SELECTIVE OXIDATION OF POLYNUCLEAR AROMATIC HYDROCARBONS

Thesis submitted in accordance with the requirements of
Cardiff University for the degree of

Doctor of Philosophy

EWA NOWICKA

July 2012

DECLARATION

This work has not been submitted in substance for any other degree or award at this or any other university or place of learning, nor is being submitted concurrently in candidature for any degree or other award.

Signed ………………………………………… (candidate) Date ....

STATEMENT 1

This thesis is being submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Signed ………………………………………… (candidate) Date …………………………

STATEMENT 2

This thesis is the result of my own independent work/investigation, except where otherwise stated. Other sources are acknowledged by explicit references.The views expressed are my own.

Signed ………………………………………… (candidate) Date …………………………

STATEMENT 3

I hereby give consent for my thesis, if accepted, to be available for photocopying and for inter-library loan, and for the title and summary to be made available to outside organisations.

Signed ………………………………………… (candidate) Date …………………………

STATEMENT 4: PREVIOUSLY APPROVED BAR ON ACCESS

I hereby give consent for my thesis, if accepted, to be available for photocopying and for inter-library loans **after expiry of a bar on access previously approved by the Academic Standards & Quality Committee.**

Signed ………………………………………… (candidate) Date …………………………

“You never fail until you stop trying.”

Albert Einstein

Abstract

This thesis targets the selective oxidation of polynuclear aromatic compounds, which is considered as a preliminary step of upgrading of heavy oils, resids and bitumens to higher value materials in the liquid phase using different catalytic systems.

Oxidation studies concentrated on simple model polyaromatic compounds and their alkylated derivatives. Ruthenium ion catalyzed oxidation chemistry has the potential to selectively oxidize PAHs and this system was studied in great detail with particular attention made to the reaction solvent system. Through careful studies it was found that the use of a monophasic solvent system led to the selective oxidative opening of an aromatic ring to produce the dialdehyde derivative. It was demonstrated that under standard conditions the rate of oxidation increased with the size of the fused ring system. ^{1}H NMR methodology was developed to quantify the percentage of alkyl chain hydrogens preserved after reaction. It was found that the ruthenium based system demonstrated a high affinity for the oxidation of aromatic carbon with a low tendency to oxidise aliphatic carbon. These studies formed the basis of a detailed investigation into the mechanism of ruthenium ion catalyzed oxidation of PAHs.

Investigation into another catalytic system which uses a homogeneous tungsten catalyst with hydrogen peroxide as the oxidant was also performed. Early studies showed that the H_2WO_4/H_2O_2 catalytic system exhibits high solvent dependant selectivity towards preferential oxidation of aromatic carbon. What is more, studies using alkylated aromatics with a alkyl chain greater than C_8 showed that even in a non polar solvent the selectivity of oxidation is directed towards the aromatic carbon.

A range of catalytic systems containing tungsten, ruthenium, heteropolyacids and their heterogenised equivalents were also applied to the oxidation of PAHs. Au-Pd supported catalysts in combination with molecular oxygen and H_2WO_4 were also used for the oxidation of PAHs and the results obtained opened a new path in the research of PAHs.

Studies on the oxidative desulfurization, denitrogenation of heteroaromatics and the demetallation of nickel and vanadium porphyrines was also performed and are reported in this thesis.

Acknowledgement

First of all I would like to express my heartfelt gratitude to my first research supervisor, Dr Stuart H. Taylor, for his support, valuable guidance throughout the period of my research and all suggestions and corrections related to my thesis. A special thank you goes to my co-supervisor, Prof. Graham J. Hutchings, whose knowledge and positive attitude towards life always put me in a better mood. I sincerely thank both of them for offering me the opportunity to study in Cardiff.

I also would like to say thank you to my industrial sponsor, Dr Manuel A. Francisco, who turned out to be not only a good partner in collaboration but also a great friend of Polish culture. I am grateful for all the support and help given to me during the last 3 years. I also would like to acknowledge ExxonMobil for Ph.D. funding.

Thanks must be given to Dr David Willock, and Prof. David Knight for their valuable advice. I am very happy to acknowledge my post doc, Dr Sankar M. Sundaram, amazing personality, brilliant researcher and my friend, who always encouraged me to do more work, gave me positive energy and made my life in Cardiff more colourful. Special thank you goes to Dr Robert L. Jenkins, who always believes that everything is possible, especially in the field of analysis. I am not able to express my gratitude toward him for all the long hours spent on my thesis corrections.

Many thanks go to the boys from the GC-MS room, Robin and Dave. It gives me great pleasure to thank my labmates and friends, who made Cardiff a memorable place, especially: Ragini, Benoit, Jean-Philipe, Julie and Polina. Several people I would like to mention because they deserve a special thank you: Tomos Clarke for help during summer 2010, Scott Davies for support while printing the thesis, Dr Julia Rogan and Dr Barry Dean for being the most helpful couple in the world, Dr Tatyana Kotionova for 'laugh and cry' times, Piotr Rutkowski for chasing me with the mechanism of SN1 and SN2, Dr James Wixey for showing me the real face of British life and Niamh Hickey for introducing me to theoretical chemistry, bell ringing and knitting.

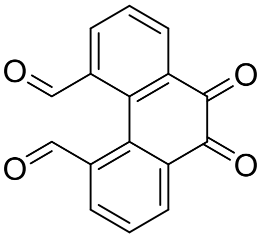
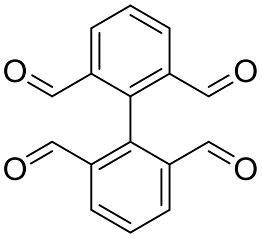
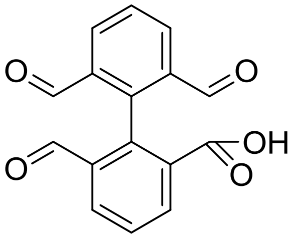
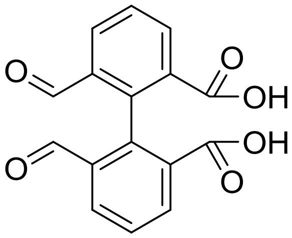
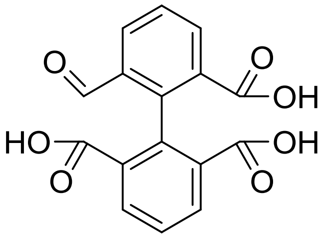
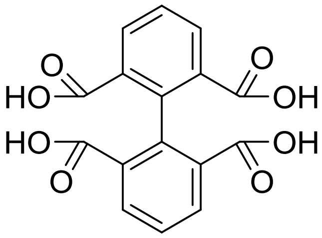
Words are not enough to express my love and gratitude to my fiancée, Jakub for his passion, support and perseverance in loving me.

Finally I would like to thank my parents for the help and love they have given me over my stay in the UK. Dziękuję.

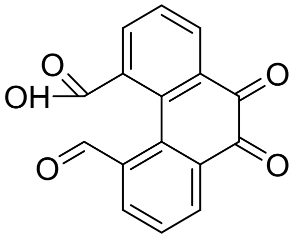
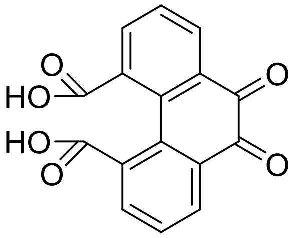
Glossary

AAS	Atomic Absorption Spectroscopy
BET	(Brunauer, Emmett, Teller) Surface Area Analysis
COSY	Correlation NMR Spectroscopy
DMSO	Dimethyl Sulfoxide
GC	Gas Chromatography
HMBC	Heteronuclear Multiple Bond Correlation
HPLC	High Performance Liquid Chromatography
HR-MS	High Resolution Mass Spectrometry
LR-MS	Low Resolution Mass Spectrometry
HSQC	Heteronuclear Single-Quantum Correlation Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IR	Infrared Electromagnetic Radiation
MS	Mass Spectroscopy
NiTPP	Nickel (II) tetraphenylporphyrin
NMR	Nuclear Magnetic Resonance
RICO	Ruthenium Ion Catalyzed Oxidation
SEM	Scanning Electron Microscopy
TBAB	Tetra-n-butylammonium Bromide
TBAF	Tetra-n-butylammonium Fluoride
TBHP	Tert-butyl Hydrogen Peroxide
TEM	Transmission Electron Microscopy
TPP	5,10,15,20-Tetraphenyl 21H,23H-porphine
UV-Vis	Ultraviolet-Visible Electromagnetic Radiation Spectroscopy
VOTPP	Vanadyl tetraphenylporphyrin
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Nomenclature

IUPAC	Name in THESIS	Structure
9,10-Dioxo-9,10-dihydrophenanthrene-4,5-dialdehyde	Pyrene-4,5-Dialdehyde-9,10-Dione	
Biphenyl-2,2',6,6'-tetraaldehyde	Pyrene-4,5,9,10-Tetraaldehyde	
2',6,6-Triformyl-2-carboxylic acid	Pyrene-4,5,9-Trialdehyde-10-Monoacid	
6,6'-Diformylbiphenyl-2,2'-diacarboxylic acid	Pyrene-4,5-Dialdehyde-9,10-Diacid	
6'-Formylbiphenyl-2,2',6-tricarboxylic acid	Pyrene-4-Monoaldehyde-5,9,10-Triacid	
Biphenyl-2,2',6,6'-tetracarboxylic acid	Pyrene-4,5,9,10-Tetraacid	

Nomenclature

IUPAC	Name in THESIS	Structure
5-Formyl-9,10-dioxo-9,10-dihydrophenanthrene-4-carboxylic acid	Pyrene-4-Monoacid-5-Monoaldehyde -9,10-Dione	
9,10-Dioxo-9,10-dihydrophenanthrene-4,5-dicarboxylic acid	Pyrene-4,5-Diacid-9,10-Dione	

Contest

1. Introduction 1

2. Experimental 31

1. Introduction

1.1. General information about Polynuclear Aromatic Hydrocarbons (PAHs)

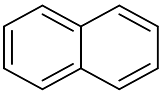
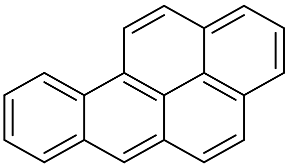
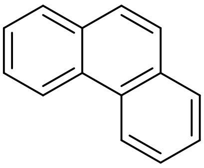
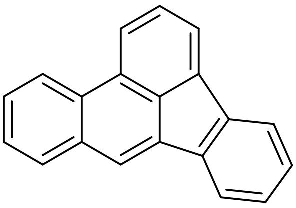
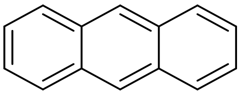
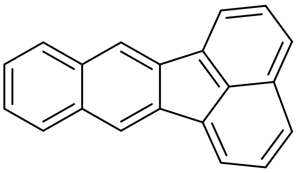
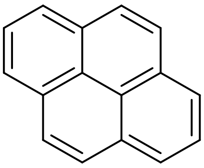
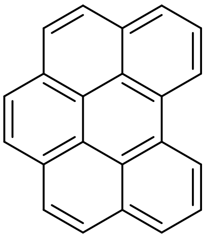
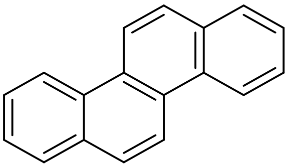
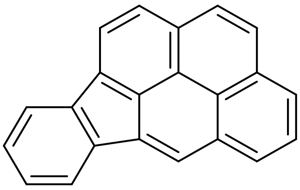
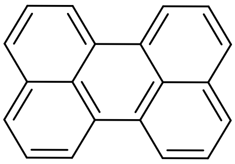
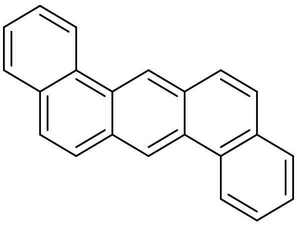
Polynuclear Aromatic Hydrocarbons are also named Polyaromatic Hydrocarbons or Polycyclic Aromatic Hydrocarbons (PAHs). They are compounds that comprise of two or more benzene rings arranged in various configurations and do not contain any heteroatoms [1].

There are two sources of PAHs: natural and anthropogenic. The major natural source of PAHs are materials derived from volcanic eruptions, meteorites, crude oil and coal deposits, thus PAHs are closely related to the petroleum industry [2-3]. Anthropogenic PAHs, which are one of the world's most widespread organic pollutants, are by-products derived from petroleum processing or through the combustion of hydrocarbons, such as coal and gasoline [4]. It is worth emphasizing that some PAHs compounds have been classified as cancerogenic, teratogenic and mutagenic, what most probably is related to the K-region electrons [5]. A table showing PAHs used in present studies, as well as PAHs being monitor in environment, is given below (Table 1-1) [6].

It is important to emphasize, that research based on PAHs is related to molecules that contain up to six aromatic rings. However, molecules with a higher number of aromatic rings (>6) exhibit similar biological activity as smaller PAHs. It has been reported that most of these chemicals have no known use except for research purposes. A few PAHs are used in medicines and to make dyes, plastics and pesticides. Other PAHs are contained in asphalt which is used in road construction [7].

Research related to PAHs is associated mainly with the degradation of these compounds. PAHs adsorb strongly to small particles in aqueous media and the soil, where they can accumulate resulting in serious contamination problems [8]. Approximately two-thirds of the PAHs found in surface water are particle-bound and can be removed by sedimentation, flocculation or via filtration processes. The remaining one-third of the dissolved PAHs usually need to be oxidized to enable their removal or transformation [7].

Table 1-1: Name and structure of the most frequently monitored PAHs [6]

Chemical Compound	Structure	Chemical Compound	Structure
Naphthalene		Benzo[*a*]Pyrene	
Phenanthrene		Benzo[*a*] fluoranthene	
Anthracene		Benzo[*k*] fluoranthene	
Pyrene		Benzo[*ghi*]perylene	
Chrysene		Indeno[1,2,3-*cd*] pyrene	
Perylene		Dibenzo[*a,h*] anthracene	

Regarding degradation of PAHs in soil and coal, many different methods have been reported. Biodegradation is one of those methods, it is a low cost method and has many technical advantages [9-12]. However, this system works only for small molecules, while high-molecular weight PAHs are resistant to this treatment (>6R) [13-14]. Chemical oxidation was found to be an alternative to the biological application with ozone used as an electrophilic oxidant [15-16]. A combined chemical and biological approach has been highlighted as the most effective way of PAHs remediation [8, 17-18].

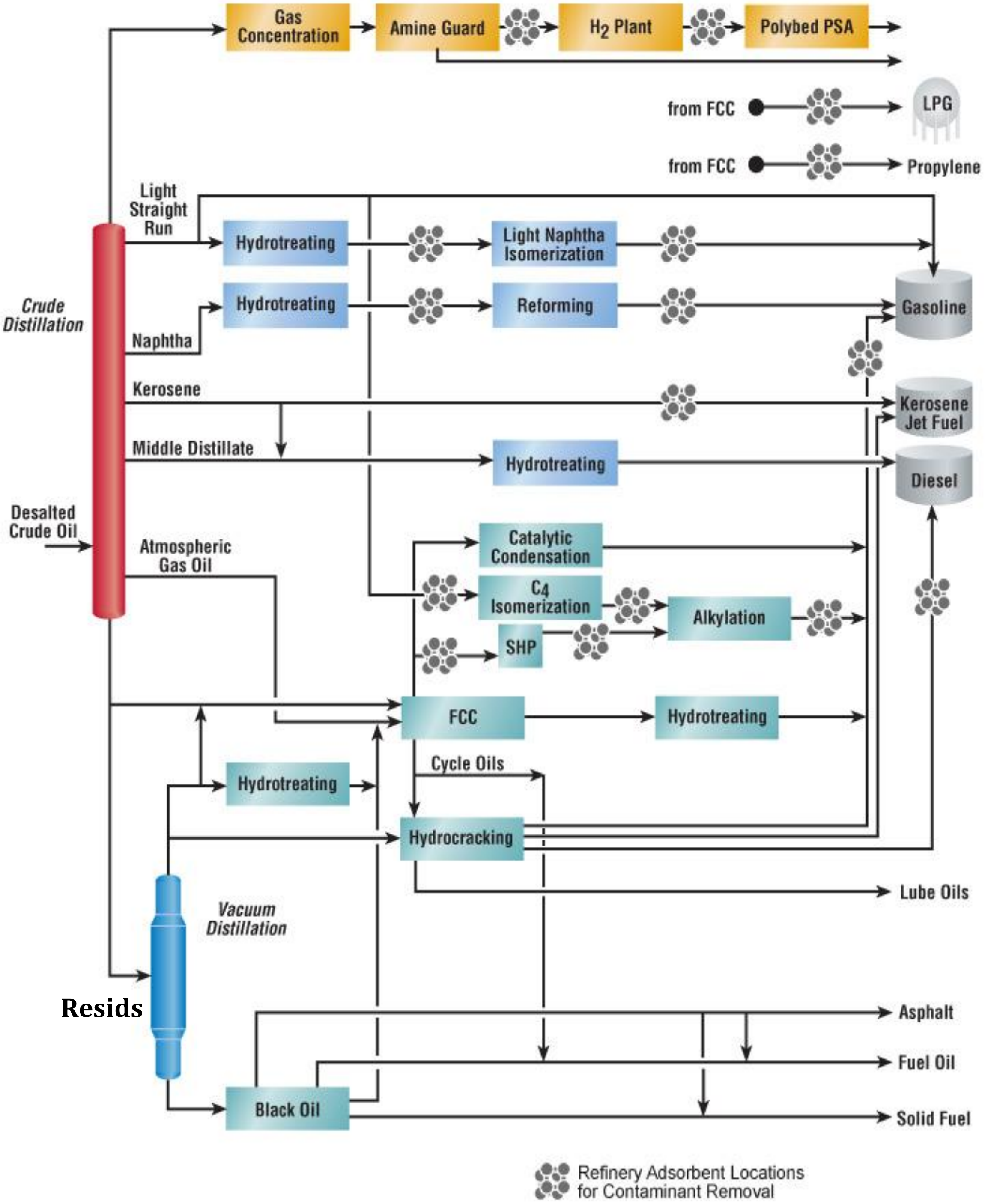
As can be seen from the examples given above, PAHs are considered as an unwanted group of compounds, considered as environmental pollutants and their degradation is required. However, taking into account the presence of PAHs in the petroleum industry, their high carbon and hydrogen content, it has to be highlighted that in the perspective of decreasing amount of fossil fuel, PAHs can play a very important role as energy donors.

1.2. Heavy oils, resids, bitumens upgrading

1.2.1. General Information

Heavy oils, resids and bitumens are petroleum resources that differ from whole crudes. These compounds typically display high density, high boiling point and high content of nitrogen, sulphur and metals. Bitumens, also called native asphalt or extra heavy oil are semisolid materials, that can exist in nature with no mineral impurity or with mineral matter contents that exceed 50% by weight. Both, heavy oils and bitumens are naturally occurring materials that contain very little volatile material. However, resids (residuum, residua) are the residual, non volatile materials left behind after the distillation of a crude oil under atmospheric pressure (atmospheric residuum) or under reduced pressure (vacuum residuum)[19] as shown in scheme 1-1. These materials contain a higher concentration of molecules that produce low value coke and gas in the refinery processes, e.g.: PAHs. It is important to highlight that the economic conversion of these materials to high value liquid fuels is relatively difficult [19-21]. However, due to their easy access and low price they are getting more attention and soon may be used in a place of whole crudes [22].

.



Scheme 1-1: The refinery flowchart [23]

1.2.2. Common methods of heavy crudes upgrading

The process of petroleum residuals upgrading was studied for many years. It was important to find a simple and economical process, which would convert the “bottom of the barrel” compounds into more useful materials. There are three major methods of heavy feed upgrading: deep oil fluid catalytic cracking, thermal cracking and hydrocracking with desulfurization. Fluid catalytic cracking converts the high boiling feedstock to more useful petroleum compounds with the use of high temperature, moderate pressure and the most important, fluidized powdered catalyst. Thermal cracking refers to methods where no catalyst or chemicals are added and only high temperature is used. Thermal cracking can be distinguished into three processes: visbreaking, thermal cracking and coking. Coking is the lower cost process among all of them, however, molecules containing critical sized core fragments will, under coking conditions, lose aliphatic side chains until there is nothing left but methylated and substituted aromatic cores and will lead to coke production. Molecules which have a critical core size, equal to four or more fused aromatic rings are multirings, heteroaromatic compounds containing organic sulphur, nitrogen, oxygen and metals. These compounds are also too stable to crack into smaller, more volatile fragments, therefore they cores remain in the high temperature zone until they form coke [24-25].

The hydrocracking process is often combined with thermal cracking. Hydrocracking has the possibility to transform ≥4R aromatic cores into smaller fragments, but this requires expensive high pressure hydrogen. What is more, overcracking and formation of low value gas during this process is a major drawback [26]. In addition, the critical cores of these multiring hetroaromatics are resistant to hydrocracking as they are electron rich molecules. The addition of hydrogen involves adding more electrons to the system which is only accomplished under forcing conditions i.e.: high temperature and pressure which leads to an non-selective reaction. However, multiring heteroaromatic cores are much more reactive to oxygen.

Coking and hydrocracking can waste carbon and hydrogen as coke or gas. Therefore, it is highly desirable to develop a chemical process which can selectively reduce ≥ 4R to 3R aromatic cores without losing carbon and hydrogen from the system.

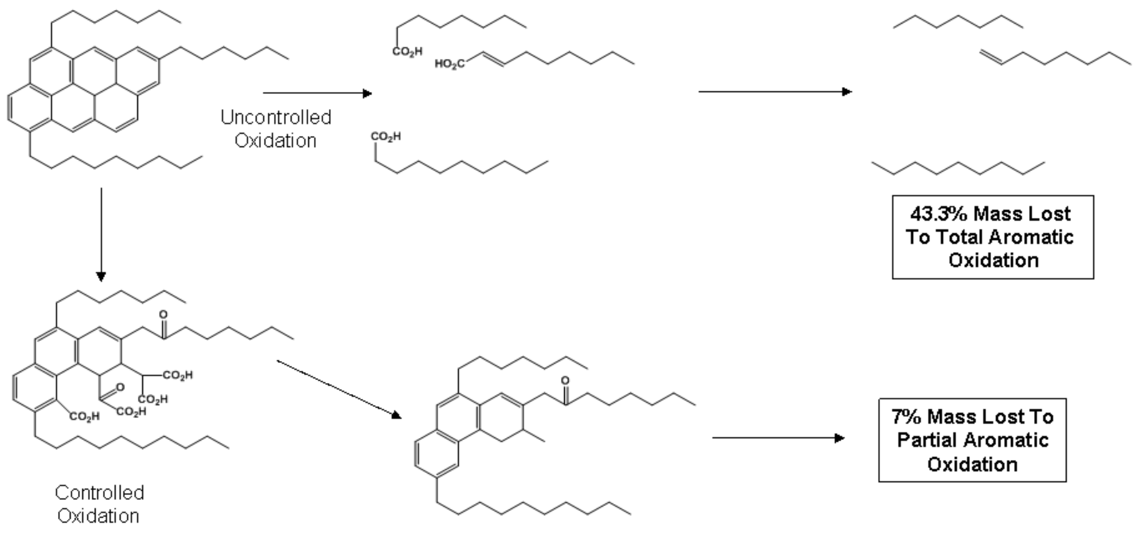
1.2.3. Oxidation as a possible pathway in upgrading of "bottom of the barrel" compounds

Oxidation appears to display the reactivity required to activate electron rich aromatics, however, controlling this oxidation can prove difficult. Comparing literature studies on the uncontrolled oxidation of molecules larger than 6 R, it was observed that >43% of the mass of the molecule was converted to CO_2 and H_2O. Coking of the 6R aromatic resulted in a mass loss of > 53% to low value coke. From this data, it is clear that even uncontrolled oxidation is better than coking [27].

Among the requirements for a selective oxidation process the most important points are:

1) To selectively target aromatic carbon and not aliphatic carbon.
2) The rate of oxidation has to be faster for aromatics with more fused rings (4R > 3R).
3) One aromatic ring at a time should be oxidized and subsequently ring-opened.
4) Over oxidation is minimized so that 4R is oxidized to 3R and not to 2R [20].

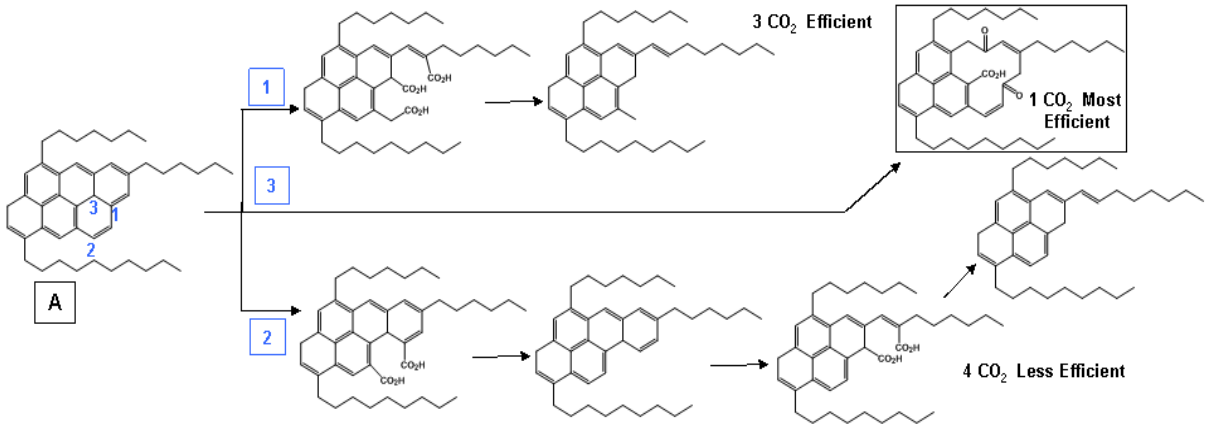
Scheme 1-2 compares the theoretical results of uncontrolled and controlled catalyzed oxidation of molecules with critically large aromatic cores and illustrates how the oxidation process affects the core structure. The coking and mass balance values are based on theoretical calculations [28].



Scheme 1-2: Effect of oxidation on aromatic cores [27]

If oxidation of the resids and bitumens could be controlled, it would convert the 6R aromatic moiety to a three ring aromatic system with a 7% loss of mass as CO_2 and H_2O, which is a much more efficient system than coking or uncontrolled oxidation. Comparing the controlled oxidation process of the 6R aromatic system with a hydrocracking process, it is clear that hydrocracking produces similar products to that seen under controlled oxidation. However, this process would require significant amounts of high pressure hydrogen and may overcrack the aromatic materials to produce low value gas. Controlled or uncontrolled oxidation will incorporate some organic oxygen and olefinic double bonds into the products which can be removed with further refinery processing [27].

There are three possible levels of oxidation selectivity illustrated in scheme 1-3. The selectivity is associated with the first aromatic carbon that is attacked. Attack at carbon #1 (bridgehead aromatic carbon) results in the loss of three aromatic carbons to go from a 6R aromatic system to a 4R system. Four aromatic carbons are lost when attack takes place at carbon #2 (outer aromatic carbon). This is less efficient than attack at carbon #1. Only one aromatic carbon is lost if the attack takes place at carbon #3 (inner aromatic carbon) with the ring size subsequently reduced from six to three. Attack at any aromatic carbon offers more selectivity than coking or hydrocracking with attack at the inner aromatic carbon being the most efficient and this is the ultimate research objective [28].



Scheme 1-3: Aromatic carbon selectivity [28]

There are many articles in the open literature on selective oxidation [29]. Most focus on the selective oxidation of aliphatic carbon. Some studies have investigated the oxidation of aromatic carbon, however, the desired selectivity was either not achievable or was never investigated.

1.3. Chemistry of selective oxidation

1.3.1. General Information

Selective oxidation has been an active area of research for many years, the challenge facing the chemist is to achieve high activity whilst minimizing over-oxidation [30-31]. In an attempt to achieve these aims, a wide range of oxidizing agents and methods of oxidation have been reported. These include chromium and manganese based stoichiometric oxidants [32-33], the Swern method [34], *o*-iodobenzoic acid (IBX)[35], Dess-Martin periodinane (DMP) [36], Parikh-Doering oxidation [37], Corey-Kim oxidation [38] and many more. These methods have one or more of the following disadvantages: the need for stoichiometric amounts of costly oxidant, low reactivity, low selectivity and lack of substrate tolerance. Efforts are continually being made to uncover an oxidizing system which overcomes most or all of these disadvantages.

1.3.2. Ruthenium Ion Catalyzed Oxidation

In 1953, Djerassi reported a ruthenium tetroxide catalytic system for the oxidation of various organic substrates [39]. This seminal discovery opened up an entirely new area of chemistry in the oxidation of organic compounds. This system was later named Ruthenium Ion Catalysed Oxidation (RICO), where RuO_4 is generated *in situ* via the combination of a ruthenium ion and an oxidizing agent in a solution of dichloromethane and water [40-41]. RuO_4 forms yellow crystals and can be generated *in situ* from $RuCl_3 \cdot xH_2O$, RuO_2 and $NaIO_4$, NaOCl, HIO_4, $NaBrO_3$, Oxone, O_3, $Ce(SO_4)_2$, $K_2S_2O_8$ [42-49].

There are a number of parameters which influence the stability and catalytic activity of RuO_4. The most important parameter is the pH of the reaction medium. RuO_4 is stable at a pH below 9 and subsequently reduced to the less oxidizing species, $[RuO_4]^-$ as shown overleaf (Figure 1-1) [50].

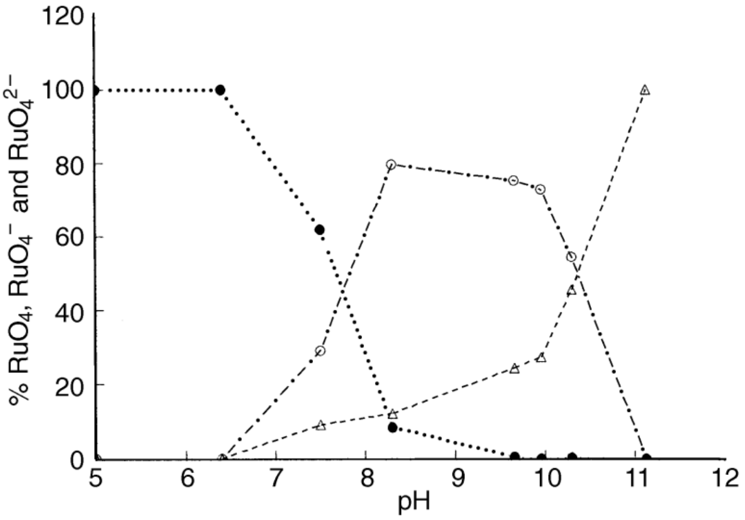
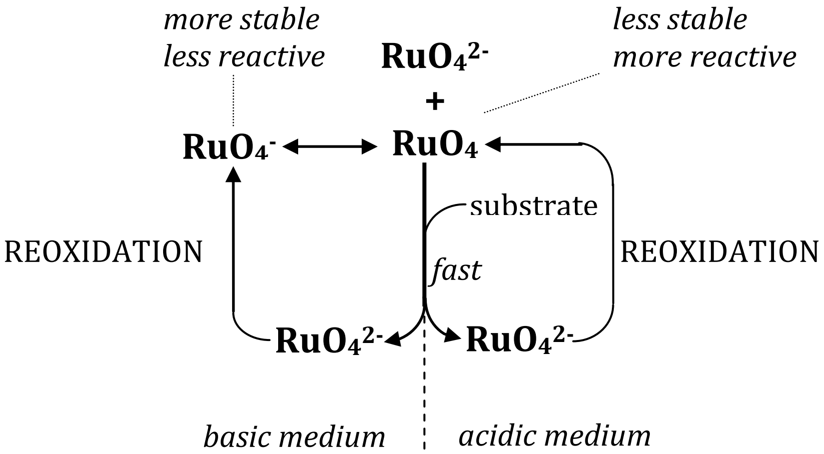


Figure 1–1: Proportion (%) of RuO_4*(●), [*RuO_4*]*$^-$*(o) and trans-[Ru(OH)*$_2O_3$*]*$^{2-}$*(△) at different pH [50]*

It is also known that the nature of the oxidant plays an important role during the RICO reaction. When Ru (VIII) is reduced to Ru (VI), a weaker single-electron oxidant can further reoxidise freshly formed Ru (VI) to RuO_4^-. This species can undergo further disproportionation reaction as outlined below (Scheme 1-4).



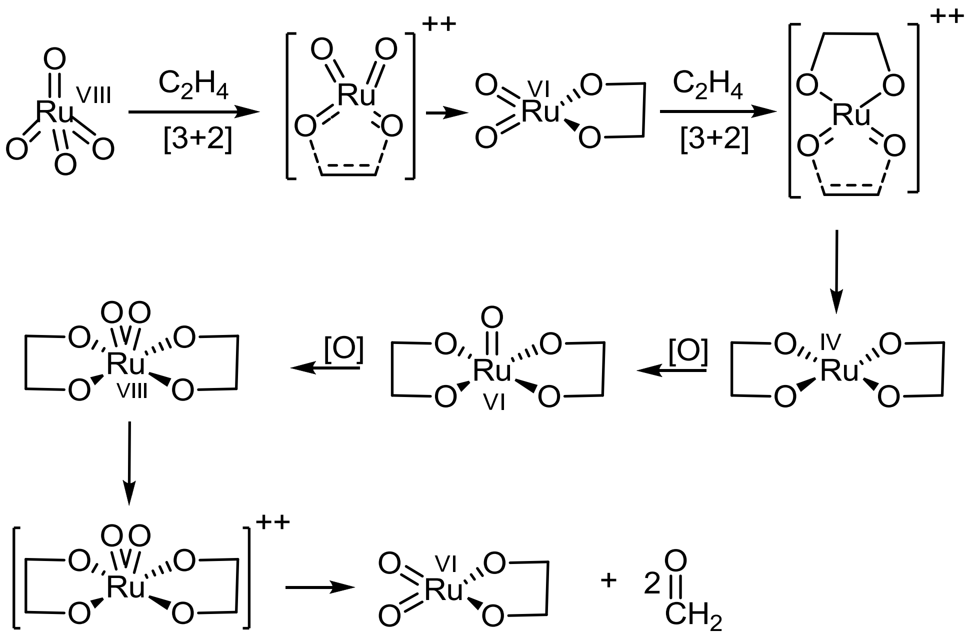
Scheme 1-4: RuO_4*-catalyzed oxidation under slightly basic conditions [51]*

Other parameters which influence reaction rate and product distribution are temperature and *oxidant : substrate* molar ratio [52]. Mills *et al.*, have also reported that the rate of oxidation increases with an increase in stirring speed or when the reaction is subjected to ultrasound radiation [50].

Initially, RICO chemistry was used mainly for the oxidative fragmentation of C=C bonds and aromatic compounds. The RICO system was found to be extremely reactive resulting in the digestion of polyaromatic compounds rather than their selective oxidation. In spite of this, many researchers have tried to utilize RICO chemistry and improve its selectivity.

Sharpless *et al.*, reported that by adding acetonitrile as a co-solvent, the selectivity of reaction, as well as the activity of oxidation, could be improved even at a much lower catalyst loading [53]. His explanation of this phenomena was based on the assumption that carboxylate complexes, formed as side-products during the oxidation process, can deactivate the catalyst by acting as coordinating ligands. The presence of acetonitrile, which reduces the formation of complexes, increased the catalyst lifetime and activity. Consequently, after this observation, RICO chemistry has been reported to be effective for many reactions, including C-H bond activation [54], dihydroxylation of olefins [55-56], dehydrogenation of alcohols and amines [57], selective mono-oxidation of vicinal diols [58-59], ketohydroxylation [60], oxidative cyclization of polyenes [61-62], oxidative cleavage of double and triple bonds [53, 63], oxidation of heteroatoms [64-65] and oxidation of saturated hydrocarbons and aromatic hydrocarbons [52, 66]. Amongst the oxidation reactions mentioned above, the oxidation of saturated hydrocarbons is intriguing, because of the high stability of the C-H bond and the potential use of this oxidation system in various industrial processes [67-68]. Wide range of oxidizing agents have been reported to oxidise hydrocarbons, however, RICO is unique because of its high reactivity and functional group tolerance [69-70].

The mechanism of RICO chemistry was proposed by many researchers [51, 71]. Until now, there was no concrete evidence for the detailed mechanism of oxidative cleavage of the double bond, which would be of special interest for this project and oxidation of polynuclear aromatic hydrocarbons. So far, there was some speculation that C=C scission could be involved in the first step of the reaction. Frenklin proposed in his theoretical investigation that Ru (VI) is formed via subsequent 3+2 cycloaddition to the olefins as shown below (Scheme 1-5), however, his theory was not confirmed by experiments. Although, this mechanism is consider to be also valid for the oxidation of aromatic compounds, no concrete evidence was given so far to prove it.



Scheme 1-5: Suggested mechanism for RuO_4 catalyzed cleavage of C=C bond [72]

Coudret *et al.*, reported that RICO chemistry occurs regioselectively at the most electron-rich C-H bond with retention of configuration [73]. It was well known that RuO_4 selectively attacks sp^2 carbons in organic substrates [74]. This high regioselectivity is remarkable and is much higher than that observed in any other catalytic oxidation system.

The regioselectivity of RICO, has been exploited in two different research areas. The first is the oxidative fragmentation of aromatic compounds to carboxylic acids in synthetic organic chemistry [63, 75] and the second is the selective oxidation of alkylated aromatics, where the aromatic moiety is oxidized to CO_2 and H_2O leaving the aliphatic chain intact as a carboxylic acid [40].

1.3.2.1. RICO in petroleum industry

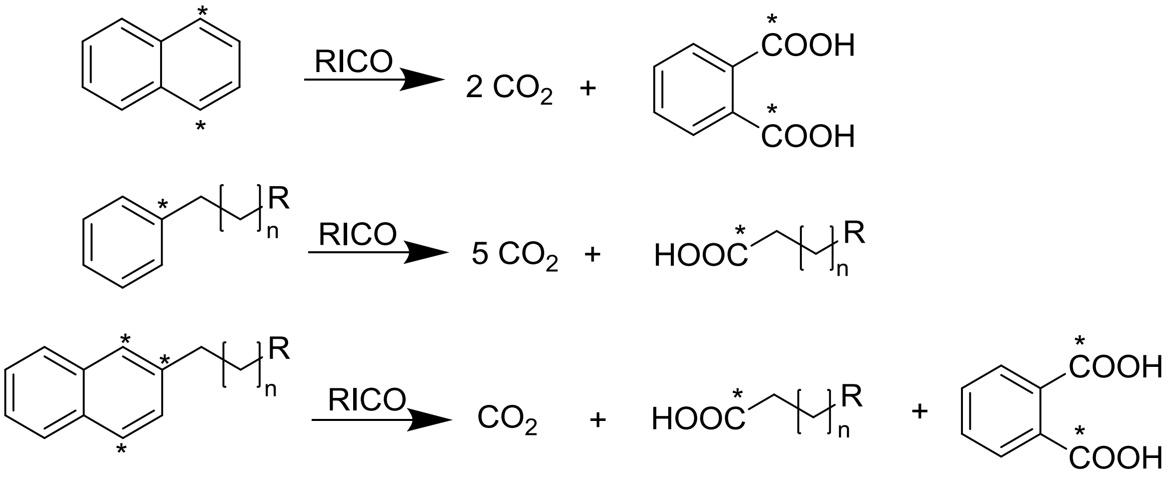
Ruthenium catalyzed oxidation has been reported for many years to characterize aliphatic side chains in multiring heteroaromatics in the petroleum [76-78] and coal industries [41, 74, 79-82]. A number of papers have been published using this methodology to identify the aliphatic chains in coal and asphaltenes. [77, 83]

This approach is based on three different hypotheses:

1) The aromatic hydrocarbons are oxidized to CO_2 and H_2O in high yield,

2) Oxidation occurs exclusively at the aliphatic carbon atom attached to the aromatic ring,
3) The aliphatic chain is not oxidized.

As a result of the oxidation, the aromatic carbon located in the position of aliphatic chain attachment becomes a carboxylic carbon on the carboxylic acid as shown below (Scheme 1-6) [77].



Scheme 1-6: Scheme presenting the basics of RICO in the petroleum chemistry [84]

Although these hypotheses have been tested using a limited range of substrates, only an estimate quantitative investigation has been previously reported in the literature [80, 85-86]. To quantify and determine the number of carbons preserved in the aliphatic chains, usually a number of procedures were applied. First the carboxylic acids formed during the oxidation reaction, were converted into the corresponding esters. The efficiency of methylation was reported not to be sufficient and the process needed to be repeated at least three times. Only then were GC and GC-MS analysis carried out. The second step in analysis was done via chromatography separation. Also NMR analyses were employed to calculate the ratio of alkyl carbon versus total carbon present in the oxidation products. Based on this methodology, it was possible to characterize different coal types, bitumens, heavy asphaltenes as well as quantify the sulphur and nitrogen content.

This ruthenium system appears to have the potential to deliver the required selectivity for controlled oxidation of PAHs and further upgrading of heavy oils, resids and bitumens. It targets only the aromatic carbon of the PAHs and the cationic nature of the chemistry suggests that the greater the number of the aromatic cores, the faster these fused rings will oxidize. The control of this chemistry and its selectivity has received limited attention. There are publications where authors report studies performed on several PAH model compounds, however, those experiments were run without *in situ* studies. For example Mendez *et al.*, reported studies on phenanthrene, with sample analysis after 6, 12 and 18h of reaction with no intermediate analysis reported [87].

1.3.3. H_2O_2 used as oxidant

H_2O_2 is considered to be one of the most attractive oxidants with high oxygen content as shown below (Table 1-2). It is relatively cheap and its controlled use does not lead to unwanted waste products with water being its only by-product [88]. What is more, its aqueous solution can be easily and safely transported and stored.

Table 1-2: Popular oxidants and their active oxygen content [45]

Oxidant	Active oxygen content (wt%)	Waste product
Oxygen O_2	100	-
H_2O_2	50	H_2O
NaOCl	21.6	NaCl
tBuOOH (TBHP)	17.8	tBuOH

1.3.3.1. H_2O_2 for PAHs degradation

The first report of using H_2O_2 in the oxidation of aromatic hydrocarbons was made in 1881 by Leeds. He obtained ß-naphthol from naphthalene and antraquinone from anthracene [89]. From that moment, the use of H_2O_2 has been studied more and more extensively.

Milas and Sussman introduced OsO_4 to the H_2O_2 system and it was found to be very active for the oxidation of olefins in the presence of *tert*-butanol (Milas's reagent) [90]. This system was further applied by Cook and Schoental to the oxidation of polynuclear aromatic hydrocarbons [91]. When the system was applied to the oxidation of naphthalene and phenanthrene, the authors observed the presence of diols and acids, indicating C=C bond cleavage. Moreover, it was also reported that the oxidation of pyrene with H_2O_2 resulted in a mixture of quinones, pyrene-3,8-quinone and pyrene-3,10-quinone. The authors emphasized the absence of products having oxidized carbons in positions 1 and 2, which are exclusively attacked when using OsO_4 in benzene-pyridine solvent mixture [91]. The chemical structure of pyrene along with the carbon numbering as presented in Cook's publication is shown below (Figure 1-2).

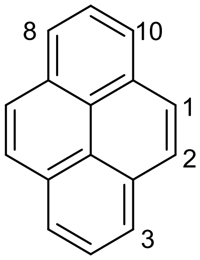


Figure 1–2: Chemical structure of pyrene with carbons numbered in accordance with Cook's publication [91]

The use of H_2O_2 for the oxidation of aromatic compounds in the presence of trace amounts of $RuCl_3$, was reported by Tandon *et al.* Using a 50% H_2O_2 solution and a *substrate : catalyst* ratio of 1488:1, Tandon was able to oxidize naphthalene to α-naphthol with a yield of 15% [92]. Tandon also observed an increased yield when the amount of catalyst used in the reaction was lowered. Oxidation of phenanthrene using the same catalyst in the presence of acetic acid gave phenanthrene 4,5-quinone and diphenic acid as oxidation products [93].

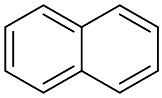
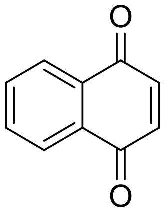
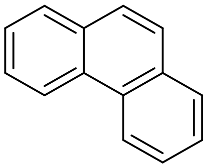
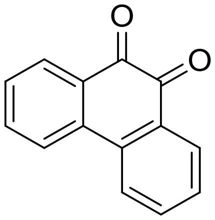
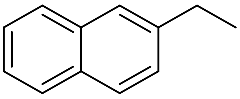
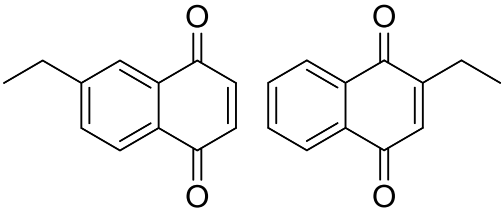
Although OsO_4 and RuO_4 are considered to be similar oxidising species, based on the above reported publication, it can be found that different carbons can be attacked when changing the oxidant. Oberender and Dixon performed studies on pyrene using three systems: OsO_4 in combination with H_2O_2, OsO_4 with $NaIO_4$ and RuO_2 with $NaIO_4$. They noticed different activities of the systems, but pointed out that carbons in position 4 and 5 were mainly attacked. Comparing the products obtained by Oberender and Dixon with those reported by Cook and Schoental, it can be seen that contradictory results are reported, emphasizing oxidation of carbons in different positions (Table 1-3)[91, 94].

Table 1-3: Pyrene oxidation product distribution using different oxidation systems

Authors	**OsO_4/H_2O_2**	**$OsO_4/NaIO_4$**	**$RuO_2/NaIO_4$**
Oberender/ Dixon [94]	• Pyrene-4,5-quinone	• Pyrene-4,5-quinone • Lactol 4-formylphenanthrene-5-carboxylic acid	• Pyrene-4,5-quinone • Pyrene-1,6-quinone • Lactol 4-formylphenanthrene-5-carboxylic acid
Cook/ Schoental [91]	• Pyrene-1,6-quinone • Pyrene-3,6-quinone		

Beller *et al.*, reported the application of Ru complexes and H_2O_2 for PAHs oxidation as a novel and convenient process [95-96]. The most active complex in this study was Ru(II)tetrapyridine(2,6-pyridinedicarboxylate), which transformed naphthalene to naphthalene quinone and phenanthrene to phenanthrene 9,10-quinone (Table 1-4). The result which is of special interest to this project, is related to the oxidation of 2-ethylnaphthalene, as when this catalyst was used in the presence of tributylbenzylammonium chloride, no products with an oxidized alkyl chain were observed. Also when 2-methylnaphthalene was treated with 30% H_2O_2 is the presence of Ru(II)tetrapyridine(2,6-pyridinedicarboxylate) only corresponding methyl quinones were detected. This suggest that the above mentioned complex is very selective in the oxidation of aromatic carbon [95].

Table 1-4: Oxidation of naphthalene derivatives [95-96]

Substrate	Product	Conversion [%]	Yield [%]
		100	63
		100	34
	 **2.3 : 1**	55	50

In 1953 O'Connor and Moriconi investigated the oxidation of phenanthrene using 50% H_2O_2 in a glacial acetic acid solution combined with 40% peracetic acid. They observed a 70% yield to 2,2'-diphenic acid at reaction temperatures in the range 100-110°C [97].

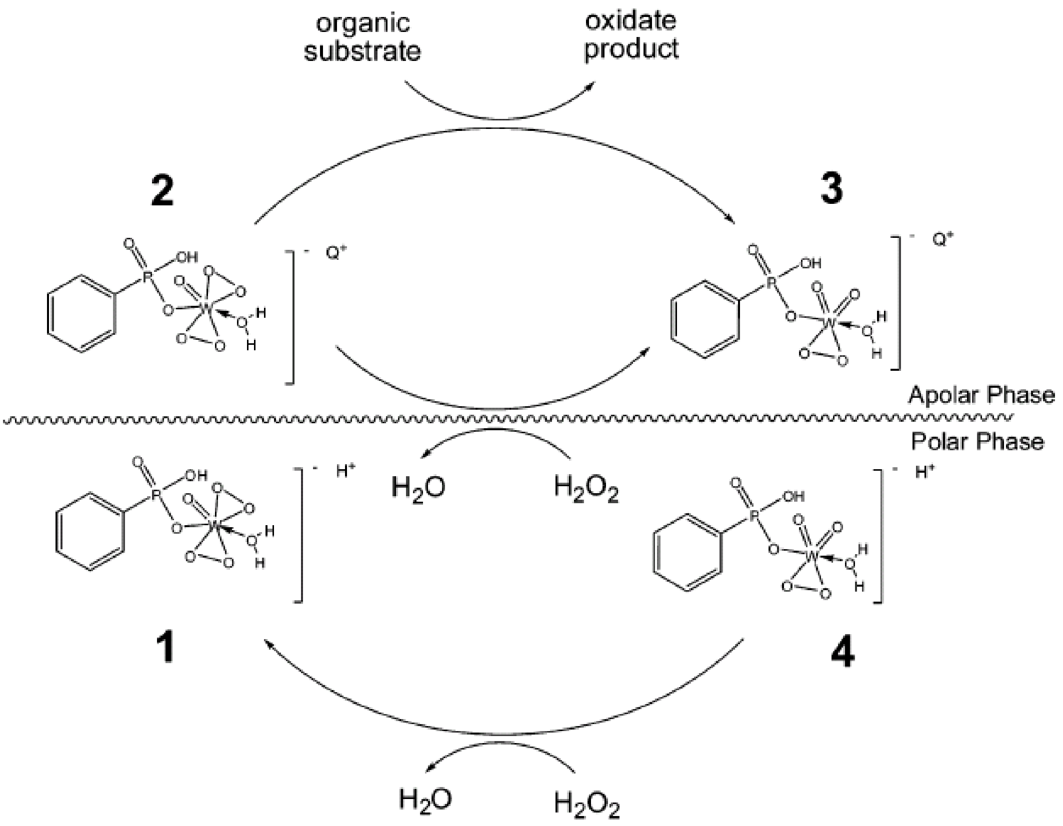
H_2O_2 was also used in combination with heteropolyacids. This system was found to be useful for epoxidation of olefins and allylic alcohols, ketonization of alcohols and diols and in the oxidative cleavage of 1,2-diols and olefins [98-100]. Surprisingly, the number of publications on the use of polyoxometalates in PAHs oxidation is limited. However, one such report is based on the use of mono-substituted Keggin-type polyoxometalates with H_2O_2 [68]. In the oxidation of 2-ethylnaphthalene, the authors used acetonitrile as a solvent and observed that oxidation of 2-ethylnaphthalene occurred predominantly at the alkyl side chain. Bordoloi *et al.*, immobilized the polyoxometalate, molybdovanadophosphoric acid on mesoporous silica and used it in the oxidation of anthracene. The reaction was found to be 100% selective to 9,10-antraquinone with catalyst leaching studies confirming the heterogeneous nature of the catalyst [101]. Lukasiewicz *et al.* also used tungstoboric acid immobilized on SiO_2 for anthracene oxidation. In the presence of H_2O_2 this system was irradiated in a microwave reactor to give 9,10-antraquinone in a 96% yield [102].

The successful oxidation of PAHs was also reported using a combination of H_2O_2 and iron (III) porphyrins. Giri *et al.*, applied 5,10,15,20-tetraarylporphyrinatoiron (III) chloride for the oxidation of several PAHs using dichloromethane and acetonitrile as a solvent over a period of 6h at room temperature. These experiments, in the presence of H_2O_2, resulted in the production of diols and ketones with no ring-opened products observed. Interestingly, pyrene was oxidized to pyrene-4,5-dione and pyrene-4,5,9,10-tetraone under these reaction conditions [103].

1.3.3.2. H_2O_2 in the combination with H_2WO_4

One of the most selective PAHs oxidation reactions was achieved using H_2O_2 as an oxidant in conjunction with a catalyst derived from WO_4^{2-}. The addition of a phase transfer catalyst to the system, was also necessary for reaction to occur, as H_2O_2 is only available as an aqueous solution while the substrates only dissolve in an organic medium. The phase transfer catalyst can be a quaternary ammonium or phosphonium salts, which should have an appropriate partition coefficient, to interact with both the aqueous and organic media [104]. This system was first proposed by Payne *et al.*, who applied it to the hydroxylation of cyclohexane and epoxidation of acids [105-106]. In their first experiments they used tungstic acid in the presence of 90% H_2O_2. They also mentioned that a slightly modified system was also found to be useful in the oxidation of alcohols [107-108], in the oxidation of aldehydes to carboxylic acids [109], olefin epoxidation [110-111] and in the oxidation of sulphides to sulfoxides [112].

The mechanism of the active complex formation and the transfer from aqueous to organic phase is quite complicated. Based on previously reported experimental findings and theoretical calculations, presented by Barrio *et al.*, it is postulated that first, H_2WO_4 is oxidized by H_2O_2 to form a bisperoxotungstate complex in the aqueous phase. This complex reacts further with phosphonic acid to form compound **1** (Scheme 1-7). Freshly formed complex is then transported via the phase transfer catalyst to the organic phase (**2**) where oxidation of the substrate takes place. In the next step, the monoperoxo tungstate ion marked as **3** is transferred back to the aqueous layer where it is oxidized by H_2O_2 to reform the anion **4** [113].



Scheme 1-7: Proposed mechanism for the oxidation of organic compounds with H_2O_2 and H_2WO_4 [113]

The application of WO_4^{2-} and H_2O_2 for the selective oxidation of arenes to aromatic dicarboxylic acids in the liquid phase in the presence of phase transfer catalyst was patented in 1989 by Saito *et al.* He used this catalytic system to selectively oxidize phenanthrene to biphenyl-2,2'-dicarboxylic acid and pyrene to phenanthrene-4,5-dicarboxylic acid. The reaction selectivity was seen to be dependant on reaction pH, catalyst, acid and the phase transfer catalyst used as can be seen below (Table 1-5) [114]. Young and Funk reported the oxidation of pyrene to phenanthrene-4,5-dicarboxylic acid as a step in the synthesis to pyrene-4,5-dione. The yield to the diacid was reported as 91% [115].

Table 1-5: Oxidation of pyrene to phenanthrene 4,5-dicarboxylic acid: reaction conditions dependence

Conversion [%]	Selectivity [%]	Catalyst	Phase transfer catalyst	pH	Acid
88	72.7	H_2WO_4	N-methyl-di-n-octylamine	1.6	30% H_2SO_4
97.1	80.6	H_2WO_4	Tri-n-octylamine	<1.5	10% H_3PO_4
95.4	79.5	$(NH_4)_{10}(W_{12}O_{41})\cdot 5H_2O$	Tri-n-octylmethylammonium chloride	<0.7	10% H_3PO_4
92.2	80.7	$Na_2WO_4\cdot 2H_2O$	Tri-n-octylmethylammonium chloride	<1.9	10% H_3PO_4

1.3.4. Molecular oxygen as an oxidant

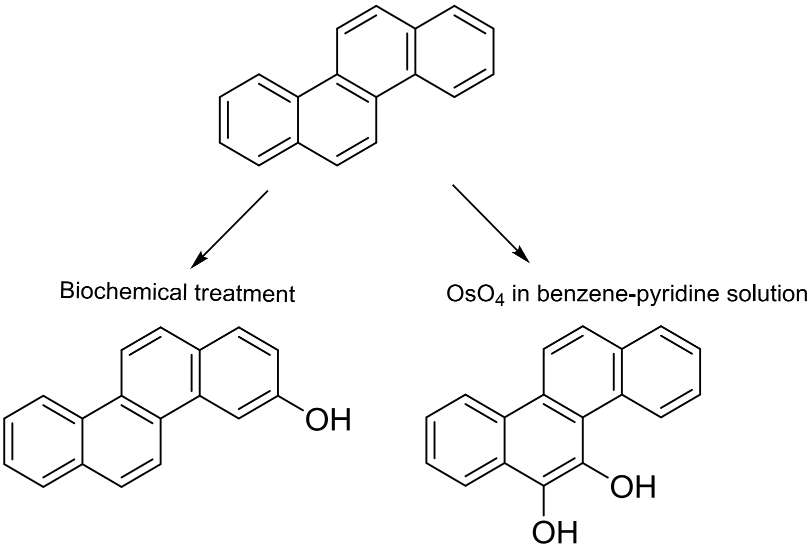
The use of molecular oxygen as an oxidant is of great interest to the field of catalytic chemistry. The biggest advantage being that oxygen is readily available. Air is made up of 21% of oxygen and its use does not lead to the waste production. Unfortunately, the capability of oxygen or air to work as an oxidant is not alone sufficient; therefore the presence of a metal or radical initiator is required. There are thousands of publications related to the selective oxidation of alcohols or aldehydes, however, there are few reports describing the use of molecular oxygen in the oxidation of PAHs. The current literature mainly describes the use of molecular oxygen over a heterogeneous catalyst for the total oxidation of PAHs to CO_2.

Zhang *et al.,* tested a series of metal supported catalysts for naphthalene oxidation. The 1% Pt, 1%Pd, 1% Ru, 5% Co, 5% Mo and 5% W-alumina supported catalysts exhibited different activities for the total oxidation of naphthalene, at temperatures in excess of 200°C [116]. Ntainjua *et al.*, performed a similar set of experiments which also saw the total oxidation of naphthalene to CO_2 [117].

It is important to highlight that these total oxidation reactions were mainly reported for naphthalene and not for heavier compounds. What is more, the total oxidation of PAHs is not the aim of this project.

1.3.5. Other oxidation systems

As was said before, osmium tetroxide (OsO_4) is considered to have similar chemical properties to RuO_4, yet its reactivity towards olefins is lower than that observed with RuO_4 [51]. Cook *et al.*, compared the oxidation of PAHs using a biochemical process to when the oxidation was performed using OsO_4 and noticed that different positions in the molecules were attacked, thus revealing different reactive centres for these two oxidation methods. As an example result they used work of Berenblum *et al.*, who converted chrysene to 3-hydroxychrysene using biochemical methods [118]. When reaction was performed with OsO_4 in benzene-pyridine solution, chrysene was oxidized to 1,2–dihydroxychrysene. Generally all the products of oxidation with OsO_4 were mainly alcohols (diols), indicating a relatively mild oxidation process [119].



Scheme 1-8: Chrysene oxidation: Products obtained under different treatment

It was also found that ozone yields similar products to RuO_4 in the oxidation of alkenes [120]. Ozone has been used in PAHs oxidation for many years. In 1905 Harris reported the ozonolysis of phenanthrene [121]. The group of Moriconi and O'Conor continued Harris's work and performed ozonolysis on phenanthrene and benozo[a]pyrene [122-123]. When phenanthrene underwent ozonolysis biphenyl 2,2'-dialdehyde and biphenyl 2,2'-diacid were obtained as oxidation products.

Cataldo and Keheyan reported the degradation of 18 different PAHs using γ-radiation combined with ozonolysis. This work was performed in acetonitrile in contrary to previous reports, where water was used as a solvent. The authors observed that a change of solvent contributed to better compound degradation [124].

Iodoxybenzene was also used as a reagent for the oxidation of polynuclear aromatics yielding quinones as the only products. Ranganathan *et al.* considered iodoxybenzene to be a remarkably close ozone equivalent. He reported that pyrene was oxidized in nitrobenzene for 8h at a temperature of 170°C yielding pyrene-4,5-dione (14%), pyrene 1,6-quinone (12%) and pyrene 3,6-quinone (15%). Phenanthrene, however was oxidized to phenanthrene 4,5-quinone [125].

Jeyaraman *et al.*, reported the production of arene oxides by the caroate-acetone system with the involvement of dioxiranes formation. In their studies the dimethyldioxiranes, considered as an oxygen donor, were formed in the reaction with acetone, potassium peroxymonosulfate, tetra-n-butylammonium hydrogen sulphate and phosphate buffer. Although pyrene, chrysene, phenanthrene and their derivatives were oxidized to the corresponding oxides, the procedure was relatively complicated with no ring opened products observed [126].

There are only a few publications related to the oxidation of aromatic compounds catalyzed by metalloporhyrins [127]. One such publication describes the oxidation of aromatic compounds using 2,6-dichloropyridine N-oxide catalyzed by ruthenium porphyrin. The authors reported the oxidation of phenanthrene to phenanthrene 4,5-quinone with a yield of 40% [128].

1.4. Oxidation of heteroaromatics and metalloporphyrins

1.4.1. Sulphur and Nitrogen removal from crude oil

The presence of sulphides and nitrites in the petroleum industry has been known for many years to be problematic. The sulphur and nitrogen content in fuels is problematic because its combustion leads to production of hazardous gases and its presence can reduce effectiveness of catalytic processes in petrol feedstocks [129]. Therefore, the removal of sulphur and nitrogen has gained much of attention.

The most popular method of sulphur removal on an industrial scale is hydrodesulfurization (HDS). Although this process is efficient, it can not be applied to systems which contain dibenzothiophene and its alkylated derivatives. Other processes which can be used as a substitute for HDS are: microbial transformations, selective adsorption and the most "green" method, oxidative desulfurization (ODS). The greatest advantage of ODS is that the sulphides are oxidized to sulfones, which are easily removed by adsorption, extraction or distillation [129]. These separation processes rely on the altered chemical properties e.g. solubility, volatility and reactivity of the sulfones in comparison to the original sulphur compounds [130]. Lately literature reports describes the possibility of sulfones adsorption on activated carbon [131].

Many different types of oxidative systems have been reported in the literature. Djerassi found that RuO_4 is the perfect active species for the oxidation of sulfides to sulfones [39]. A similar observation was reported by Tabatabaeian *et al.*, who selectively oxidized 1-benzothiophene to the corresponding sulfone. However, oxidation of 3-methyl-indole resulted in the formation of a complex mixture of compounds [71].

Kwon *et al.* proposed the use of mesoporous silica adsorbents as a method for clean fuel production. Kwon's solution was based on the selective adsorption of nitrogen and sulphur-containing compounds during the refinery processes [132].

Hydrogen peroxide was also reported as an active oxidant in the oxidation of heteroaromatic compounds [133]. Its use was reported in the selective oxidation of sulfides to corresponding sulfodixes or sulfones in the presence of: cyanuric chloride [134], boric acid [135], cerium (VI) triflate [136], Cr(III) [137], tungstic acid [129], titanium molecular sieves [138] and vanadium silicates [139].

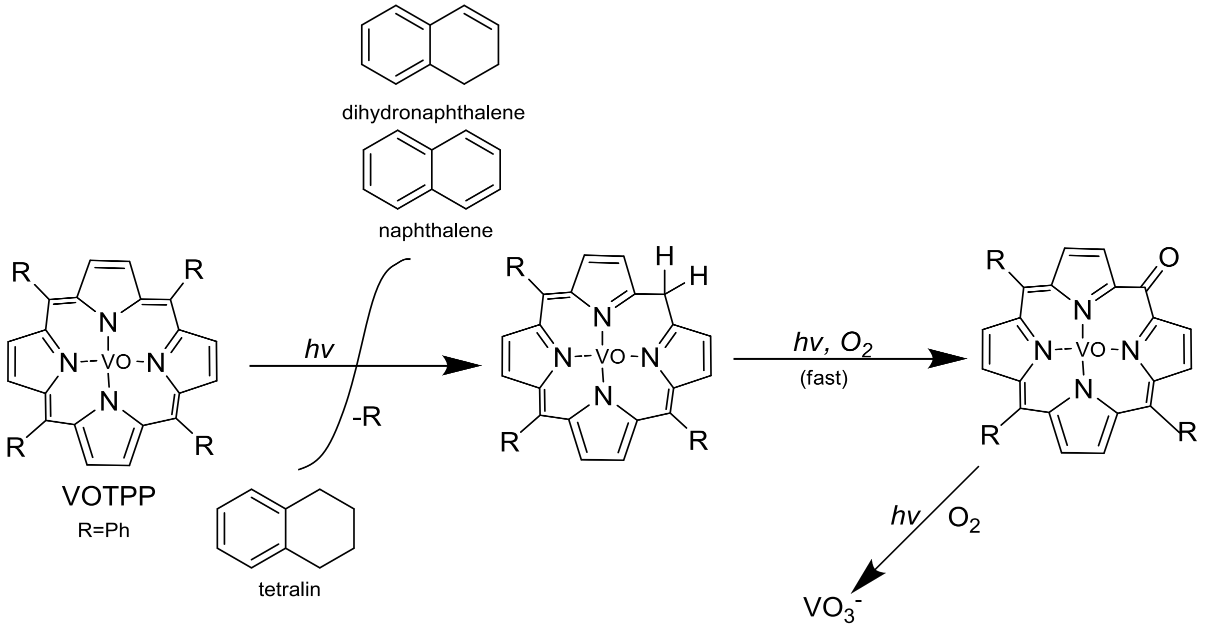
Aerobic oxidation of sulfides to sulfoxides by molecular oxygen is also possible even under atmospheric pressure conditions [140-141]. Bosch and Kochi reported the oxidation of alkyl and aryl thioethers to sulfoxides using molecular oxygen in the presence of catalytic amounts of nitrogen dioxide (NO_2) [142].

1.4.2. Removal of metals from metalloporhyrins

Demetallation of crudes remains a problematic issue in the petroleum industry. As with sulphur and nitrogen, metals like: vanadium and nickel are elements detrimental to petroleum processing. It is important to emphasize that the process of demetallation can be performed simultaneously with desulfurization and denitrogenation during hydroprocessing [143].

Several different methods have been proposed to remove these unwanted matalloporphyrins from the petroleum refinery process [144-145]. Pin Tu *et al.*, proposed a chemical assisted ultrasound method as a way of degradation and demetallation of the porphyrins using H_2O_2 as a radical source [146].

Shiraishi *et al.* investigated new method of demetallation by applying photochemical reaction combined with a liquid-liquid extraction [147]. During this process, the porpyrins in tetralin solution are irradiated with the different wavelengths as shown below (Scheme 1-9). It is worth emphasizing, that the addition of 2-propanol remarkably enhanced the photodecomposition of the metalloporhyrins.



Scheme 1-9: Proposed photodecomposition pathway for VOTPP [147]

1.5. Thesis aims

The objective of this thesis was to develop the chemistry associated with selective oxidation of heavy aromatic compounds so as to upgrade heavy oils, resids and bitumens into more valuable materials and to use this as a pre-treatment step or as a replacement of the coking and hydrocracking processes. Initial work focused on the oxidation of model multiring aromatics compounds (PAH). These model compounds are not as complex as those found in heavy oils, resids and bitumens but they are representative of the aromatic core ring size of PAHs found in nature. In addition, detailed product characterization was carried out in conjunction with material balance studies to determine if the aromatic rings of the PAHs are opened under the reaction conditions employed and fulfil the selective oxidation requirements. A further aim was to adapt ruthenium ion catalysed chemistry for PAHs oxidation and to obtain the required reaction selectivity, simultaneously investigating the limits and potential of this chemistry. Apart from RICO, also H_2WO_4/H_2O_2 system was studied in details for PAHs oxidation. The oxidation of heteroaromatics and the removal of metal from metalloporhyrins became a side aims of this thesis. Next aim of the present work, was to perform studies on variety of chemical system, and find those which fulfil the requirement of selective oxidation chemistry.

1.6. Thesis overview

This thesis describes several methods for the selective oxidation of Polynuclear Aromatic Hydrocarbons and heteroaromatics in conjunction with the removal of metal from metalloporphyrins. This thesis is made up of seven different chapters.

Chapter 1 gives a general introduction into the chemistry of PAHs and the subsequent upgrading of petroleum resids. Literature review of RICO chemistry and other selective catalytic oxidation systems has also been compiled.

Chapter 2 describes the experimental procedures in the synthesis of the compounds, catalysts, reactions and techniques to quantify and identify the products of PAHs oxidation.

Chapter 3 provides details of the investigations on oxidation of PAHs using Ruthenium Ion Catalyzed Oxidation in monophasic solvent system. The main idea by introducing this system was to explore RICO chemistry in better selectivity control.

Chapter 4 further explores RICO chemistry, using a biphasic solvent system. Biphasic solvent system is based on mixture of dichloromethane, acetonitrile and water. Studies in this system investigated product distribution and comparison between product obtained in mono and in biphasic system. What is more, data presented in chapter 4 are related to mechanistic investigation, further application of this system for metal removal and heteroaromatics oxidation.

Chapter 5 introduces the use of H_2WO_4/H_2O_2 chemistry for the selective oxidation of PAHs and the subsequent removal of metals from metalloporphyrins. This chemistry is presented as an alternative to RICO chemistry.

Chapter 6 tries to show different substitutes for RICO and H_2WO_4/H_2O_2 chemistry, especially emphasizing the use of heterogeneous catalysis.

Chapter 7 summarizes the conclusions reached in this thesis and provides suggestions for further research.

1.7. References

1. USEPA, U.S.E.P.A., *Polycyclic Aromatic Hydrocarbons (Pahs)*. 2008.
2. Blumer, M. and Youngblood, W.W., *Science*, **1975**, 188(4183), 53
3. White, C.M. and Lee, M.L., *Geochimica Et Cosmochimica Acta*, **1980**, 44(11), 1825
4. Fetzer, J.C., *Polycyclic Aromatic Compounds*, **2007**, 27(2), 143
5. Registry, A.f.T.S.a.D. *Polycyclic Aromatic Hydrocarbons (PAHs)*. Available from: http://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=25.
6. Lerda D., *Polycyclic Aromatic Hydrocarbons (Pahs) Factsheet*. 2010, European Commission
7. *Toxicological Profile for Polycyclic Aromatic Hydrocarbons*. 2005, U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES: Atlanta.
8. Zeng, Y., Hong, P.K.A., and Wavrek, D.A., *Water Research*, **2000**, 34(4), 1157
9. Joshi, M.M. and Lee, S.G., *Energy Sources*, **1996**, 18(2), 167
10. Joshi, M.M. and Lee, S.G., *Energy Sources*, **1996**, 18(3), 291
11. Ashok, B.T., Saxena, S., Singh, K.P., and Musarrat, J., *World Journal of Microbiology & Biotechnology*, **1995**, 11(6), 691
12. Khanna, G.P., Goyal, D., and Khanna, S., *Bioremediation Journal*, **2011**, 15(1), 12
13. Schneider, J., Grosser, R., Jayasimhulu, K., Xue, W.L., and Warshawsky, D., *Applied and Environmental Microbiology*, **1996**, 62(4), 1491
14. Schneider, J., Grosser, R., Jayasimhulu, K., Xue, W., and Warshawsky, D., *Applied and Environmental Microbiology*, **1996**, 62(1), 13
15. Beltran, F.J., Ovejero, G., Garciaaraya, J.F., and Rivas, J., *Industrial & Engineering Chemistry Research*, **1995**, 34(5), 1607
16. Beltran, F.J., Ovejero, G., Encinar, J.M., and Rivas, J., *Industrial & Engineering Chemistry Research*, **1995**, 34(5), 1596
17. Scott, J.P. and Ollis, D.F., *Journal of Environmental Engineering-Asce*, **1996**, 122(12), 1110
18. Pizzul, L., Sjogren, A., Castillo, M.D., and Stenstroem, J., *Biodegradation*, **2007**, 18(5), 607
19. Speight, J.G., *The Chemistry and Technology of Petroleum*. 4th ed **2006**, Taylor & Francis Group.
20. Hsu, S.C. and Robinson, P.R., *Practical Advances in Petroleum Processing*. **Vol. 2nd 2006**, Springer Science, Business Media Inc.
21. Wang, B. and Manos, G., *Journal of Catalysis*, **2007**, 250(1), 121
22. Dixon, T.W., *Us Refining Economics - a Model Based Approach*, in *Light Metals 2009*, G. Bearne, **2009**. p. 941.
23. *Uop a Honeywell Company*. Available from: http://www.uop.com/refining-flowscheme-2/.
24. Jones, D.S.J. and Pujado, R.P., *Handbook of Petroleum Processing*. **2006**, Dordrecht, Springer.

25. Sawarkar, A.N., Pandit, A.B., Samant, S.D., and Joshi, J.B., *Canadian Journal of Chemical Engineering*, **2007**, 85(1), 1
26. Leyva, C., Rana, M.S., Trejo, F., and Ancheyta, J., *Industrial & Engineering Chemistry Research*, **2007**, 46(23), 7448
27. Francisco, M.A., Garcia, R., Hutchings, G.J., Taylor, S.H., Willock, D.J., Jenkins, R., Sankar, M., Nowicka, E., and Hickey, N., *Upgrading of Heavy Oils, Resids and Bitumens with Selective Oxidation 2*. 2011, Exxon Mobil: New Jersey.
28. Francisco, M.A., Freund, H., Joshi, Y., Siskin, M., Garcia, R., Hutchings, G.J., Taylor, S.H., Willock, D.J., Sankar, M., Nowicka, E., and Hickey, N., *Upgrading of Heavy Oils, Resids and Bitumens with Selective Oxidation 1*. 2010, ExxonMobil: New Jersey.
29. Hermans, I., Spier, E.S., Neuenschwander, U., Turra, N., and Baiker, A., *Topics in Catalysis*, **2009**, 52(9), 1162
30. Hudlicky, M., *Acs American Chemical Society Monograph No. 186. Oxidations in Organic Chemistry*, in *Hudlicky, M. Acs*. **1990**.
31. Centi, G., Corberan, V.C., Perathoner, S., and Ruiz, P., *Catalysis Today*, **2000**, 61(1-4), 1
32. Corey, E.J. and Suggs, J.W., *Tetrahedron Letters*, **1975**(31), 2647
33. Sedelmeier, J., Ley, S.V., Baxendale, I.R., and Baumann, M., *Organic Letters*, **2010**, 12(16), 3618
34. Omura, K. and Swern, D., *Tetrahedron*, **1978**, 34(11), 1651
35. Frigerio, M., Santagostino, M., and Sputore, S., *Journal of Organic Chemistry*, **1999**, 64(12), 4537
36. Dess, D.B. and Martin, J.C., *Journal of Organic Chemistry*, **1983**, 48(22), 4155
37. Parikh, J.R. and Doering, W.V.E., *Journal of the American Chemical Society*, **1967**, 89(21), 5505
38. Corey, E.J. and Kim, C.U., *Journal of the American Chemical Society*, **1972**, 94(21), 7586
39. Djerassi, C. and Engle, R.R., *Journal of Organic Chemistry*, **1953**, 75, 3838
40. Strausz, O.P., Mojelsky, T.W., and Lown, E.M., *The Chemistry of Alberta Oil Sand Bitumen*. International Symposium on Heavy Oil and Residue Upgrading and Utilization : Proceedings, ed. C.R. Han and C. Hsi **1992**. 29.
41. Stock, L.M. and Kwok-tuen, T., *FUEL*, **1983**, 62, 974
42. Wolfe, S., Hasan, S.K., and Campbell, J.R., *Journal of the Chemical Society D-Chemical Communications*, **1970**(21), 1420
43. Orita, H., Hayakawa, T., and Takehira, K., *Bulletin of the Chemical Society of Japan*, **1986**, 59(8), 2637
44. Caputo, J.A. and Fuchs, R., *Tetrahedron Letters*, **1967**(47), 4729
45. Backvall, J.E., *Modern Oxidation Methods*. **2004**, Weinheim, WILEY-VCH.
46. Bailey, A.J., Griffith, W.P., Marsden, S.P., White, A.J.P., and Williams, D.J., *Journal of the Chemical Society-Dalton Transactions*, **1998**(21), 3673
47. Giddings, S. and Mills, A., *Journal of Organic Chemistry*, **1988**, 53(5), 1103
48. Paquette, L.A., Dressel, J., and Pansegrau, P.D., *Tetrahedron Letters*, **1987**, 28(42), 4965
49. Schroder, M. and Griffith, W.P., *Journal of the Chemical Society-Chemical Communications*, **1979**(2), 58
50. Mills, A. and Holland, C., *Journal of Chemical Research-S*, **1997**(10), 368
51. Plietker, B., *Synthesis-Stuttgart*, **2005**(15), 2453
52. Hu, J., Zhang, D., and Harris, F.W., *Journal of Organic Chemistry*, **2005**, 70(2), 707

53. Carlsen, P.H.J., Katsuki, T., Martin, V.S., and Sharpless, K.B., *Journal of Organic Chemistry*, **1981**, 46(19), 3936
54. Coudret, J.L., Zollner, S., Ravoo, B.J., Malara, L., Hanisch, C., Dorre, K., deMeijere, A., and Waegell, B., *Tetrahedron Letters*, **1996**, 37(14), 2425
55. Piccialli, V., Smaldone, D.M.A., and Sica, D., *Tetrahedron*, **1993**, 49(20), 4211
56. Shing, T.K.M., Tam, E.K.W., Tai, V.W.F., Chung, I.H.F., and Jiang, Q., *Chemistry-a European Journal*, **1996**, 2(1), 50
57. Yamaoka, H., Moriya, N., and Ikunaka, M., *Organic Process Research & Development*, **2004**, 8(6), 931
58. Morikawa, K., Park, J., Andersson, P.G., Hashiyama, T., and Sharpless, K.B., *Journal of the American Chemical Society*, **1993**, 115(18), 8463
59. Momiyama, N. and Yamamoto, H., *Journal of the American Chemical Society*, **2003**, 125(20), 6038
60. Plietker, B., *European Journal of Organic Chemistry*, **2005**(9), 1919
61. Bifulco, G., Caserta, T., Gomez-Paloma, L., and Piccialli, V., *Tetrahedron Letters*, **2003**, 44(29), 5499
62. Bifulco, G., Caserta, T., Gomez-Paloma, L., and Piccialli, V., *Tetrahedron Letters*, **2002**, 43(50), 9265
63. Yang, D., Chen, F., Dong, Z.M., and Zhang, D.W., *Journal of Organic Chemistry*, **2004**, 69(6), 2221
64. Petride, H., Costan, O., Draghici, C., Florea, C., and Petride, A., *Arkivoc*, **2005**, 18
65. Su, W.G., *Tetrahedron Letters*, **1994**, 35(28), 4955
66. Imajo, S., Kuritani, H., Shingu, K., and Nakagawa, M., *Journal of Organic Chemistry*, **1979**, 44(20), 3587
67. Thomas, J.M., Raja, R., Sankar, G., and Bell, R.G., *Nature*, **1999**, 398(6724), 227
68. Estrada, A.C., Simoes, M.M.Q., Santos, I.C.M.S., Neves, M.G.P.M.S., Cavaleiro, J.A.S., and Cavaleiro, A.M.V., *Chemcatchem*, **2011**, 3(4), 771
69. Bakke, J.M. and Braenden, J.E., *Acta Chemica Scandinavica*, **1991**, 45(4), 418
70. Tenaglia, A., Terranova, E., and Waegell, B., *Journal of Organic Chemistry*, **1992**, 57(20), 5523
71. Tabatabaeian, K., Mamaghani, M., Mahmoodi, N.O., and Khorshidi, A., *Catalysis Communications*, **2008**, 9(3), 416
72. Frunzke, J., Loschen, C., and Frenking, G., *Journal of the American Chemical Society*, **2004**, 126(11), 3642
73. Coudret, J.L. and Waegel, B., *Inorganica Chimica Acta*, **1994**, 222(1-2), 115
74. Murata, S., Uesaka, K., Inoue, H., and Nomura, M., *Abstracts of Papers of the American Chemical Society*, **1994**, 208, 63
75. Lee, D.G., Spitzer, U.A., Cleland, J., and Olson, M.E., *Canadian Journal of Chemistry-Revue Canadienne De Chimie*, **1976**, 54(13), 2124
76. Wang, Z.J., Que, G.H., Liang, W.J., and Qian, J.L., *Abstracts of Papers of the American Chemical Society*, **1998**, 215, U136
77. Ma, A., Zhang, S., and Zhang, D., *Organic Geochemistry*, **2008**, 39(11), 1502
78. Artok, L., Su, Y., Hirose, Y., Hosokawa, M., Murata, S., and Nomura, M., *Energy & Fuels*, **1999**, 13(2), 287
79. Zhang, H., Yan, Y., Cheng, Z., and Sun, W., *Petroleum Science and Technology*, **2008**, 26(16), 1945
80. Stock, L.M., Tse, K.T., and Wang, S.H., *Abstracts of Papers of the American Chemical Society*, **1985**, 190(SEP), 113

81. Murata, S., Uesaka, K., Inoue, H., and Nomura, M., *Energy & Fuels*, **1994**, 8(6), 1379
82. Payzant, J.D., Lown, E.M., and Strausz, O.P., *Energy & Fuels*, **1991**, 5(3), 445
83. Huang, Y.-G., Zong, Z.-M., Yao, Z.-S., Zheng, Y.-X., Mou, J., Liu, G.-F., Cao, J.-P., Ding, M.-H., Cai, K.-Y., Wang, F., Zhao, W., Xia, Z.-L., Wu, L., and Wei, X.-Y., *Energy & Fuels*, **2008**, 22(3), 1799
84. Peng, P.a., Fu, J., and Sheng, G., *Energy & Fuels*, **1999**, 13, 266
85. Stock, L.M. and Wang, S.H., *Fuel*, **1987**, 66(7), 921
86. Stock, L.M. and Wang, S.H., *Fuel*, **1985**, 64(12), 1713
87. Mendez, A., Bermejo, J., Santamaria, R., Blanco, C.C., and Menendez, R., *Energy & Fuels*, **2000**, 14, 936
88. Noyori, R., Aoki, M., and Sato, K., *Chemical Communications*, **2003**(16), 1977
89. Leeds, A.R., *Ber. Dtsch. Chem. Ges*, **1881**, 14, 1382
90. Milas, N.A. and Sussman, S., *Journal of the American Chemical Society*, **1936**, 58, 1302
91. Cook, J.W. and Schoental, R., *Journal of the Chemical Society*, **1950**(JAN), 47
92. Tandon, P.K., Baboo, R., Singh, A.K., Purwar, G., and Purwar, M., *Applied Organometallic Chemistry*, **2005**, 19(10), 1079
93. Tandon, P.K., Baboo, R., Singh, A.K., and Gayatri, *Applied Organometallic Chemistry*, **2006**, 20(1), 20
94. Oberender, F.G. and Dixon, J.A., *Journal of Organic Chemistry*, **1959**, 24(9), 1226
95. Shi, F., Tse, M.K., and Beller, M., *Advanced Synthesis & Catalysis*, **2007**, 349(3), 303
96. Wienhoefer, G., Schroeder, K., Moeller, K., Junge, K., and Beller, M., *Advanced Synthesis & Catalysis*, **2010**, 352(10), 1615
97. Oconnor, W.F. and Moriconi, E.J., *Industrial and Engineering Chemistry*, **1953**, 45(2), 277
98. Neumann, R. and Gara, M., *Journal of the American Chemical Society*, **1995**, 117(18), 5066
99. Ishii, Y., Yamawaki, K., Ura, T., Yamada, H., Yoshida, T., and Ogawa, M., *Journal of Organic Chemistry*, **1988**, 53(15), 3587
100. Kamata, K., Yonehara, K., Sumida, Y., Yamaguchi, K., Hikichi, S., and Mizuno, N., *Science*, **2003**, 300(5621), 964
101. Bordoloi, A., Lefebvre, E., and Halligudi, S.B., *Journal of Catalysis*, **2007**, 247(2), 166
102. Lukasiewicz, M., Bogdal, D., and Pielichowski, J., *Molecular Diversity*, **2006**, 10(3), 491
103. Giri, N.G. and Chauhan, S.M.S., *Catalysis Communications*, **2009**, 10(4), 383
104. Lane, B.S. and Burgess, K., *Chemical Reviews*, **2003**, 103(7), 2457
105. Payne, G.B. and Smith, C.W., *Journal of Organic Chemistry*, **1957**, 22(12), 1682
106. Payne, G.B. and Williams, P.H., *Journal of Organic Chemistry*, **1959**, 24(1), 54
107. Jacobson, S.E., Muccigrosso, D.A., and Mares, F., *Journal of Organic Chemistry*, **1979**, 44(6), 921
108. Sato, K., Aoki, M., Takagi, J., Zimmermann, K., and Noyori, R., *Bulletin of the Chemical Society of Japan*, **1999**, 72(10), 2287
109. Sato, K., Hyodo, M., Takagi, J., Aoki, M., and Noyori, R., *Tetrahedron Letters*, **2000**, 41(9), 1439
110. Venturello, C., Alneri, E., and Ricci, M., *Journal of Organic Chemistry*, **1983**, 48(21), 3831

111. Quenard, M., Bonmarin, V., and Gelbard, G., *Tetrahedron Letters*, **1987**, 28(20), 2237
112. Sato, K., Hyodo, M., Aoki, M., Zheng, X.Q., and Noyori, R., *Tetrahedron*, **2001**, 57(13), 2469
113. Barrio, L., Campos-Martin, J.M., and Fierro, J.L.G., *Journal of Physical Chemistry A*, **2007**, 111(11), 2166
114. Saito, Y., Shinichi, A., Yoshio, S., and Naoji, K., *Process for Producing Aromatic Dicarboxylic Acids*. **1989**: United States.
115. Young, E.R.R. and Funk, R.L., *Journal of Organic Chemistry*, **1998**, 63(26), 9995
116. Zhang, X.W., Shen, S.C., Yu, L.E., Kawi, S., Hidajat, K., and Simon Ng, K.Y., *Applied Catalysis A: General*, **2003**, 250, 341
117. Ntainjua, E.N., Davies, T.E., Garcia, T., Solsona, B., and Taylor, S.H., *Catalysis Letters*, **2011**, 141(12), 1732
118. Berenblum, I. and Schoental, R., *Biochemical Journal*, **1945**, 39(5), R64
119. Cook, J.W. and Schoental, R., *Journal of the Chemical Society*, **1948**, 2, 170
120. Dean, F.M. and Knight, J.C., *Journal of the Chemical Society*, **1962**(DEC), 4745
121. Harries, C., *Justus Liebigs Annalen Der Chemie*, **1905**, 343(1/3), 311
122. Moriconi, E.J., Rakoczy, B., and Oconnor, W.F., *Journal of the American Chemical Society*, **1961**, 83(22), 4618
123. Schmitt, W.J., Moriconi, E.J., and Oconnor, W.F., *Journal of the American Chemical Society*, **1955**, 77(21), 5640
124. Cataldo, F. and Keheyan, Y., *Journal of Radioanalytical and Nuclear Chemistry*, **2006**, 267(3), 679
125. Ranganathan, S., Ranganathan, D., and Ramachandran, P.V., *Tetrahedron*, **1984**, 40(16), 3145
126. Jeyaraman, R. and Murray, R.W., *Journal of the American Chemical Society*, **1984**, 106(8), 2462
127. Meunier, B., *Chemical Reviews*, **1992**, 92(6), 1411
128. Higuchi, T., Satake, C., and Hirobe, M., *Journal of the American Chemical Society*, **1995**, 117(34), 8879
129. Campos-Martin, J.M., Capel-Sanchez, M.C., and Fierro, J.L.G., *Green Chemistry*, **2004**, 6(11), 557
130. Zhang, T., Anand, N., and Hoover, T.S., *Sulfone Removal from an Oxidized Hydrocarbon Fuel*. **2012**: U.S.
131. Lim, S.M., Kim, J.N., Park, J., Han, S.S., Park, J.H., Jung, T.S., Yoon, H.C., Kim, S.H., and Ko, C.H., *Energy & Fuels*, **2012**, 26(4), 2168
132. Kwon, J.M., Moon, J.H., Bae, Y.S., Lee, D.G., Sohn, H.C., and Lee, C.H., *Chemsuschem*, **2008**, 1(4), 307
133. Kaczorowska, K., Kolarska, Z., Mitka, K., and Kowalski, P., *Tetrahedron*, **2005**, 61(35), 8315
134. Lakouraj, M.M., Abdi, H., and Hasantabar, V., *Journal of Sulfur Chemistry*, **2011**, 32(5), 435
135. Rostami, A. and Akradi, J., *Tetrahedron Letters*, **2010**, 51(27), 3501
136. Raju, B.R., Sarkar, S., Reddy, U.C., and Saikia, A.K., *Journal of Molecular Catalysis a-Chemical*, **2009**, 308(1-2), 169
137. Supale, A.R. and Gokavi, G.S., *Catalysis Letters*, **2008**, 124(3-4), 284
138. Hulea, V., Fajula, F., and Bousquet, J., *Journal of Catalysis*, **2001**, 198(2), 179
139. Shiraishi, Y., Naito, T., and Hirai, T., *Industrial & Engineering Chemistry Research*, **2003**, 42(24), 6034

140. Iwahama, T., Sakaguchi, S., and Ishii, Y., *Tetrahedron Letters*, **1998**, 39(49), 9059
141. Boring, E., Geletii, Y.V., and Hill, C.L., *Journal of the American Chemical Society*, **2001**, 123(8), 1625
142. Bosch, E. and Kochi, J.K., *Journal of Organic Chemistry*, **1995**, 60(10), 3172
143. Callejas, M.A. and Martinez, M.T., *Energy & Fuels*, **1999**, 13(3), 629
144. Sugihara, J.M. and Garvey, R.G., *Analytical Chemistry*, **1964**, 36(12), 2374
145. Eisner, U. and Harding, M.J.C., *Journal of the Chemical Society*, **1964**(NOV), 4089
146. Tu, S.P. and Yen, T.F., *Energy & Fuels*, **2000**, 14(6), 1168
147. Shiraishi, Y., Hirai, T., and Komasawa, I., *Industrial & Engineering Chemistry Research*, **2000**, 39(5), 1345

2. Experimental

2.1. Introduction

This chapter provides information about the reactions carried out in this thesis. The first section describes the chemicals and reactors used in the experiments. The synthesis of compounds and catalysts are also explained. The last section of this chapter is dedicated to the description of experiments and the qualitative and quantitative chemical analysis techniques used.

2.2. Chemicals used

All the chemicals purchased from commercial sources were of high purity and were used without further purification. Chemicals provided by ExxonMobil were of unknown purity and were used without further purification. A full list of the chemicals used in this study is provided below.

Table 2-1: List of chemicals used in the experiments

Chemical	**Purity**	**Supplier**
Acetonitrile	99.95%	Fisher Scientific
Dichloromethane	99.5%	Fisher Scientific
Toluene	99%	Fisher Scientific
H_2O		HPLC grade, Sigma-Aldrich
Propionitrile	99%	Aldrich
Chloroform-D	99.8%D	Euriso-Top
Acetonitrile-D3	98%D	Cambridge Isotope Laboratories Inc
DMSO	98%D	Euriso-Top
D_2O	99.9%	Euriso-Top
$NaIO_4$	>99%	Sigma-Aldrich
$RuCl_3 \cdot xH_2O$ (used name: $RuCl_3$)	98%	Aldrich
H_2WO_4	99%	Aldrich
Aliquat 336	100%	Aldrich
2-Butanol	>99.5%	Fluka
Ethylbenzene	99.8%	Sigma-Aldrich
2-Ethylnaphthalene	99%	Sigma-Aldrich

Naphthalene	99%	Aldrich
Phenanthrene	98%	Aldrich
Pyrene	98%	Aldrich
Chrysene	92%	Aldrich
Perylene	≥99%	Fluka
Benzothiophene	99%	Acros
Dibenzothiophene	98%	Aldrich
Indole	≥99%	Aldrich
Carbazole	96%	Aldrich
Dodecyl sulfide	93%	Aldrich
1-Octadecylnaphthalene	unknown	ExxonMobil
1-Decylnaphthalene	unknown	ExxonMobil
2-Nonylphenanthrene	unknown	ExxonMobil
9-Octadecylphenanthrene	unknown	ExxonMobil
1-Octadecylpyrene	unknown	ExxonMobil
1-Butylpyrene	unknown	ExxonMobil
1-Decylpyrene	unknown	ExxonMobil
Vanadyl tetraphenylporphyrin	97%	Stream Chemicals
Nickel tetraphenylporphyrin	97%	Stream Chemicals
5,10,15,20-Tetraphenyl 21*H*,23*H*-porphine	97%	Sigma-Aldrich
H_2O_2	35%, 50%	Sigma-Aldrich
Tert-butyl hydrogen peroxide (TBHP)	70% aq. solution	Acros
$H_3PMo_{12}O_{40}$	99.99%	Sigma-Aldrich
$H_3PW_{12}O_{40}$	99.995%	Sigma-Aldrich

2.3. Preparation of compounds

2.3.1. Pyrene-4,5-dione

Pyrene-4,5-dione was synthesised following a procedure previously reported in the literature [1]. To a solution of pyrene (5mmol) in CH_2Cl_2 (20.0ml) and CH_3CN (20.0ml), $NaIO_4$ (5.0g, 23.4mmol), H_2O (25.0ml), and $RuCl_3{\cdot}xH_2O$ (0.10g, 0.48mmol) were subsequently added. The mixture was stirred for 15h at 295- 298K followed by the addition of water (200ml), the aqueous and organic phase were then separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 20ml), these CH_2Cl_2 extracts were combined with the organic phase and washed with H_2O (50ml) to yield a dark orange solution. The solvent was removed under reduced pressure to afford a dark orange solid. Column chromatography gave bright orange crystals. Melting point: 308°C (lit. 299-302°C),^{13}C NMR (500MHz, $CDCl_3$): δ 180.5, 135.9, 132.1, 130.2, 130.20, 128.5, 128.1, 127.4, ^1H NMR (400MHz, $CDCl_3$): δ 8.42 (dd, 2H, J=8Hz), 8.11 (dd, 2H, J=8Hz), 7.78 (s, 2H), 7.72 (t, 2H, J=8Hz), calculated mass for $C_{16}H_8O_2$ is 232.05, found 232.07 (EI) (Appendix 8.1).

2.3.2. Pyrene-4,5,9,10-tetraone

Synthesis of pyrene-4,5,9,10-tetraone was carried out following a previously reported literature method [1]. To a solution of pyrene (5 mmol) in CH_2Cl_2 (20.0 ml) and CH_3CN (20.0 ml), $NaIO_4$ (9g, 40.4 mmol), H_2O (25.0 ml) and $RuCl_3{\cdot}xH_2O$ (0.6 g, 0.6 mmol) were added. The dark brown suspension was heated at 308K overnight. The cooled reaction mixture was poured into a flask of H_2O (100ml) and the resultant solid recovered by filtration and washed with H_2O (250ml). The organic and aqueous phase of the filtrate were subsequently separated and the aqueous phase extracted with CH_2Cl_2 (3 x 25ml). The organic extracts were combined with the organic phase of the filtrate and washed with H_2O (3 x 50 ml) to give a dark green solution. The solvent was removed under vacuum to yield more green material, which was combined with the dark green product previously isolated by filtration. After column chromatography a bright yellow orange powder was obtained with a melting point mp >350 °C. ^1H NMR spectrum: (400 MHz, DMSO-d_6) δ 8.34 (d, 4H, J=8Hz), 7.73 (t, 2H, J=7.7Hz). No ^{13}C NMR spectra was obtained because of the poor product solubility. Calculated mass for $C_{16}H_6O_4$ is 262.03, mass found 262.0262 (EI) (Appendix 8.2).

2.4. Preparation of catalyst

2.4.1. 1%, 20%WO_3/TiO_2

The WO_3/TiO_2 catalyst was prepared following the procedure previously reported in the literature [2]. TiO_2 (1g, P25, Degusa) was dissolved in a 1M ammonia solution (50 ml) containing the appropriate amount of H_2WO_4 (0.27g or 0.0136g). The slurry obtained was evaporated to dryness at 80-100°C under vigorous stirring. The powder formed was calcined at 400°C for 4h in static air. The heating rate was set at 5°C/min. The furnace was allowed to cool to room temperature and the catalyst in the form of a white powder removed from the furnace and used in the reaction.

2.4.2. Ion exchange of polyoxometalates

Cs salts of the heteropolyacids ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$) were prepared via the addition of the desired amount of aqueous Cs_2CO_3 (≥98%, Fluka) to an aqueous solution of the heteropolyacids ($H_3PMo_{12}O_{40}$, $H_4PW_{12}O_{40}$)(0.14g Cs_2CO_3 to 1g $H_4PW_{12}O_{40}$/0.223g Cs_2CO_3 to 1g $H_3PMo_{12}O_{40}$). The addition of the Cs_2CO_3 solution to the free heteropolyacid was carried out dropwise using a pipette. After the slow evaporation of the slurry (without filtration), the solid material was dried in static air for 20 hours at 120˚C [3].

Preparation of Cs exchanged polyoxometalates supported on ZrO_2 was carried out following the procedure previously reported in the literature [4-6]. Firstly, ZrO_2 was prepared by hydrolyzing an aqueous solution of $ZrOCl_2 \cdot H_2O$ (0.5M) with ammonia (10M) to a pH of 10. The precipitate was filtered and washed with deionised water. The precipitate was dried at 120°C for 36h in static air. The next step of the preparation was to support HPA on ZrO_2 via a impregnation method. The required amount of $H_3PW_{12}O_{40}$ or $H_3PMo_{12}O_{40}$ (0.4g) was dissolved in water and added dropwise to the aqueous solution of ZrO_2 (3.6g ZrO_2 in 5 ml H_2O). The solution was allowed to rest for 3h and the excess water evaporated using a heated water bath, dried at 120°C for 12h and finally calcined in static air at 300°C for 2h. Cs was exchanged with the protons of the TPA supported on ZrO_2 in the ratio of 2.5:1, this value being theoretically calculated (0.028g Cs_2CO_3 added to 1g 20%$H_3PW_{12}O_{40}/ZrO_2$ / 0.045g to 1g 20%$H_3Mo_{12}O_{40}P/ZrO_2$). The required quantity of Cs_2CO_3 was dissolved in water and added dropwise to HPA/ZrO_2. The excess water was removed via evaporation on a heated water bath, the material was dried at room temperature in air for 12h before being calcined at 300°C for 2h in static air. The active component deposited on the ZrO_2 was kept at a constant value, 20 wt %.

2.4.3. Supported metal catalysts

2.4.3.1. Preparation of 5%Ru/TiO_2

A 5% Ru/TiO_2 catalyst was prepared via a impregnation method. Firstly, $RuCl_3$ (0.102g) was added to a vessel containing TiO_2 (1g, P25, Degussa) dissolved in 5ml of H_2O, the contents of the flask was stirred for 20mins and the excess water removed via evaporation. The resultant catalyst was dried in static air at 120°C for 12h. After drying 0.1g of the prepared catalyst was used in the reaction. A further 0.5g portion of the catalyst was calcined at 400°C for 4h in flowing air. The heating rate was set at 10°C/min. The furnace was allowed to cool to room temperature and the catalyst was removed from the furnace and used in the reaction. The photograph of calcinations furnace and its description is shown below, Figure 2-1.

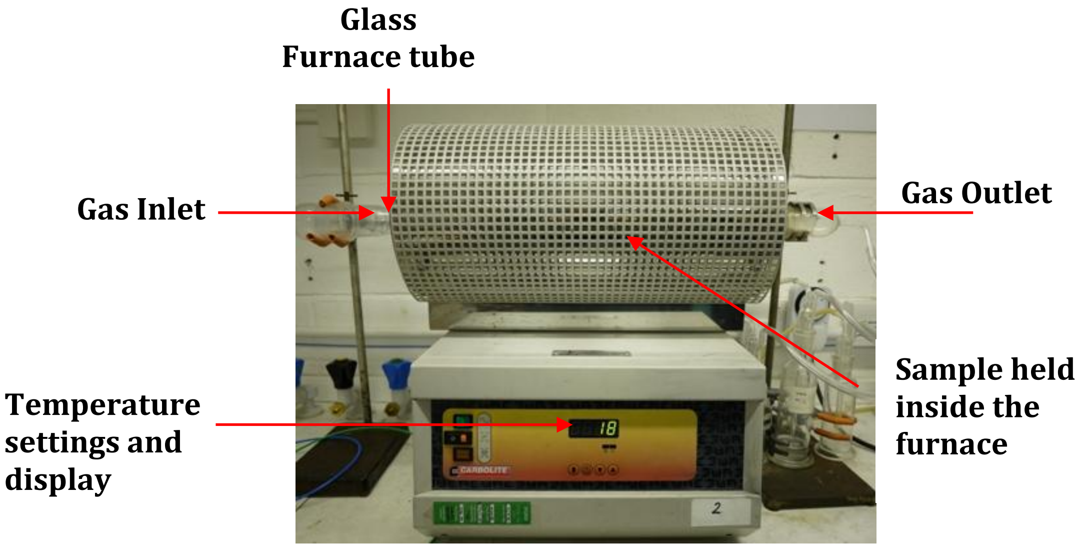


Figure 2–1: Photograph of calcination furnace

2.4.3.2. Preparation of 2.5% Ru/Co_3O_4

A 2.5% Ru supported on Co_3O_4 catalyst was prepared via an adsorption precipitation method previously reported in the literature [7]. Co_3O_4 (1g, 99.5%, Aldrich) was added to an aqueous solution of $RuCl_3$ (0.0524g in 30 ml). The suspension was stirred for 1h at room temperature. Subsequently an aqueous solution of NaOH (1M) was added dropwise to the solution to adjust the pH level to 13, the resultant suspension was further stirred for 1h. The solid catalyst was recovered by filtration and washed thoroughly with deionised water. The resultant solid was washed with ethanol and then dried at room temperature in a vacuum oven. After 24 hours the catalyst was removed from the oven and used in the reaction.

2.4.3.3. Preparation of nano-Ru on hydroxyapatite

The preparation of this catalyst was carried out following a procedure previously published by Fievet *et al.*[8]. Firstly, 0.32 mmols of $RuCl_3·xH_2O$ was dissolved in 50 ml of 1,2-propanediol solution, followed by the addition of 1mmols $NaOAc·3H_2O$, the contents of the flask was heated to 150°C until the solution changed colour from dark red to dark brown. The mixture was transferred to a separating funnel and extracted with toluene and dodecane thiol. After separating the toluene and thiol from the aqueous layer, 0.4g of hydroxyapatite was added to the organic phase and stirred for 24h in air at room temperature. The resultant colloids were filtered, washed with H_2O and the grey-brown solid generated was dried for 24h in a vacuum oven at 110°C prior to its use.

2.4.3.4. Preparation of Au-Pd catalysts: Sol Immobilisation

Au–Pd supported materials were prepared via a sol-immobilisation method. Aqueous solutions of $PdCl_2$ (6mg/ml), $HAuCl_4·3H_2O$ (8.9mg/ml),polyvinyl alcohol (PVA) (1 wt% aqueous solution, (Aldrich, MW=10 000, 80% hydrolyzed) and an aqueous solution of $NaBH_4$ (0.1M) were prepared. To a 800ml of H_2O, aqueous $PdCl_2$ (1.17ml) and $HAuCl_4$ solution (1.46ml) of the desired concentration were added under continuous stirring. Then 1.3ml of a PVA solution (1 wt%) (PVA/(Au + Pd) (w/w) = 1.2) and a freshly prepared solution of $NaBH_4$ (0.1M, $NaBH_4$/(Au + Pd) (mol/mol) = 5)(6.6ml) was added to form a dark-brown sol. After 30min of sol generation, the colloid was immobilized via the addition of the support, 1.98g of TiO_2 (Degussa, P25/ Graphite G60) (acidified to a pH of 1 by sulphuric acid) under vigorous stirring. The amount of support material required was calculated so as to have a total final metal loading of 1%wt. The metal ratio for the 1wt%Au+Pd on TiO_2 catalyst was 1 : 1molar. After 2h, the resultant slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 120°C in the oven overnight under static air [9].

2.4.3.5. Preparation of Au-Pd catalysts: Modified Impregnation

$HAuCl_4·3H_2O$ (Sigma Aldrich) was used as the gold precursor and dissolved in deionised water to give a gold solution at a gold concentration of 8.9mg/ml. The $PdCl_2$ (Sigma Aldrich) salt was dissolved in aqueous HCl solution (0.58M) with gentle warming and vigorous stirring to form a Pd solution at concentration of 6mg/ml. This solution was cooled and used as the palladium precursor. During the synthesis, the requisite amount of gold (1.46ml) and palladium solution (1.17ml) were transfered to a clean round bottom flask (50ml) fitted with a magnetic stirrer bar. The volume of the solution was adjusted using deionised water to give a total volume of 16ml. The round bottom flask was immersed in an oil bath sited on a magnetic stirrer hot plate. The solution was stirred vigorously at 1000rpm and the temperature of the oil bath raised from 27°C to 60°C over a period of 10min. Once the solution was at 60°C, the desired metal oxide support material (1.98g) [TiO_2 (Degussa Evonik P25), C (Darco G60, Sigma Aldrich), MgO (BDH)] was slowly added over a period of 8-10min with constant stirring. After the complete addition of the support, the slurry was stirred at 60°C for an additional 15min. The temperature of the oil bath was subsequently raised to 95°C and the slurry stirred at this temperature for 16h or until all the water evaporated to yield a dry solid. The solid powder was transferred to a mortar and pestle and ground thoroughly to form a uniform mixture. This catalyst was stored and designated as a “dried-only” sample. A portion of the “dried-only” sample (400mg) was transferred to a glass calcination boat (30cm in length). The temperature of the furnace was raised from 30°C to 400°C at a heating rate of 10°C/min under a steady flow of 5%H_2 in Ar and held at 400°C for 4hrs. The furnace was allowed to cool to room temperature and the “reduced” sample used as a catalyst [10].

2.5. Reactors and equipment

Three different reactors: jacketed reactor, Parr autoclave reactor and glass reactor were used in the oxidation of PAHs. A detailed description of each reactor is given below.

2.5.1. Jacketed reactor

Catalytic oxidation reactions were performed in a 50 ml, jacketed glass round bottom flask sealed with a rubber septum. The reaction mixture was stirred using a magnetic stirrer bar. The jacket of the reactor was connected to a thermostated water bath (Julabo F25-ME Refrigerated/Heating Circulator) fitted with a water pump which circulated the water around the reaction vessel at the desired reaction temperature (Figure 2-2). The temperature was maintained at 22°C for all reactions unless stated otherwise, the stirring speed was set at 500rpm for the RICO reaction.

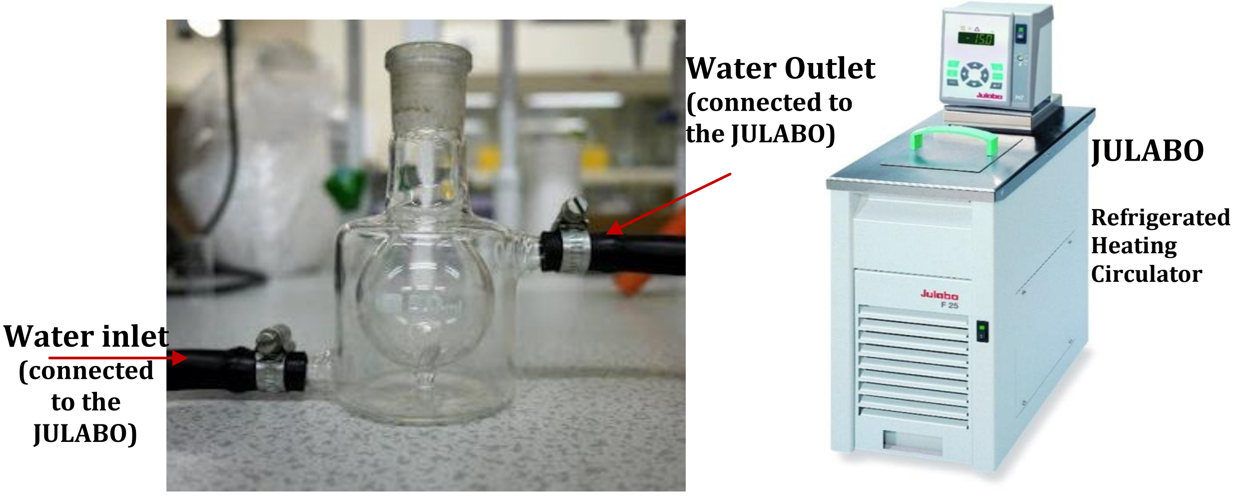


Figure 2–2: Photograph of the Glass Jacketed Reactor (left) and the JULABO thermostated water bath (right)

2.5.2. Parr autoclave reactor

High pressure oxidation of pyrene or 2-ethylnaphthalene was carried out in a 50ml Parr autoclave system over a temperature range 90-150°C. Detailed information about the reaction conditions employed is provided in chapter 6. The picture of reactor with description of apparatus is given below, Figure 2-3. The reaction system was always purged prior to use with oxygen and the oxygen reaction pressure was maintain in the range 20-30bar. The solvent volume used in the reaction was 10ml. The oxidation of 2-ethylnaphthalene was carried out under solvent free conditions. The reaction time was varied between 4 and 48 hours. Stirring speed was maintained at 1000rpm.

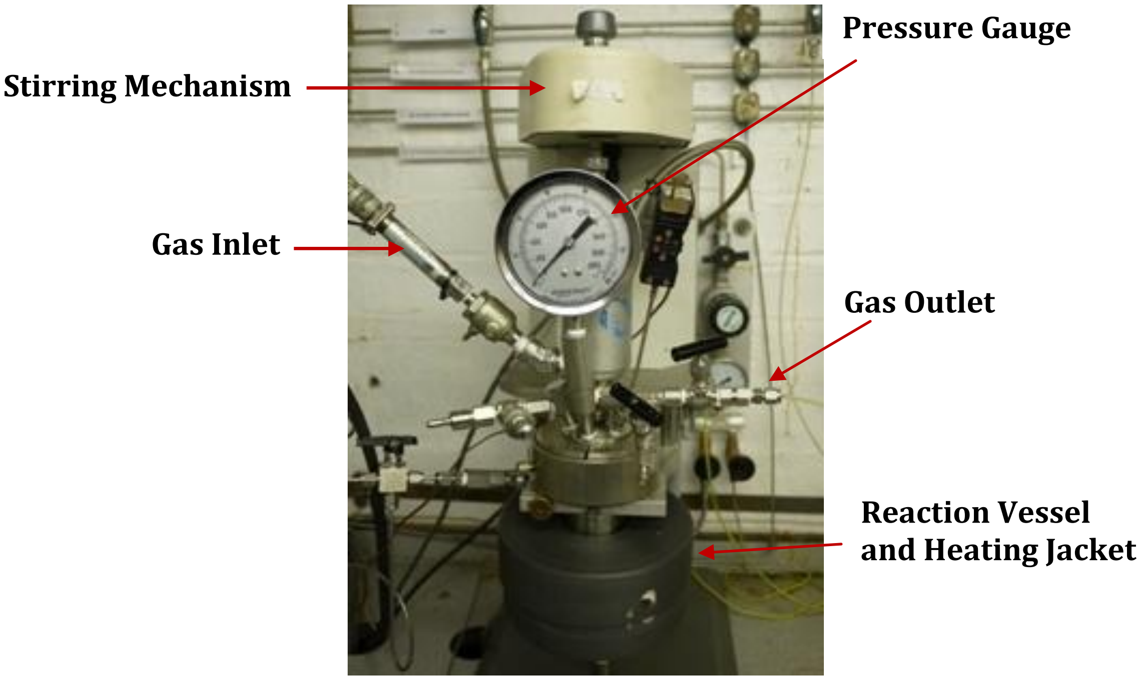


Figure 2–3: Photograph of Parr autoclave reactor

2.5.3. Glass reactor

Oxidation reactions were also carried out in a glass round bottom flask (10-100ml) fitted with a water cooled condenser or sealed with a rubber septum. The glass reactor was heated using either a heated oil or water bath. Stirring was achieved via a magnetic pellet held inside the reactor and set to run at either 500,700 or 1000rpm.

2.6. Description of oxidation procedures

2.6.1. Ruthenium Ion Catalyzed Oxidation

As previously mentioned Ruthenium Ion Catalyzed Oxidation refers to the active species RuO_4, generated *in situ* by combination of a ruthenium ion and an oxidizing agent. In reactions presented in this chapter, $RuCl_3 \cdot xH_2O$ was used as the ruthenium source and as a catalyst with $NaIO_4$ as the oxidant.

2.6.1.1. Monophasic solvent system

Reactions conducted in a monophasic solvent system consisted of two solvents which are miscible, i.e.: water and acetonitrile. In a typical reaction, the jacketed reactor was charged with the requisite amount of substrate (0.164mmols) and the solvent acetonitrile (20ml) and the reaction temperature was set for 22°C. To this solution, an aqueous solution of $NaIO_4$ (280mg, 1.312mmols dissolved in 10ml H_2O) was added and stirred for 1 min (Stirring speed: 500rpm). The solid $RuCl_3 \cdot xH_2O$ (2.5mg, 0.012mmols) was added to the above mixture and this denoted the start of the reaction. During the course of the reaction, small aliquots of the reaction mixture (0.5ml) were withdrawn at regular time intervals and quantitatively analyzed by gas chromatography. For accurate kinetic data, the samples were quenched, immediately after withdrawal, via the addition of an aqueous solution of Na_2SO_3 (0.1ml, 1.403mmols in 6 ml H_2O). A 0.3ml portion of the quenched sample was added to 0.03ml of the external standard, 2-butanol and shaken vigorously. 0.1µl of this solution was injected into the GC fitted with VF-5ht (30m, 0.25mm) column.

For HPLC analysis the reaction was run in a mixture of acetonitrile (30 ml) and H_2O (10 ml). The amount of substrate used in the reaction was limited by its solubility in MeCN and was kept at a concentration of $3.5x10^{-5}$ mols. The *substrate: oxidant: catalyst* ratio was kept at 1 : 8 : 0.1. For kinetic measurements, the samples (1 ml) were quenched by adding 0.1ml of an aqueous Na_2SO_3 solution(0.065g in 5ml H_2O) and combined with 0.1ml of the external standard, naphthalene (0.015g in MeCN). 5µl of this solution was injected on the HPLC column (Zorbax Eclipse Plus Phenyl-Hexyl 4.6x150mm, 3.5µm) via an autosampler.

2.6.1.2. Biphasic solvent system

All reactions performed in biphasic solvent system used dichloromethane (16ml), acetonitrile (7ml) and H_2O (7ml) as a solvent system. Product identification and kinetic studies were carried out using the same methodology as previously describe in section 2.6.1.1. First, the round bottom flask of jacketed reactor was charged with substrate (0.131mmols) dissolved in DCM and MeCN, then an aqueous solution of $NaIO_4$ (224mg, 1.048mmols dissolved in 7ml H_2O) was added and stirred for 1 min (Stirring speed: 500rpm). Addition of $RuCl_3$ (0.01mmol) commenced the reaction. All samples taken for analysis were withdrawn from the organic layer unless stated, as the substrates are not soluble in the aqueous phase which was proven by the following procedure. Three substrate samples of different weight (10mg, 25mg and 50mg) were dissolved in a acetonitrile (3ml), dichloromethane (3ml) and H_2O (5ml) solvent mixture. The mixtures were stirred for 10mins and a 1ml portion extracted from the organic layer of each solution was taken and combined with an external standard (2-butanol, 0.1 ml), shaken vigorously and injected (0.5µl) into the GC. The same procedure was carried out for the aqueous layer. The area derived from the GC trace of the organic and aqueous layers were integrated and normalized. The percentage distribution of the substrate in the organic layer was calculated to be 99% for pyrene, 98% for phenanthrene and 95% for naphthalene.

HPLC-MS was used to determine the products of pyrene oxidation in a biphasic solvent system. After the desired reaction time, the reaction was quenched and the organic and aqueous layers separated. The organic layer was evaporated to dryness, the resultant solid was redissolved in 1ml of acetonitrile and added to a solution of the external standard, benzophenone (0.1ml, C=0.001 mol dm^{-3}) prior to analysis by HPLC-MS. For the aqueous layer a portion of the sample (0.6 ml) was combined with MeCN (0.4ml) and solution (0.1ml, C=0.001 mol dm^{-3}) to make a total volume of 1.1 ml. The injection volume used for both phases was 0.5µl.

Samples analyzed by GC-MS were always directly withdrawn from the reaction mixture, both organic and aqueous layer and analyzed without any workup.

2.6.1.3. Porphyrins oxidation using RICO

Three porphyrins were used in this study: 5,10,15,20-Tetraphenyl 21H,23H-porphine, vanadyl tetraphenylporphyrin (VOTTP) and nickel tetraphenylporphyrin (NiTPP). Stock solutions of these substrates were prepared by adding the desired amount of compound to dichloromethane to obtain a solution concentration of $C=1.19\times10^{-4}$ mol dm^{-3}. For the purpose of reaction, a 12 ml stock solution was mixed with $NaIO_4$ in 5 ml of H_2O having different concentration (C_1=0.187M, C_2=0.0187M, C_3=0.00187M) and $RuCl_3$ (0.02g, 0.002g, 0.0002g) used as a catalyst. At the end of reaction samples were withdrawn from the organic layer and analyzed by UV-Vis spectroscopy, previously calibrated with a known solution concentration of the substrate. Samples from the aqueous layer of the reaction were analyzed for the presence of Ni using AAS and ICP-AES. The aqueous layer from the reaction with VOTTP was analyzed for V presence only by using ICP-AES.

2.6.2. Oxidation using H_2WO_4 and H_2O_2

2.6.2.1. Polynuclear Aromatic Hydrocarbons oxidation

Oxidation reactions were carried out in a glass reactor over the temperature range 65°C to 85°C in a variety of different solvents: C_6H_5Cl, $C_6H_5CH_3$, CH_3CN, C_2H_5CN, C_4H_9Cl. The reaction mixture was stirred using a magnetic bar, held inside the reactor (700rpm). In a typical reaction the round bottom flask was firstly charged with the substrate (PAHs, 18.8mmols) and the desired solvent (8ml). The catalyst (H_2WO_4, 0.614mmols), 10%H_3PO_4 (0.14ml) and Aliquat 336 (0.24ml) were subsequently added and the reaction mixture left to stir for 2mins. H_2O_2 (30%, 12ml) was then added dropwise under continuous stirring, the flask containing reaction mixture was then transferred to a preheated oil bath and was fitted with a water cooled condenser. For quantitative analysis samples (0.2ml) were withdrawn from the organic layer at the desired time interval and mixed with external standard, 2-butanol (20μl) prior to GC analysis. To enable the withdrawal of the sample, stirring was stopped so as to obtain a visible separation between the two phases. Reaction time was varied between 6h and 20h for the different substrates tested. Samples for GC-MS analysis were withdrawn from both, organic and aqueous layer.

2.6.2.2. Oxidation of PAHs with long alkyl chain for NMR analysis

NMR analysis of PAHs with long alkyl chain required a clean ^{1}H NMR spectra, which was dependent on the Aliquat 336 used, phase transfer catalyst used as it masks signals from products in the aliphatic region. This was possible due to lowering the concentration of aliquat and introduction of small scale experiment. Oxidation reaction were carried out in a glass reactors for 16 hours, unless otherwise stated. First, substrate (0.1mmol) was dissolved in toluene (1ml), then H_2WO_4 (0.019g, 0.077mmol), H_3PO_4 10% 0.01ml, Aliquat 336 (0.0012g, solution in toluene, 5ml) were added and mixed together. In the last step of the reaction H_2O_2 35% (2ml) was added under continuous stirring. Reaction was run at a temperature of 80°C. Firstly, 1-octadecylpyrene, then 2-nonylphenanthrene were used as a substrate in the reaction. After the required time of reaction, two phases were separated and organic phase was washed with water (3x20ml). The aqueous phase was washed with toluene (3x20ml) and the organic as well as aqueous filtrates were combined with organic or aqueous layer. The organic phase was dried over anhydrous Na_2SO_4, the solid filtered and the filtrate evaporated to the dryness. The aqueous phases were also evaporated to dryness. For NMR analysis the residues were dissolved in D_2O or $CDCl_3$, respectively for aqueous and organic phase.

In the oxidation of 9-octadecylphenanthrene, the following conditions were used. First substrate 0.043g (0.1mmol) was dissolved in 3ml of C_6H_5Cl, then H_2WO_4 0.038 g

(0.154mmol), H_3PO_4 10% 0.02ml, Aliquat 336 (0.0024g) (solution in toluene) were added and stirred for few minutes. Then H_2O_2 50% (4ml) was added dropwise. Reaction was performed at T=110°C. Obtained conversion was 46%. Post reaction steps were the same as above.

2.6.2.3. Porphyrins oxidation

The reaction and work up was performed following a procedure previously reported by Tu and Yen [11]. Three porphyrins were used in this study: 5,10,15,20-tetraphenyl 21H, 23H-porphine, vanadyl tetraphenylporphyrin (VOTTP) and nickel tetraphenylporphyrin (NiTPP). First, 3 solutions of NiTPP (8ml, $C=1.19\times10^{-4}$ moldm^{-3} in chlorobenzene) were treated with different *substrate : oxidant & catalyst* ratios in the presence of Aliquat 336 (0.0024g) and H_3PO_4 (20μl, 10%). In experiments a *substrate : catalyst* ratios of 1:4 (H_2O_2 35% 0.1ml, H_2WO_4 0.001g), 1:40 (H_2O_2 35% 1ml, H_2WO_4 0.01g) and 1:80 (H_2O_2 35% 2ml, H_2WO_4 0.02g) were used. At the end of reaction samples were withdrawn from the organic layer and analyzed by UV-Vis spectroscopy, previously calibrated with a known solution concentration of the substrate. In a reaction without the catalyst, H_2O_2 (2ml, 35%) was added to porphyrin solution (8ml, $C=1.19\times10^{-4}$mol dm^{-3} in C_6H_5Cl). Reactions were performed in a glass reactor under continuous stirring at a temperature of 80°C, for 20 hours. After the desired reaction time samples from the organic layer were withdrawn and analyzed using UV-Vis spectroscopy.

To determine the free metal content of the solution, the organic layer was separated from the aqueous phase which was subsequently submitted for ICP-AES analysis. To enable metal analysis using X-Ray Photoelectron Spectroscopy, the reaction was scaled up by a factor of three and at the end of the reaction the aqueous layer was kept for further work up. 0.1M NaOH and 0.18M EDTA were added to the aqueous phase prior to extraction with chloroform. Following the separation, the aqueous upper layer was collected, the water evaporated and the resultant solid dried in air at 120°C for 5h and submitted for XPS analysis.

2.6.2.4. Heteroaromatics oxidation

The oxidation of compounds, which contain heteroatoms (S or N) were studied as well. The heteroaromatic compounds: benzothiophene, dibenzothiophene, indole, carbazole and dodecyl sulfide were first dissolved in either toluene or chlorobenzene. The reaction protocol employed was the same as that described in paragraph 2.6.2.1. To enable GC-MS analysis samples were withdrawn after 20h reaction and diluted with toluene or dichloromethane. To obtain a sample for elemental analysis the reaction mixture was treated as follows: the organic layer was separated from the aqueous phase and the organic solvent evaporated to obtain a dry sample. In the case of the aqueous layer, solvent removal was not required and the sample was sent for analysis without modification. Elemental analysis was performed by Warwick Analytical Centre, Coventry, UK.

2.6.3. Heterogeneous catalysts for PAHs oxidation

Reaction with the use of WO_3, WO_3/TiO_2, heteropolyacids, supported HPAs and Ru supported catalyst were performed in a glass reactor fitted with water cooled condenser in temperature range 22-140°C. The details of each reaction can be found in chapter 6. Testing of catalyst containing Au-Pd metals were carried out in a 50 ml Parr autoclave reactor. In a typical reaction, the requisite amount of catalyst and substrate held in the desired solvent were charged to the reactor which was then sealed and purged 3 times with oxygen. The reactor was pressurized to the required oxygen pressure and the temperature of the reactor raised to the desired temperature. The reaction mixture was started with the commencement of stirring at a rate of 1000rpm. After the desired reaction time, the stirring was stopped and the reactor cooled in an ice bath. After the temperature reached below 40°C, the reactor was depressurized and the contents of the reactor filtered to yield a solution of the product. An aliquot of this clear supernatant (0.2 ml) was added to 2-butanol (0.02 ml, external standard for GC analysis). For ^1H NMR analysis the solvent was evaporated and the obtained residue re-dissolved in 1ml of $CDCl_3$, 0.7ml was transferred to the NMR tube. For HPLC analysis the residue was dissolved in acetonitrile and transferred to the vial.

2.7. Qualitative and quantitative analysis techniques

2.7.1. Gas chromatography (GC)

Gas chromatography is a type of chromatography widely used in analytical chemistry for separating and analyzing mixtures of chemical compounds. The sample is vaporized and injected onto the head of a column. Elution is brought about by a flowing of a mobile phase. The mobile phase which is an inert gas, e.g.: helium or nitrogen, does not interact with the analyte, as its sole role is to carry the sample thought the column. The stationary phase which is an adsorbent or a liquid phase on an inert material, is usually held in tubes made of glass or quartz. Generally there are two types of column: packed (diameter: 3 to 8mm, length: 1 to 3m) and capillary column (length up to 100m, diameter of 0.2 to 1mm).

There are several techniques available for introducing the sample onto the capillary column. Split injection allows only a small fraction of the sample (around 2%) to pass onto the column, while a splitless injection avoids the problems of low sensitivity. With a 'on column' injection system a small amount of liquid sample is placed directly into the cooled top of the column, which is subsequently heated to volatilize the compounds.

A gas chromatograph consists of a carrier gas supply, sample injection port, flow controller, a column held inside a oven, detector and a processing unit. There are a number of detectors which can be used, but the most widely applicable detector is the flame ionization detector (FID). Here, the eluent from the column is mixed with hydrogen and air and then burned. The organic compounds, when pyrolyzed by the flame, produce ions and electrons that can conduct electricity through the flame. Above the flame, is a built in collector electrode and the resulting current is directed into a operational amplifier and measured. The number of ions produced is proportional to the number of reduced carbon atoms in the flame, making quantitative analysis possible [12-13].

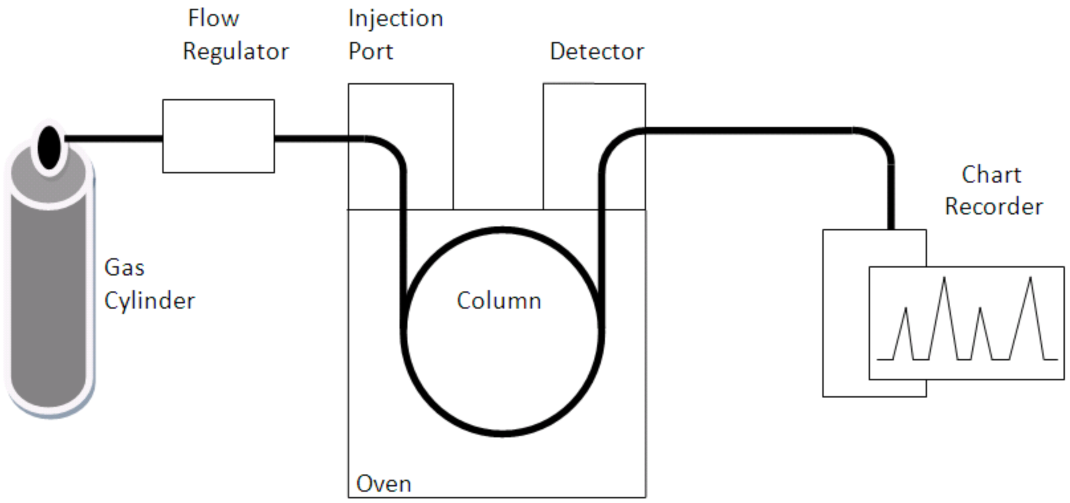


Figure 2–4: Scheme of Gas Chromatograph
(Based on: Pieper and Rutledge, Laboratory Techniques for Pharmacists, Upjohn 1989, page 20, figure 2)

Reaction samples were analyzed quantitatively using a Varian 450 gas chromatograph with a VF-5ht (30m, 0.25mm) column and a FID detector, helium was used as the carrier gas. The injector temperature was set at 375°C and the split ratio set as 1:20. The GC oven temperature was increased from 70°C to 410°C at a heating rate of 20°C. The detector temperature was set at 420°C. The analysis time was typically set to 30mins. A simple GC chromatogram is shown below (Figure 2-5).

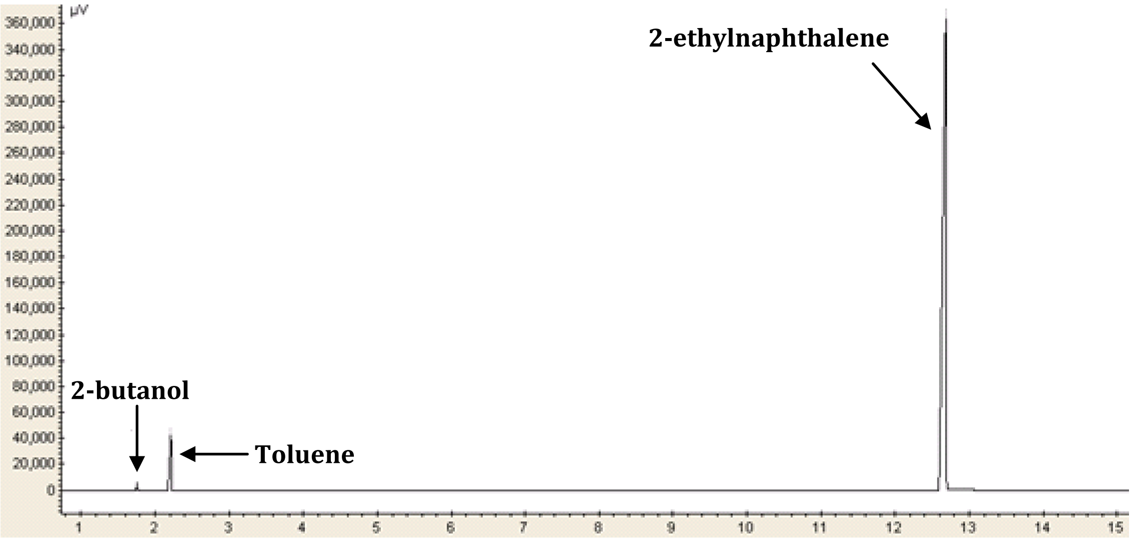


Figure 2–5: An example of GC chromatogram

2.7.1.1. Quantitative kinetic studies using GC

For kinetic studies of PAHs, samples (0.5ml-0.2ml depending on reaction) were withdrawn from the reaction mixture and combined with an external standard (2-butanol) and injected into GC system as described earlier (sections: 2.6.1., 2.6.2.). To determine the changes in substrate concentration during kinetic studies, the normalized areas of the substrate before and after reaction were compared. The conversion was calculated as follows:

$$Conversion= (\frac{N.A.So-N.A\ Sx}{N.A.So}\ x\ 100)\% \qquad (Equation\ 2\text{-}1)$$

Where:

N.A. S_0 *= Normalized area of substrate before reaction*

N. A. S_x *= Normalized Area of substrate after or during the reaction (*$sample_x$ *withdrawn from the reaction mixture)*

The numbers of mols of substrate present during or after the reaction was calculated using equation 2-2:

$$n_{Sx} = n_{So} - \frac{conversion}{100\%} \; x \; n_{So} \qquad \text{(Equation 2-2)}$$

Where:

n_{Sx} *= Number of mols of substrate at the moment of sample withdrawal*
n_{So} *= Number of mols of substrate before the reaction*

2.7.1.2. Error in GC analysis

The major quantitative error in GC is due to inaccurate integration, poor peak detection and false base line positioning. Often the error can be minimised by several injections of the same sample. Here, the reaction conversion was calculated based on at least 2 GC injections of the same sample. GC analysis of a six time injected sample of naphthalene showed that the standard deviation was better than 0.00167. A graph showing GC injection reproducibility is shown below (Figure 2-6). Based on this experiment, it can be said that conversion data obtained from GC are reliable and the error is negligible.

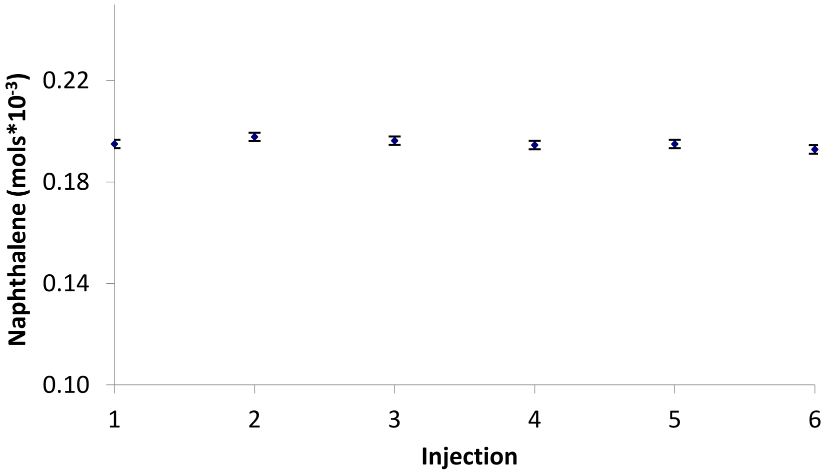


Figure 2–6: Naphthalene solution GC injection reproducibility

For the purpose of clarity, no error bars were used on the graphs displaying kinetic data. However, as shown above, the error in GC analysis is negligible.

2.7.2. High Performance Liquid Chromatography (HPLC)

HPLC is a type of column chromatography used frequently in analytical chemistry to separate, identify and quantify mixtures of compounds. An HPLC device consists of four main components: an injection system, a pump that moves the mobile phase through the column (producing a pressure of up to 400 atm), a separation column that holds the chromatographic packing material (stationery phase) and a detector with a processing system, which displays the retention time of the separated compounds. Retention time varies depending on the interactions between the stationery phase and the molecules being analysed, the temperature of the column and the solvent used.

Many different detectors can be used in conjunction with a HPLC but the most popular is a variable λ UV spectrometer. There are 2 main types of HPLC: normal and reverse phase. Normal-phase HPLC (NP-HPLC) separates analytes based on adsorption to a stationary surface chemistry and by polarity. NP-HPLC uses a polar stationary phase and a non-polar, non-aqueous mobile phase and works effectively for separating analytes readily soluble in non-polar solvents. Reversed phase HPLC (RP-HPLC or RPC) has a non-polar stationary phase and an aqueous, moderately polar mobile phase. One common stationary phase is silica which has been treated with RMe_2SiCl, where R is a straight chain alkyl group such as $C_{18}H_{37}$ or C_8H_{17}. With these stationary phases, the retention time is longer for molecules which are less polar, while polar molecules elute more readily [13-14].

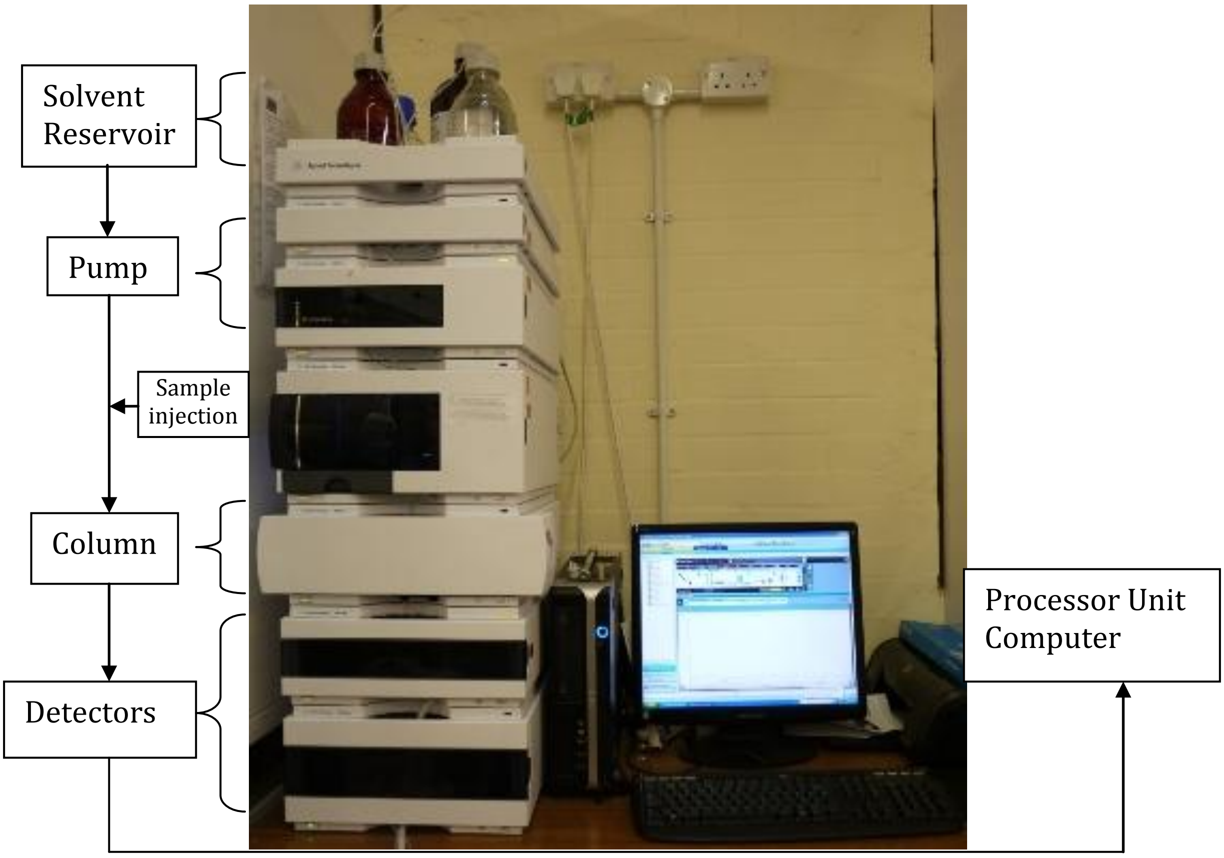


Figure 2–7: Scheme and photograph of a HPLC instrument

HPLC analysis were performed on an Agilent 1200 Series HPLC using a Zorbax Eclipse Plus Phenyl-Hexyl 4.6x150mm, 3.5μm column. Water (solvent A) and acetonitrile (solvent B) were used as the mobile phase at a flow rate of 1 ml/min. The solvent gradient was programmed as follows: 100% A for 2 min and then a linear gradient to 40% A, 60% B over the next 8 minutes and kept at this solvent composition for an additional 16 min. The column temperature was kept at constant 30°C and the injection volume used was 5μl. An example of HPLC chromatogram is illustrated below (Figure 2-8).

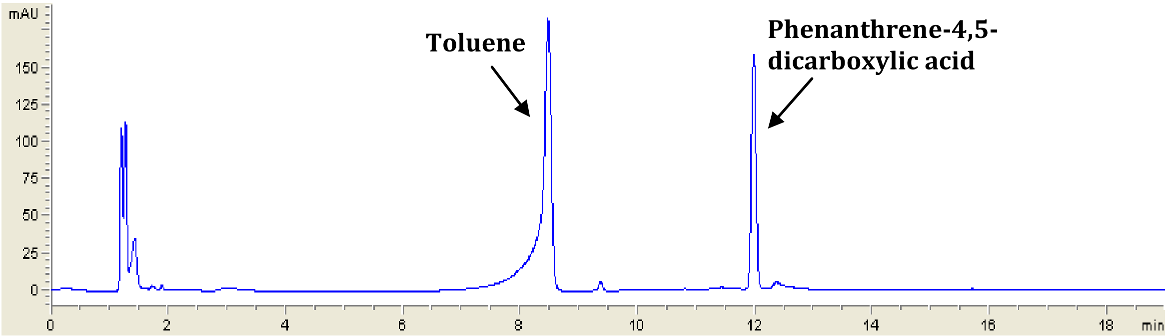


Figure 2–8: An example of a typical HPLC chromatogram

2.7.2.1. Quantification using HPLC analysis

For the purpose of kinetic studies, the HPLC system was calibrated with solutions of a known concentration of pyrene, pyrene-4,5-dione and pyrene-4,5,9,10-tetraone. A calibration curve for pyrene-4,5-dione is shown below (Figure 2-9).

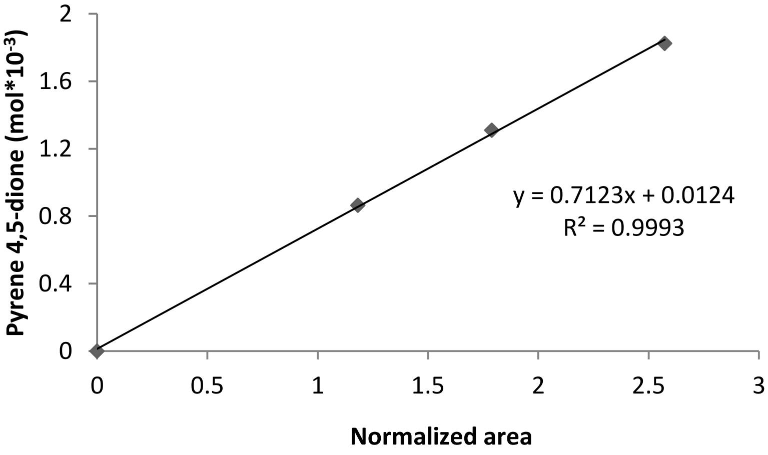


Figure 2–9: A HPLC calibration curve for pyrene-4,5,-dione

The number of mols of substrate or product present in a reaction was calculated based on a response factor, calculated as follows:

$$n_{S/P} = \frac{N.A.\ s/p}{Rf} \qquad \text{(Equation 2-3)}$$

Where:

$n_{S/P}$= number of mols of substrate or product

$N.A._{S/P}$ = normalized area (area of compound/area of external standard)

Rf =response factor

The conversion of a reaction determined by HPLC was calculated in a similar way to that previously described in section 2.9.1.1.

$$Conversion = \left(\frac{nSo - n\,Sx}{nSo} \times 100\right)\% \qquad \text{(Equation 2-4)}$$

Where:

n_{So}=number of mols of substrate before reaction

n_{Sx}= number of mols of substrate after or during the reaction (sample$_x$ withdrawn from the reaction mixture)

Number of mols of all products was calculated as shown in equation below.

$$n_{px} = \frac{Conv}{100\%} \times n_{so} \qquad \text{(Equation 2-5)}$$

Where:

n_{So}= number of mols of substrate before reaction

n_{px}= number of mols of products obtained during the reaction

Conv=Conversion

Selectivity towards product x was calculated based on the following equation:

$$Selectivity = \left(\frac{n\ px}{n\ p}\right) \times 100\% \qquad \text{(Equation 2-6)}$$

Where:

n_{px} = number of mols of product x

n_p = number of mols of products

In some reactions the conversion was calculated based on a normalized area calculation using the equation 2-1.

2.7.3. Mass Spectrometry (MS)

In mass spectrometry the molecular masses of compounds are determined. The principles consist of ionizing compounds to generate charged molecules and measuring their mass to charge ratio. Each mass analysis includes sample vaporization, ionization, separation based on mass and detection of the ions generated as shown in figure 2-10 [15]. In our studies mainly electron ionization (EI) and electrospray (ESI) ionization techniques were used.

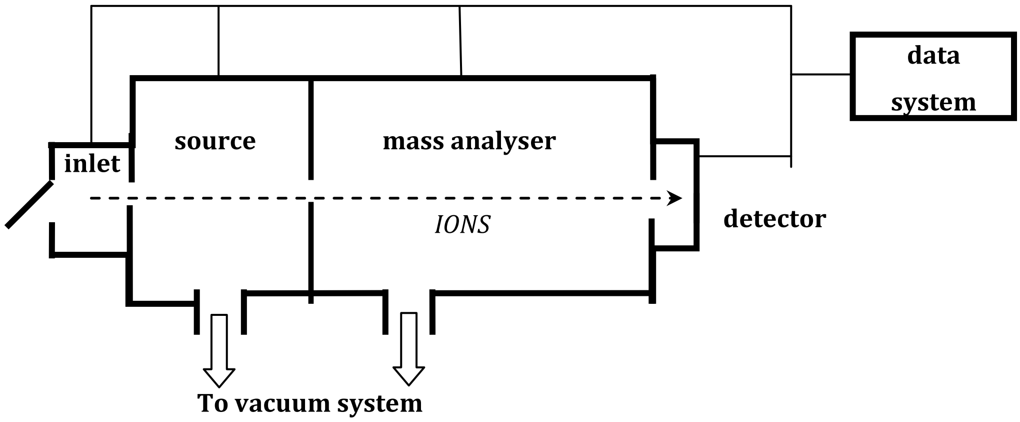


Figure 2–10: Scheme of mass spectrometer [16]

Apart from the EI and ESI ionization techniques it is worth mentioning other MS ionizaton techniques such as: plasma desorption, fast atom bombardment (FAB) and matrix-assisted laser desorption/ionisation (MALDI), which is the most popular technique used in bioscience. The Electron Ionisation technique is the most well-known ionization technique used in organic chemistry. The source contains a heated metal filament, made of rhenium or tungsten [15]. Electrons which are emitted from the surface of the metal filament are accelerated towards an anode. On their way to the anode, the electrons interact with vaporised sample molecules resulting in their electronic excitation and the expulsion of an electron from the sample molecule. The molecular ion formed can fragment to form smaller ions, which can also undergo fragmentation [15-16].

Electrospray Ionisation is a technique which involves the creation of an aerosol of highly charged micro droplets in a strong electric field. The process of droplet creation is called nebulisation. This technique requires a continuous flow of solution containing the analyte, therefore this technique is often coupled to an HPLC system [16].

Mass analysers employ an electric field, sometimes in conjunction with a magnetic field, to enable discrimination between the ions of differing mass-to-charge ratio (m/z). There are five main types of mass analysers: magnetic sector, quadrupole, ion trap, TOF (time of flight) and FTICR (Fourier transform ion cyclotron resonance). High resolution MS includes double focusing, FTICR and orbitrap mass spectrometers [15].

Analysis were performed using a Waters LCT Premier XE (ES) while EI data was generated using Waters GCT Premier EI (EI) instrument. An example of a MS spectrum is shown below (Figure 2-11).

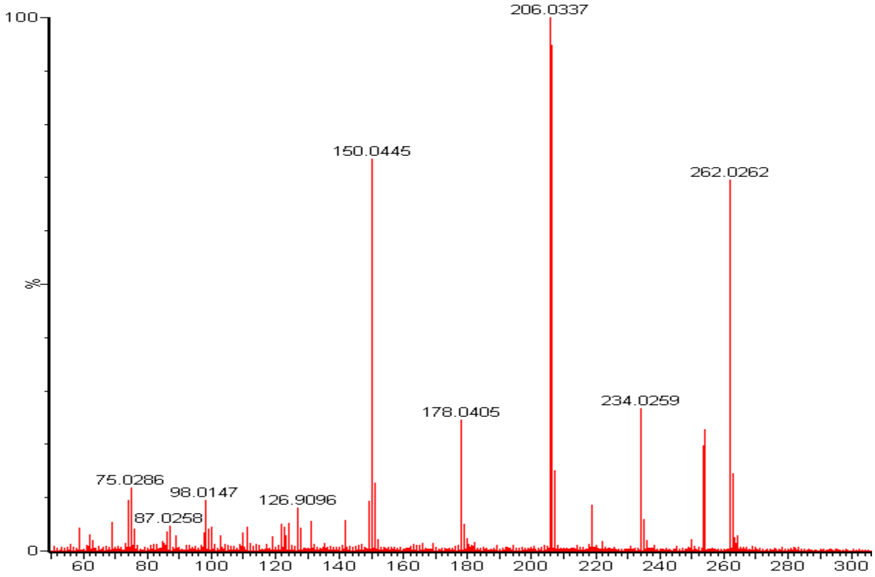


Figure 2–11: MS spectrum of pyrene-4,5,9,10-tetraone (Mw=262 g/mol)

2.7.3.1. Techniques combined with MS

A) Gas Chromatography coupled with Mass Spectrometry (GC-MS)

GC-MS technique is used to separate and identify chemical compounds in a mixture. Each GC-MS system is equipped with a library of reference spectra which helps to identify unknown compounds. Firstly, compounds are separated in the GC column, the separated components enter the ionization chamber of the MS system where they interact with an electron beam from a tungsten filament. This interaction leads to the generation of gas-phase ions, which are transferred to the mass analyser for separation according to their mass to charge ratio. The lower the mass of an ion, the faster it will reach the detector. The detector registers and counts the arriving ions [16].

GC-MS analyses were performed using a Waters GCT premier instrument fitted with an Agilent HP-5MS column. The length and internal diameter of the column were 30m and 0.25µm, respectively. The temperature program was set from 40°C to 280°C, the carrier gas was helium (flow 1ml/min). At the end of the run, the mass spectra of the unknown compounds were compared with spectra held in the mass spectral library database as a means of determining their identity.

B) High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS)

HPLC coupled with an MS instrument is often used in organic chemistry. The principles of this technique are very similar to GC-MS. However, in HPLC-MS there is continuous flow of solvent which moves the analyte through the LC column and into the electrospray ionization source.

HPLC-MS analysis were carried out using a Waters HPLC system fitted with a reverse phase C18 column (4.6mm x 17.5mm) and a UV detector (λ=254nm) coupled to a ZQ mass spectrometer. The mobile phase was: 95% H_2O / 5% ACN changing to 95% ACN and 5% H_2O over a 20min period, the flow rate was set as 1ml/min. The techniques used for analysis were: electrospray negative ($M-H^+$) and electrospray positive ($M+H^+$). Samples from the organic and aqueous layers were prepared for analysis as previously described in section 2.6.1.2.

2.7.4. Nuclear Magnetic Resonance

NMR spectrometry is widely used for the identification and structural analysis of organic materials. It is based on the absorption of electromagnetic radiation in the radio-frequency region of the spectrum (wavelength range 0.6-10m) which results in changes in the orientation of the nuclei spin in an applied magnetic field. The absorption of this radiation can be observed for those nuclei, which are considered to spin about their own axes. Nuclei are assigned the spin quantum number I which may be zero, half-integral or integral, but only those with a quantum number $I \neq 0$ have a magnetic moment μ meaning they are NMR active. The nucleus also possesses angular momentum I and for each isotope the relative values of μ and I determine the frequency at which energy can be absorbed. The angular momentum associated with nuclear spin is quantized both in magnitude and direction. In the presence of an applied magnetic field, the momentum vector can assume only those orientations in space which result in its component aligning in the direction of the field. Hence for any given nucleus, there is a total of $2S + 1$ angular momentum states.

If a nucleus is placed in a magnetic field, however, the interaction between the nuclear magnetic moment and the external magnetic field means the two states no longer have the same energy. The energy of interaction between magnetic moment μ when in a magnetic field B_0 is given by:

$$E=-\mu_z B_0=-m_I \gamma \frac{h}{2\pi} B \qquad \text{(Equation 2-7)}$$

Where:

μ =magnetic moment

B_0 =magnetic field

m_I =magnetic quantum number

γ=magnetogyric (gyromagnetic)ratio

h=Planck constant

For a ^{1}H or ^{13}C nucleus I is 1/2 therefore, m_I can be only ± 1/2 and 2 energy levels are produced.

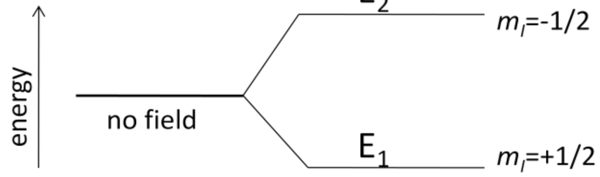


Figure 2–12: Nuclear spin energy levels for ^{1}H or ^{13}C nuclei

For energy to be absorbed, radiation at a frequency equal to E_2-E_1 must be supplied. The absorption frequency is then proportional to the applied magnetic field at the nucleus.

The width of an absorption band is determined by the rate at which the nuclei absorbing the higher energy (E_2) return to the lower level. This process is called relaxation. During relaxation a decaying emission signal is detected by Fourier Transformation spectrometers and processed by a computer.

Chemical shift plays a very important role in NMR spectrometry. It is important to emphasize that the shielding effect, which is related to the binding ratios of the particular atoms, is responsible for protons in different chemical environments absorbing at different values of the applied field. Differences between such absorption are referred to as chemical shift [13, 17].

^{1}H NMR spectra were recorded on a Bruker 400 MHz and 500 MHz instrument using $CDCl_3$, D_2O, CD_3CN or DMSO as solvents. ^{13}C NMR spectra were obtained using a Bruker 500MHz instrument using $CDCl_3$ and DMSO as solvents.

Samples for qualitative NMR analysis were prepared as follows: firstly the solvent used in the reaction was evaporated, the sample was then placed under vacuum until it was completely dry and a volume of approx. 1ml of deuterated solvent added to the dry residue to dissolve it. The solution (0.5-0.7 ml) was subsequently transferred to the NMR tube. An example of ^{1}H NMR spectra is given below (Figure 2-13).

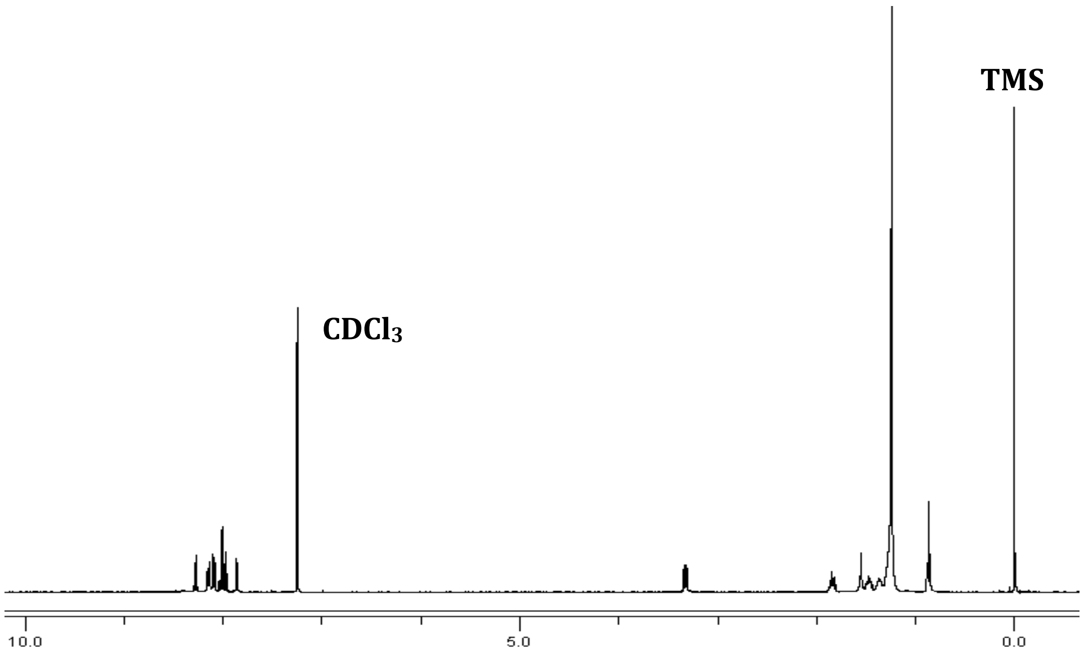


Figure 2–13: ^{1}H NMR spectra of 1-octadecylpyrene with TMS and $CDCl_3$

2.7.4.1. Kinetic NMR studies on the oxidation of aliphatic vs aromatic protons and carbons

Water suppressed ^{1}H NMR spectra of 2-ethylnaphthalene oxidation reaction were acquired on a Bruker DPX 500 MHz, system using a 5mm auto tune broadband probe. NMR spectra were acquired over a 36 scan period using the Bruker pulse sequence 'zgpr'. A power level of 53.5 db was employed for water pre-saturation, along with a relaxation delay of 5 seconds and an acquisition time of 1.638 seconds. To a solution of 2-ethylnaphthalene (15.8 mg, 0.101mmols) in deuterated acetonitrile (2ml), an aqueous solution of $NaIO_4$ (90mg, 0.421mmols in 1 ml H_2O) was added and stirred for one minute. H_2O (2ml) was also added to the above mixture. A 0.7ml portion of this reaction mixture was transferred to an NMR tube fitted with a sealed glass insert containing a fixed quantity of 1% TMS in $CDCl_3$ (external standard for quantitative analyses). After recording the ^{1}H NMR spectra of the mixture (0h sample), the NMR tube was removed from the instrument and an aqueous solution of $RuCl_3{\cdot}xH_2O$ (20µl, 0.105mg, 0.5µmols) added to the NMR tube to start the reaction. The NMR tube was immediately transferred to the NMR instrument and ^{1}H NMR spectra recorded every 15 minutes for 9h. Each NMR peak was integrated and subsequently normalized against the TMS signal at 0 PPM.

2.7.4.2. NMR quantitative analysis for aromatics with long alkyl chain

A) Ruthenium Ion Catalyzed Oxidation (RICO)

To a solution of substrate (0.0276 mmols), $CDCl_3$ (2ml) and CD_3CN (1ml), an aqueous solution of $NaIO_4$ (44mg, 0.2065mmols dissolved in 1ml H_2O) was added and stirred for one minute. A 0.6ml portion of this reaction solution was removed from the organic layer and transferred to an NMR tube fitted with a sealed glass insert containing fixed quantity of 1%TMS in $CDCl_3$ (external standard for quantitative analyses). To this CD_3CN (0.3ml) was added and analyzed using ^1H NMR and this was denoted as sample 0. An aqueous solution of $RuCl_3{\cdot}xH_2O$ (20µl, 2µmols) was subsequently added to the round bottom flask and stirring initiated. The temperature of the reaction was maintained at 22°C using a water bath. After 4.5h of reaction, a 0.6ml portion from the organic layer was transferred to a clean NMR tube fitted with the same glass insert. CD_3CN (0.3ml) was added and the ^1H NMR spectra recorded. Each NMR peak was integrated and then normalized against the TMS signal at 0 PPM.

B) H_2WO_4/H_2O_2

To a solution of 0.1mmol of substrate in 1 ml of toluene or chlorobenzene, 0.077mmol of H_2WO_4, 0.01ml of H_3PO_4 10% and 0.0012g of Aliquat 336 were added. H_2O_2 (2ml, 35%) was added dropwise to the mixture and stirring started and allowed to continue at 80°C for 16h in the 5ml round bottom flask fitted with a water cooled condenser. After 16h, the reaction was cooled and the 2 phases separated. The organic phase was washed with H_2O (3x10ml) and the aqueous phase extracted with toluene (3 x 10ml). The organic phases were combined and dried over anhydrous Na_2SO_4. The solid was filtered and the filtrate evaporated to dryness, weighed and used for NMR analysis. The aqueous phases were also combined and evaporated to dryness and weighed. $CDCl_3$ (0.7ml) was added to the flask containing the organic products and a 0.6ml portion of the resultant solution transferred to the NMR tube fitted with a glass insert (1%TMS in $CDCl_3$). The NMR spectra obtained were compared against the spectra of the pure substrate, which was previously prepared by dissolving 0.1mmol of compound in 0.6 ml of $CDCl_3$. The NMR spectrum of this solution was recorded in the presence of the same glass insert.

2.7.4.3. Error in NMR integration analysis

The biggest source of analysis error during NMR integration lies in the wrong manual integration of the peaks. Therefore, integrations was repeated three times to avoid this problem. The standard deviation for three different samples taken from the same reaction mixture and analyzed by ^{1}H NMR was calculated to be 0.006. This number suggests that the error during quantitative NMR measurements is insignificant.

2.7.4.4. Two dimensional NMR spectroscopy

Due to the development of a variety of computer-controlled pulse sequences consisting of two or more pulses of appropriate length, frequency range, power and phase two dimensional spectroscopy plays an important role in the identification of chemical compounds. There are a number of different techniques which are widely applied in NMR analysis, here only NMR experiments used in this thesis are mentioned:

1) **COSY Correlation Spectroscopy** provides proton-proton coupling information (^{1}H-^{1}H connectivity)
2) **HSQC Heteronuclear single-quantum correlation spectroscopy** detects correlations between nuclei of two different types which are separated by one bond
3) **HMBC Heteronuclear multiple-bond correlation spectroscopy** detects heteronuclear correlations over a longer range of about 2–4 bonds.

All 2D-NMR analysis were performed using a Bruker DPX 500MHz instrument.

2.7.5. Infrared Spectroscopy (IR)

IR spectroscopy is a type of vibrational spectroscopy, which deals with the absorption of light energy in the range from 0.8 to1000µm. The spectral range is divided into three regions, near IR approximately 14000-4000cm^{-1}, mid-infrared 4000-400cm^{-1} and far infrared 400-10cm^{-1}. During measurement, different mechanical vibrations of atoms or functional groups are excited in the molecules. Usually this method is used for identification and structural analysis of organic materials.

IR analysis were performed using a Jasco FT/IR-660 spectrometer, where all wavelengths are detected and measured simultaneously.

Compounds in dichloromethane solution were deposited on the surface of a NaCl plate. The film formed on the plate was analysed directly [12, 18].

2.7.6. Raman Spectroscopy

Raman Spectroscopy is a technique used to study low frequency modes, based on the spectral distribution of inelastically scattered light. The monochromatic light interacts with the molecule, leading to molecular vibrations, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system [12, 18].

Raman spectra were obtained using a Horiba Jobin-Yvon LabRAM HR spectrometer using a 514nm line from an argon ion laser. The spectrometer was calibrated using silicon, which gave a band at 520cm^{-1}.

2.7.7. Visible and Ultraviolet Spectroscopy (UV-Vis)

The principle behind this analytical technique is based on the absorption of electromagnetic radiation in the ultraviolet-visible spectral region which results in changes to the electronic structure of the ions and molecules. The absorption of UV or visible light by an organic molecule leads to the excitation of π electrons (of double or triple bonds), n-electrons or non-binding electron pairs of O, S, N. The visible wavelength region runs from 400 to 800 nm, while the near ultraviolet UV and vacuum UV regions extends from 400 to 100 nm.

All porphyrins oxidation reactions measurements were performed using a Jasco V-570 spectrophotometer to determine the change in concentration with time, withdrawn from organic layer. An example of a UV-Vis spectra is shown below (Figure 2-14).

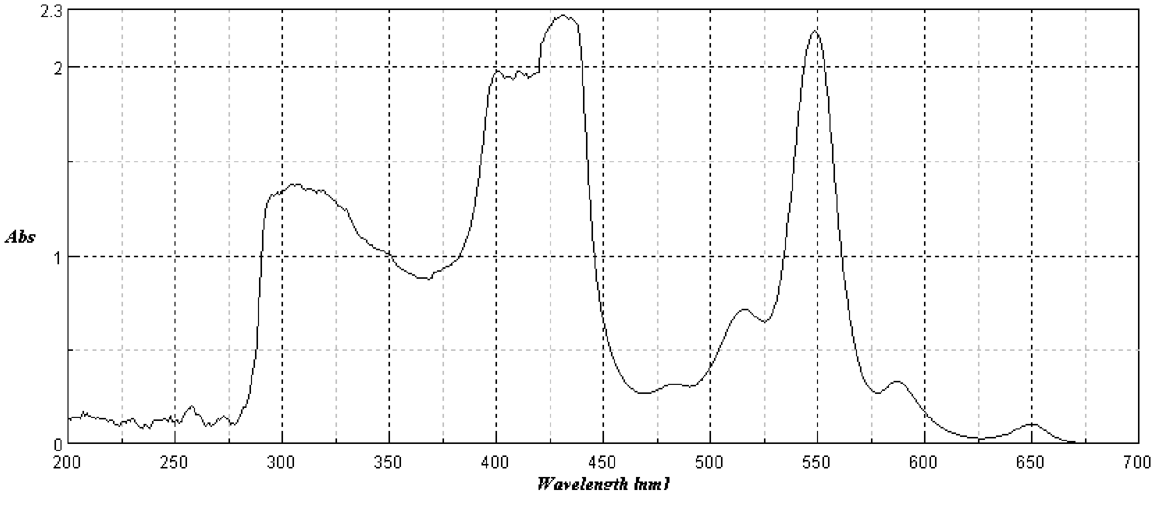


*Figure 2–14: UV-Vis spectra of NiTPP (Concentration=1.19*10^{-4}M)*

Solutions of different concentration of nickel tetraphenylporphyrin or vanadyl tetraphenylporphyrin in chlorobenzene or dichloromethane were used to calibrate the spectrometer. The calibration curve for NiTPP is shown below (Figure 2-15).

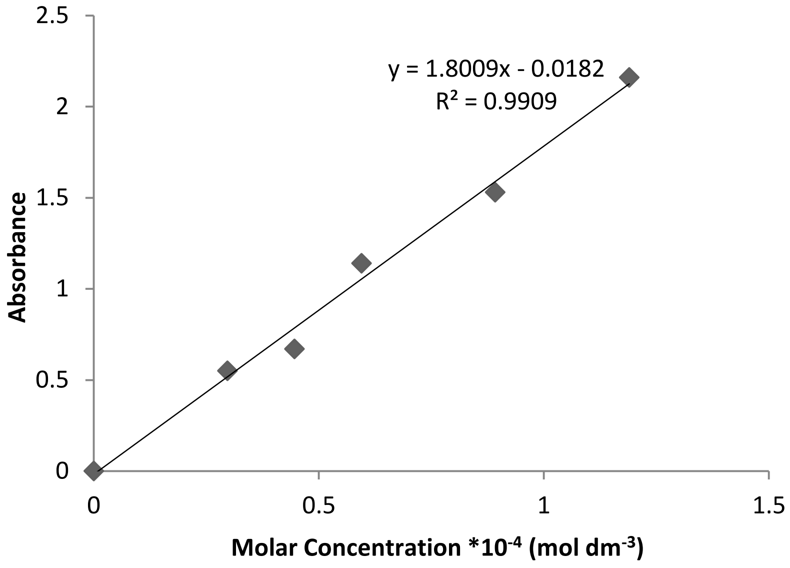


Figure 2–15: UV-Vis calibration curve for NiTPP

In UV-Vis analysis, absorbance is proportional to the concentration of the sample as seen in the equation below. Based on this relationship, it is straight forward to determine the conversion of the reaction in porphyrin oxidation.

$$A=\log (I_o/I) \qquad \text{(Equation 2-8)}$$

Where:

I=intensity of transmitted light

I_o =intensity of the incident light beam

The absorbance is defined by bellowed equation and it is proportional to the analyte concentration.

$$A=abc \qquad \text{(Equation 2-9)}$$

Where:

A=absorbance
a=wavelength
b=path length
c=analyte concentration

2.7.8. Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectroscopy is a quantitative analysis method which uses the absorption of light by free atoms to measure the concentration of atoms in the gas phase, based on the Beer –Lambert Law (Equation 2-8).

A hollow cathode lamp filled with an inert gas is aligned with the metal to be analyzed and is usually the source of light [13]. Thus for ruthenium analysis a ruthenium lamp was required and for nickel analysis, a nickel lamp was needed. Analysis was carried out using a Varian instrument with an air-acetylene flame.

Samples with different concentration of Ru were used to calibrate the instrument. All samples were prepared from an aqueous solution of $RuCl_3$. For the nickel standard, aqueous solutions containing the desired concentration of metal were prepared from $Ni(NO_3)_2 \cdot 6H_2O$.

2.7.9. Inductively Coupled Plasma-Atomic Emission Spectroscopy(ICP-AES)

This quantitative technique is used for measuring trace levels of metal in an analyte and has considerably fewer matrix effects than AAS. It can be used for the quantification of all elements at low (ppb) concentration. This analytical method is a type of emission spectroscopy that uses a inductively coupled argon plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic to a particular element. The intensity of emission is indicative of the concentration of that element within the sample [12].

ICP-AES analysis was performed at Warwick Analytical Centre in Coventry, UK. Samples containing Ru, were withdrawn directly from the reaction mixture (aqueous layer) or after solvent evaporation, then sent as a solid. Samples containing Ni and V were withdrawn directly from the reaction mixture and sent without further work up.

2.8. References

1. Hu, J., Zhang, D., and Harris, F.W., *Journal of Organic Chemistry*, **2005**, 70(2), 707
2. Tsukamoto, D., Ikeda, M., Shiraishi, Y., Hara, T., Ichikuni, N., Tanaka, S., and Hirai, T., *Chemistry-a European Journal*, **2011**, 17(35), 9816
3. Dimitratos, N. and Vedrine, J.C., *Applied Catalysis a-General*, **2003**, 256(1-2), 251
4. Rao, K.T.V., Rao, P.S.N., Prasad, P.S.S., and Lingaiah, N., *Catalysis Communications*, **2009**, 10(10), 1394
5. Jagadeeswaraiah, K., Balaraju, M., Prasad, P.S.S., and Lingaiah, N., *Applied Catalysis a-General*, **2010**, 386(1-2), 166
6. Devassy, B.M. and Halligudi, S.B., *Journal of Catalysis*, **2005**, 236(2), 313
7. Li, F., Chen, J., Zhang, Q., and Wang, Y., *Green Chemistry*, **2008**, 10(5), 553
8. Viau, G., Brayner, R., Poul, L., Chakroune, N., Lacaze, E., Fievet-Vincent, F., and Fievet, F., *Chemistry of Materials*, **2003**, 15(2), 486
9. Meenakshisundaram, S., Nowicka, E., Miedziak, P.J., Brett, G.L., Jenkins, R.L., Dimitratos, N., Taylor, S.H., Knight, D.W., Bethell, D., and Hutchings, G.J., *Faraday Discussions*, **2010**, 145, 341
10. Sankar, M., Morad, M., Pritchard, J., He, Q., Freakley, S.J., Edwards, J.K., Taylor, S.H., Carley, A.F., Knight, D.W., Kiely, C.J., and Hutchings, G.J., *ACS Nano*, **2012**, submitted,
11. Tu, S.P. and Yen, T.F., *Energy & Fuels*, **2000**, 14(6), 1168
12. Skoog, D.A., West, D.M., and Holler, F.J., *Fundamentals of Analytical Chemistry*. 7th ed **1996**, Saunders College Publishing.
13. Fifield, F.W. and Kealey, D., *Principles and Practice of Analytical Chemistry*. **2000**, Blackwell Science Ltd.
14. Schwedt, G., *The Essential Guide to Analytical Chemistry*. **1999**, John Wiley &Sons.
15. Hoffmann, E. and Stroobant, V., *Mass Spectrometry: Principles and Applications*. 3rd ed **2007**, John Wiley &Sons , Ltd.
16. Henderson, W. and McIndoe, J.S., *Mass Spectrometry of Organic and Organometallic Compounds, Tools-Technique-Tips*. **2005**, John Wiley &Sons Ltd.
17. Friebolin, H., *Basic One-and Two-Dimensional Nmr Spectroscopy*. 4th ed **2005**, Wiley-VCH.
18. Nakamoto, K., *Infrared and Raman Spectra of Organic and Coordination Compounds*. 6th ed **2009**, Wiley.

3. Ruthenium Ion Catalyzed Oxidation of PAHs in Monophasic Solvent System

3.1. Introduction

The results presented and discussed in this chapter describe the oxidation of Polunuclear Aromatic Hydrocarbons (PAHs) based on Ruthenium Ion Catalyzed Oxidation chemistry (RICO). RICO was used mainly for the oxidative fragmentation of C=C bonds and aromatic compounds, which resulted in a reputation for the chemistry being very reactive and so limited to the digestion of polyaromatic compounds rather than their selective oxidation. In spite of this negative reputation, many researchers have tried to utilize RICO chemistry by improving its selectivity and trying to understand the conditions required for RuO_4 stability [1-3]. That is why it was decided to use water and acetonitrile as reaction solvents, the importance of which was highlighted by Sharpless, who observed an enhancement in the reaction rate when MeCN was added as a co-solvent to the reaction [4]. It is postulated that, acetonitrile prevents the formation of ruthenium carboxylates, which may inhibit the oxidation process. In this chapter, it is reported, that by optimizing the reaction parameters, it is possible to selectively oxidize aromatic carbon and hydrogen in the presence of an aliphatic chain and avoid losing carbon and hydrogen of the chain as CO_2 and H_2O, demonstrated by the oxidation of suitable model compounds using the standard ruthenium ion based catalyst. The role of the solvent system on the catalytic activity and product distribution has also been extensively studied. The use of a monophasic solvent system makes it easier to accurately quantify the reactants and products during the course and at the end of the reaction, as the products are not partitioned between the immiscible organic and aqueous layers – as would be the case when using a biphasic solvent system. In addition to the selective oxidation, we report the correlation between the rate of oxidation and the ring size of polyaromatic hydrocarbons, using suitable model compounds. Attempts have been made to fully characterize the oxidation products, both qualitatively and quantitatively, using various analytical techniques including GC-MS, HPLC and HPLC-MS. Moreover, the modification of the solvent system accompanied by its simplification, has enable a mechanistic investigation to be carried out regarding the role of water using D_2O as well as $H_2{}^{18}O$. Taking into account the positive influence of acetonitrile on the oxidation process, the change in the reaction environment from a biphasic to a monophasic solvent system has not compromised catalytic activity.

3.2. Quenching studies

The use of a monophasic solvent system in the reaction significantly simplified the product analysis. However, one other important task was to stop the reaction when required for the analysis purposes. It was very important to quench the reaction, as it occurs even at room temperature. It has been proved experimentally that the oxidant ($NaIO_4$) is inactive in the absence of the catalyst ($RuCl_3 \cdot xH_2O$) and the catalyst is active only in the presence of oxidant. Therefore, two methods of quenching were possible. First method, considers deactivation of the active species, by raising pH of the reaction mixture, thus formation of *trans*-$[Ru(OH)_2O_3]^{2-}$ ruthenate, which is not the mediator during oxidation process [3]. Second method of quenching was related to the deactivation of the oxidant by the addition of a 'killing' agent. Based on this assumption, several methods of quenching were tested: the addition of an aqueous NaOH solution as well as NaOH solution in MeOH to the reaction to raise the pH between 8 and 14, addition of solid Na_2SO_3 and its solution in H_2O.

The quenching of the reaction by raising the pH from 9 to 14 seemed to be effective; however, there was a major problem in analysing of the quenched sample. Large amounts of NaOH interfered with the analysis and its presence caused column bleeding during GC-MS runs. Na_2SO_3 has been chosen as a quenching reagent. It is known that Na_2SO_3 can be easily oxidized to Na_2SO_4, what occurred here and therefore $NaIO_4$ was deactivated and transformed to $NaIO_3$. This methodology was found to be effective and practically possible in all aspects. The data demonstrating effective quenching is given below (Figure 3-1).

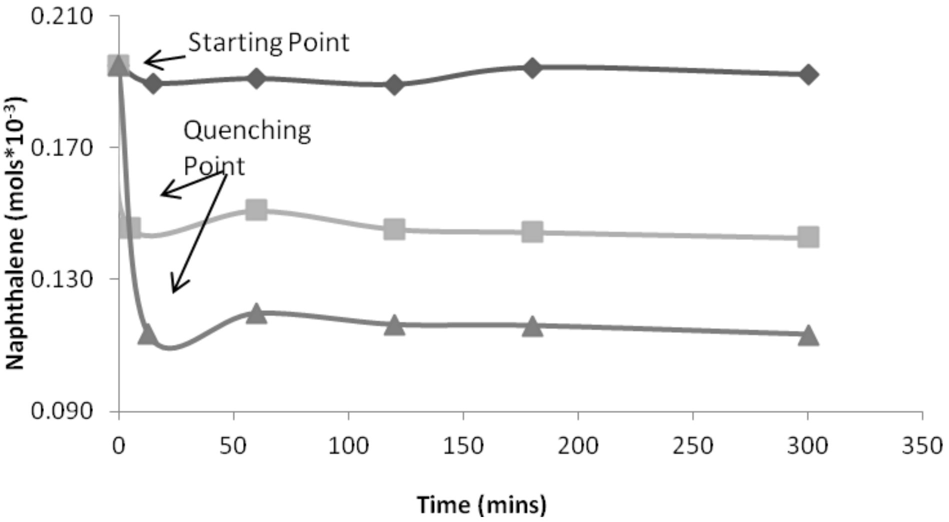


Figure 3–1: Quenching studies: Addition of Na_2SO_3 to the reaction mixture at different reaction times; Reaction 1:(◆) Na_2SO_3 added before addition of catalyst and oxidant, Reaction 2:(■) Reaction quenched after 5mins, Reaction 3:(▲) Reaction quenched after 13mins; Reaction Conditions: Substrate 0.195mmols, $NaIO_4$ 1.56 mmols, $RuCl_3$ 0.012mmols, Na_2SO_3 1.56mmols, MeCN 20ml, H_2O 10ml, T=22°C, stirring speed 500rpm

When Na_2SO_3 was added to the reaction mixture before addition of oxidant, oxidation did not occur and naphthalene concentration was maintained as the same level. Addition of quenching reagent after 5mins (Reaction 2) and 13 mins (Reaction 3) led to reaction quenching and naphthalene was not consumed further. To conclude, a minimum of 1:1 mols of Na_2SO_3 added to the oxidant was found to be needed to completely quench the reaction. A plot showing this dependence is displayed below (Figure 3-2).

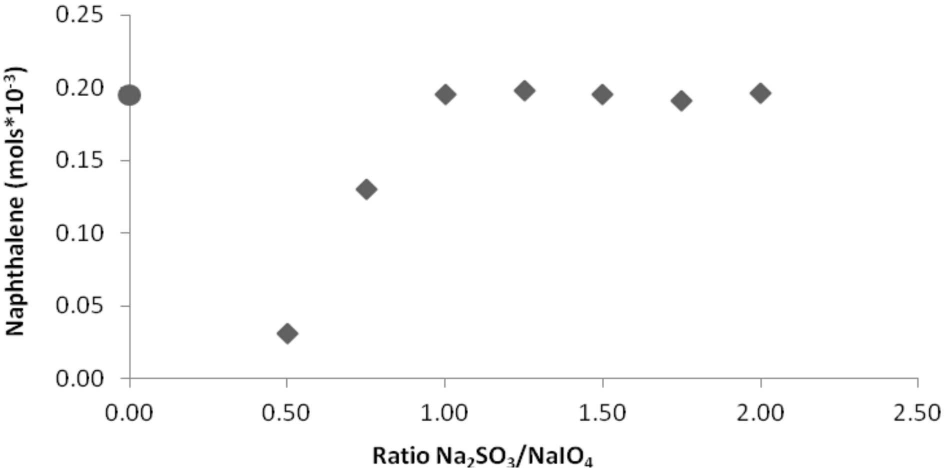


Figure 3–2: Quenching efficiency Vs molar ratio $Na_2SO_3/NaIO_4$ tested on naphthalene oxidation(◆); Reaction Conditions: Substrate 0.195mmols (initial number of mmols:●), $NaIO_4$ 1.56mmols, $RuCl_3$ 0.012mmols, Na_2SO_3 1.56mmols, (Ratio 1:1), MeCN 20ml, H_2O 10ml, T=22°C, stirring speed 500rpm

3.3. Mass balance study

One of the most important challenges of this project was to selectively oxidize molecules to the desired products with the minimum generation of CO_2. Therefore, two experiments were carried out to investigate the changes in weight during the course of the reaction and thus determine, if significant quantity of the carbon is oxidized to CO_2. Phenanthrene was chosen as a model compound for this investigation.

In both cases, the experiments were scaled up, keeping the *substrate : oxidant : catalyst* ratio constant, as previously described in section 2.6.1.1. In the first reaction (A), 1g of phenanthrene, while in the second (B), 2g of phenanthrene was used. The change in mass was determined gravimetrically by taking the weight of solid reactants before and after the reaction and the data are shown below (Table 3-1).

Table 3-1: Table presenting mass balance study performed during phenanthrene oxidation

	Reaction 1	**Reaction 2**
Substrate (Phenanthrene)	1g	2g
Oxidant ($NaIO_4$)	1.2g	2.4g
Catalyst ($RuCl_3$)	10mg	20mg
Solvents (MeCN:H_2O vol. 2:1)	60ml	120ml
Mass of reactants +flask before reaction	161.094g	205.762g
Mass of reactants +flask after reaction	160.995g	205.610g
Loss in mass (g)	0.099g	0.152g
Total loss in mass (%) (In relation to solid reactants)	4.5%	3.4%
Loss in mass (%) (In relation to substrate)	9.9%	7.6%

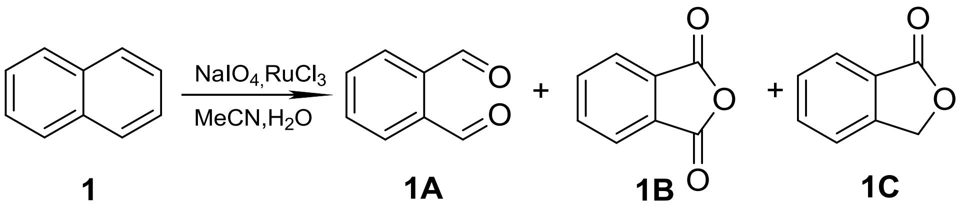
The data obtained suggested 4.5% loss in mass for the 1 g scale reaction while 3.4% loss was observed for the 2g scale reaction in relation to the total mass of reactants (oxidant and catalyst). It is assumed that the mass of oxidant and catalyst remained unchanged, thus the loss in weight for the transformation of substrate to product would be 9.9% and 7.6%, respectively. The loss in weight for reaction B, was expected to be twofold higher than for reaction A. The lower than expected percentage value for reaction B, suggests that sample A may still contain some moisture from the experiment. However, overall results obtained from this experiment show that around 90% of the substrate is converted into products.

3.4. Oxidation products identification of non alkylated PAHs

The main thrust of this section of the study was to determine the products of PAHs oxidation. Moreover, it was important to compare these products with compounds obtained when the reaction was conducted in a biphasic solvent system (Chapter 4). Four different substrates were chosen for this study: naphthalene, phenanthrene, pyrene and one of pyrene's oxidation products, pyrene-4,5-dione.

3.4.1. Naphthalene

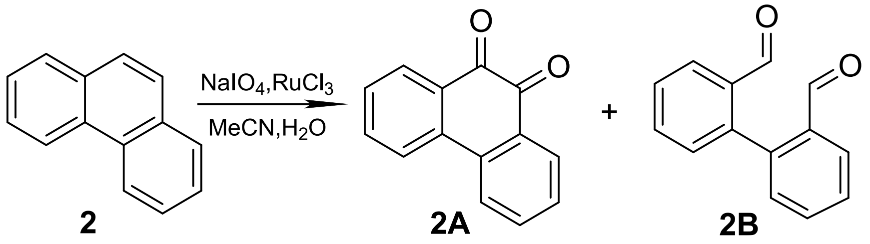
In previous literature reports a large amount of attention has been paid to the total oxidation of naphthalene to CO_2 [5-7]. Total naphthalene oxidation can be achieved in the gas phase over a heterogeneous catalyst [8]. The target of this research was completely different to that mentioned above (Chapter 1) and it is possible using RICO chemistry to convert naphthalene into desirable products having one aromatic ring open. The oxidation of naphthalene using RICO chemistry was completed within 1 hour. Reaction completion was confirmed by the disappearance of the naphthalene peak from the GC trace. GC-MS analysis of product mixture revealed that the products include phthalaldehyde (1A), phthalic anhydride (1B) and isobenzofuran 1(*3H*)-one (1C) as shown in Scheme 3-1. In all observed products only one ring has been oxidized. It is worth mentioning that phthalic anhydride was probably formed via the dehydration of phthalic acid [9]. Another compound which is formed in a similar way is the product of 2-hydroxymethyl-benzoic acid dehydration, isobenzofuran 1(*3H*)-one [10]. This was also confirmed by ^1H NMR analysis, where strong peak corresponding to acid group was detected (Appendix 8.3). In comparison to oxidation with heterogeneous catalyst, product 1B obtained in the RICO reaction was also observed as a reaction intermediate in the total oxidation of naphthalene over a 1%Pt and 5%Co/γ-Al_2O_3 [6].



Scheme 3-1: Products of naphthalene oxidation in monophasic solvent system
Reaction Conditions: Substrate 0.164mmols, $NaIO_4$ 1.312mmols, $RuCl_3$ 0.012mmols, MeCN 20ml, H_2O 10ml, T=22°C, Stirring speed 500rpm, t=4h

3.4.2. Phenanthrene

The next compound, which was used for oxidation was phenanthrene. Phenanthrene was completely transformed to its oxidative products faster than naphthalene. GC-MS analysis of the phenanthrene oxidation product mixture suggested that the main product, in the monophasic solvent system is 9,10-phenanthrenequinone (2A) along with a trace amount of biphenyl-2,2'-dicarbaldehyde (2B) (Scheme 3-2). Product 2B is obtained by the oxidative C-C bond cleavage, which is crucial for the oxidative valorisation of high molecular weight multiring residues.

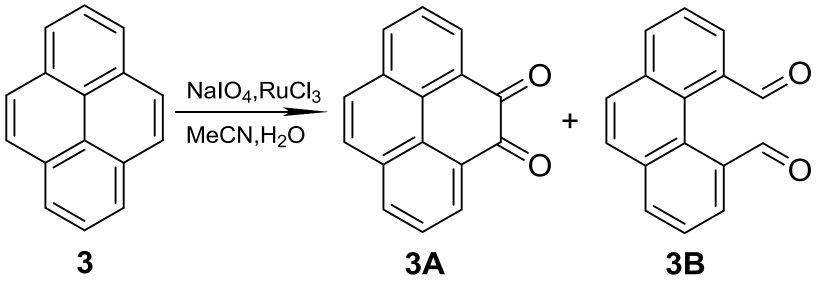


Scheme 3-2: Products of phenanthrene oxidation in monophasic solvent system
Reaction Conditions: Phenanthrene 0.164mmols, $NaIO_4$ 1.312mmols, $RuCl_3$ 0.012mmols, MeCN 20ml, H_2O 10ml, T=22°C, Stirring speed 500rpm, t=4h

The C-C bond cleavage observed under our experimental conditions is different from previously reported literature data. Tabatabaeian *et al.* did not observe any C-C bond cleavage during RICO chemistry. However, using ultrasonic-irradiation, Tabatabaeian *et al.* obtained the oxidation product, 9,10-phenanthrenequinone with a 88% yield [11]. The main differences between the work reported in literature and the catalytic system employed in this study, is the use of ultrasonification and a biphasic solvent system. As it can be concluded from the comparison between the literature reported system and used in the experiment, the product distribution is controlled by the choice of solvent and sonification.

3.4.3. Pyrene

The next PAH in the series to be studied was pyrene. Oxidation of pyrene was carried out under the same conditions as previously described in section 2.6.1., but the amount of reactants was increased by factor of 3. Oxidation in a monophasic solvent system gave two major products: pyrene-4,5-dione (3A) and phenanthrene 4,5-dialdehyde (3B) identified by HPLC-MS and ^{1}H NMR (Scheme 3-3).



Scheme 3-3: Products of pyrene oxidation in monophasic solvent system
Reaction Conditions: Pyrene 0.495mmols, NaIO$_4$ 3.936mmols, RuCl$_3$ 0.036mmols, MeCN 40ml, H$_2$O 20ml, T=22°C, Stirring speed 500rpm, t=4h

The minor product, phenanthrene-4,5-dialdehyde, is of special interest, because to the best of our knowledge, this is the first ever observation of a product of pyrene oxidation, with selective oxidative opening of only one ring using RICO chemistry. From the literature, the main products of pyrene oxidation in a biphasic solvent system are pyrene-4,5-dione and pyrene-4,5,9,10-tetraone [12]. In both these products, either one or two aromatic rings are oxidized but under our experimental conditions one aromatic ring has been selectively oxidized and subsequently undergone ring opening to the dialdehyde.

HPLC-MS (electrospray negative M-H$^+$) analysis of the resultant reaction mixture, after quenching gave a strong peak corresponding to m/z value of 233, which could be assigned to the phenanthrene-9,10-dialdehyde which has a molecular weight of 234g mol^{-1}. These products appeared in HPLC chromatogram with retention time 9.45min as shown in Figure 3-3.

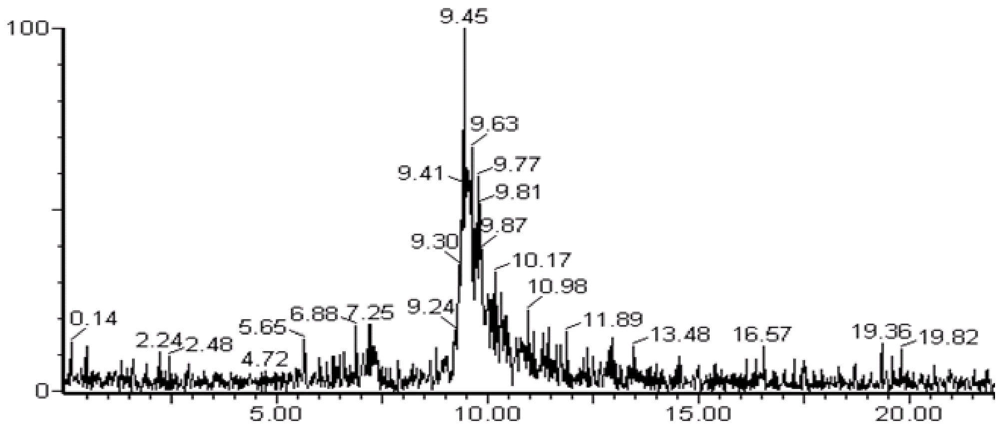


Figure 3–3: Chromatogram showing exclusively compound with signal M-H$^+$=233

^{1}H NMR spectra (Figure 3-4) proved the existence of an aldehyde group with sharp singlet peaks observed at 9.74ppm and 10.1ppm, suggesting the presence of 2 different aldehyde species in the reaction mixture.

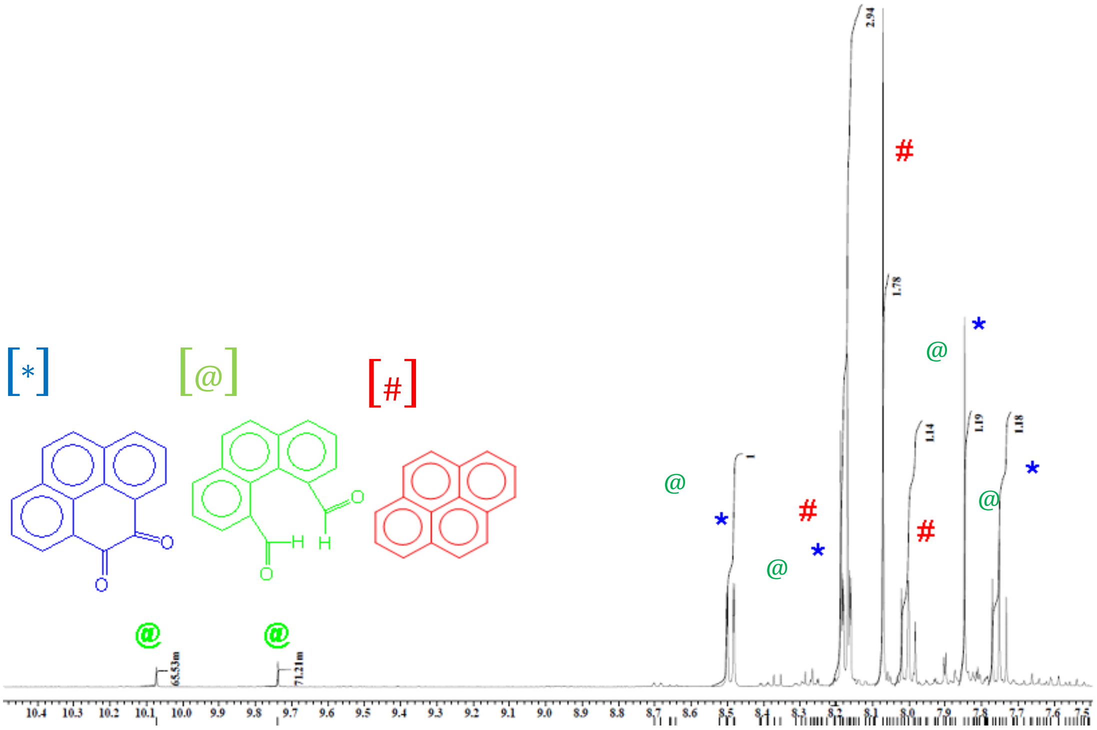
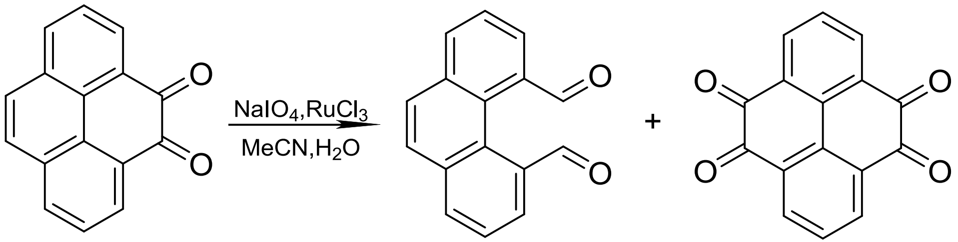


Figure 3–4: ^{1}H NMR analysis of reaction mixture, pyrene oxidation
Reaction conditions: Pyrene 0.495mmols, $NaIO_4$ 3.936mmols, $RuCl_3$ 0.036mmols, MeCN 40ml, H_2O 20ml, T=22°C, Stirring speed 500rpm, t=4h

As it was said earlier, the second major product of pyrene oxidation was pyrene-4,5-dione. It presence was identified by ^{1}H NMR analysis, where pyrene dione nuclei gave characteristic signals at 8.5ppm, 8.19ppm, 7.85ppm and 7.75 ppm marked by * (Figure 3-4).

3.4.4. Pyrene-4,5-dione

Oxidation of pyrene 4,5–dione was performed using substrate : oxidant ratio 1:5. The change is standard reaction conditions was done to avoid consecutive oxidation. The reaction resulted in the production of phenanthrene 4,5-dialdehyde (4A) and pyrene-4,5,9,10-tetraone (4B).



4 **4A** **4B**

Scheme 3-4: Pyrene-4,5-dione oxidation products
Reaction Conditions: Pyrene 4,5,-dione 0.0349mmols, NaIO$_4$ 0.174mmols, RuCl$_3$ 0.0002mmols, MeCN 20ml, H$_2$O 10ml, T=22°C, Stirring speed 500rpm

The presence of products was confirmed by HPLC and MS analysis as it can be seen in the figure 3-5. (Phenanthrene-4,5-dialdehyde: HPLC: Rt=5.72min, MS: *m/z*=234.0332; Pyrene-4,5,9,10-tetraone: HPLC: Rt=7.29min, *m/z*=262.0258). Moreover, ^{1}H NMR spectrum clearly shows doublet at 8.35ppm (4H) and triplet at 7.75ppm (2H) corresponding to pyrene-4,5,9,10-tetraone.

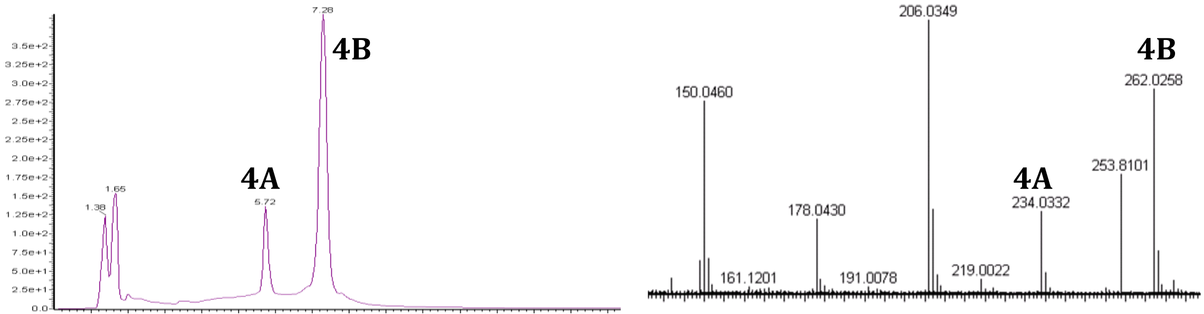


Figure 3–5: Pyrene-4,5–dione oxidation in monophasic solvent system.
UV spectra (left) from HPLC analysis and Mass Spectra (EI) analysis (right)

Through careful time on line analysis of pyrene-4,5-dione consumption, it was possible to calculate the concentration of one of the products formed, pyrene-4,5,9,10-tetraone. The HPLC system was calibrated for the dione and tetraone using synthesized standards. As it can be calculated from the data presented in figure 3-6, selectivity towards the tetraone is 81.6%. The only other product detected in this reaction was phenanthrene 4,5-dialdehyde, therefore it can be assumed that selectivity towards the dialdehyde is 18.4%.

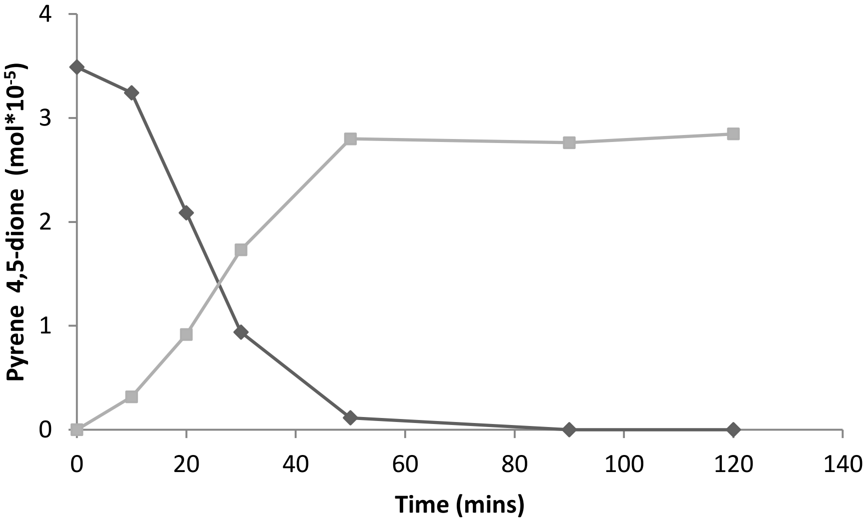


Figure 3–6: Pyrene-4,5-dione(◆) oxidation and pyrene-4,5,9,10-tetraone (■) formation Reaction Conditions: Pyrene 4,5,-dione 0.0349mmols, $NaIO_4$ 0.174mmols, $RuCl_3$ 0.0002mmols, MeCN 20ml, H_2O 10ml, T=22°C, Stirring speed 500rpm

These findings above are very interesting, as they suggest that the oxidation of only one aromatic ring can take place at any one time. That is why in case of pyrene-4,5-dione oxidation we observed products containing 2 oxygen activated rings, while products derived from the oxidation of pyrene have only one oxygenated ring.

3.5. Kinetic studies

For the purpose of valorisations of petroleum resids it is very important to oxidize aromatic molecules selectively with one ring opening at a time. It is also crucial to achieve and maintain the higher reaction rate for heavier molecules than for those with 2 aromatic rings. Thus, kinetic studies were performed to answer the questions about the rate of reaction for molecules with different numbers of aromatic rings.

3.5.1. Individual reactions

The time on line plots presenting substrate consumption: naphthalene, phenanthrene and pyrene in individual reactions are shown on the graph below (Figure 3-7).

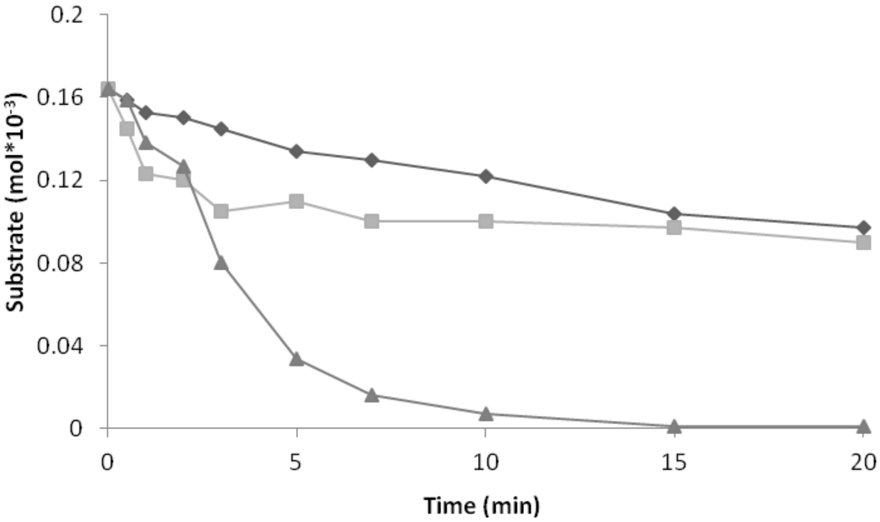


Figure 3–7 Comparison of the individual rates of oxidation of PAHs in a monophasic solvent system
Reaction conditions: Substrate: naphthalene (◆), phenanthrene (■) and pyrene (▲) 0.164mmols, $NaIO_4$ 1.312mmols, $RuCl_3$ 0.012mmols, MeCN 20ml, H_2O 10ml, T=22°C, Stirring speed 500rpm

Oxidation of PAHs in a monophasic solvent system shows a substantial difference in the rate of oxidation between pyrene and that of phenanthrene and naphthalene. Initial reaction rates calculated for first 5 mins of the reaction are tabularised below (Table 3-2).

Table 3-2: Initial rates of oxidation in monophasic solvent system

	Naphthalene	**Phenanthrene**	**Pyrene**
Initial rate (mmols/min)	0.005	0.009	0.027

As it is shown above, the order of reactivity is pyrene>phenanthrene>naphthalene. This is an important observation for the oxidative valorisation of petroleum resids, because here the employed catalytic system oxidizes the aromatics with a higher number of rings faster than their smaller counterparts. This is in agreement with literature reports which suggest that reactivity increases with the number of fused aromatic rings [13].

In addition, studies investigating the reaction rate between the substrate, pyrene and its oxidation product, pyrene-4,5-dione were also performed. For this experiment, the volume of solvent used in the reaction needed to be increased by factor of 2 in order to avoid precipitation problems. Theoretical calculations showed that energy differences for adduct formation (Ru VI) from pyrene and pyrene dione were negligible (pyrene: -35.19 kcal mol^{-1}, pyrene-4,5-dione: -31.87 kcal mol^{-1}) [14]. Experimental observation supported the expected outcome, that the reaction rate for both pyrene and pyrene-4,5-dione is similar.

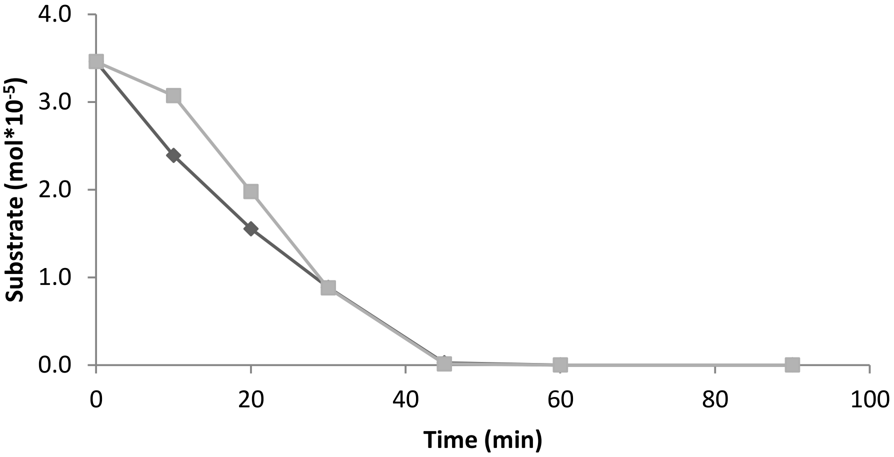


Figure 3–8: Individual oxidation of pyrene (◆) and pyrene-4,5-dione (■) in a monophasic solvent system
Reaction Conditions: Substrate 0.0349 mmols, $NaIO_4$ 0.2768 mmols, $RuCl_3$ 0.0003 mmols, MeCN 40ml, H_2O 20 ml, T=22°C, Stirring speed 500rpm

3.5.2. Competitive oxidation reactions

To perform competitive oxidation between pyrene and pyrene 4,5-dione in a one pot reaction, the solubility of the substrate in the solvent needs to be taken into account. Pyrene solubility in acetonitrile is relatively low, as ire its derivatives. Thus to perform a competitive reaction between pyrene and pyrene-4,5-dione, the relative concentration of the substrates was lowered by reducing the moles of reactants used and increasing the volume of the solvent. By careful kinetic studies, here again, it was possible to monitor product formation and substrate consumption (Figure 3-9).

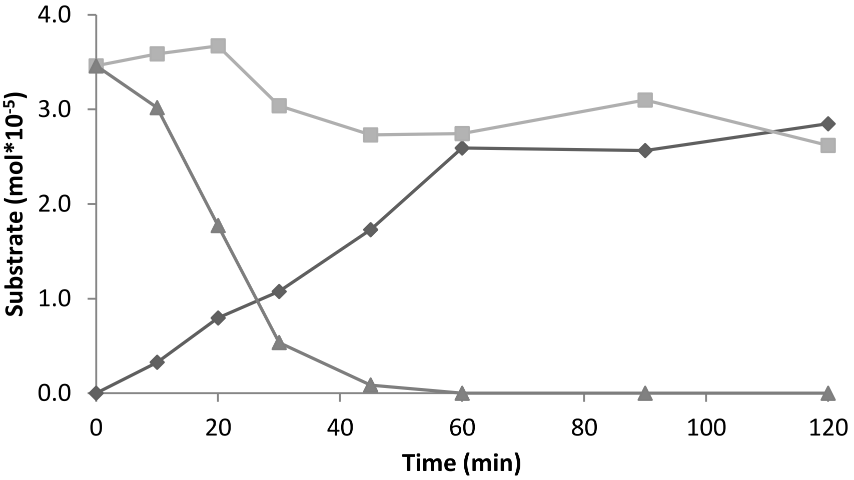


Figure 3–9: Competitive oxidation of pyrene (▲) and pyrene-4,5-dione(■) , formation of pyrene-4,5,9,10-tetraone also marked (◆)
Reaction Conditions: Substrate 0.0349mmols, $NaIO_4$ 0.554mmols, $RuCl_3$ 0.0006mmols, MeCN 40ml, H_2O 20ml, T=22°C, Stirring speed 500rpm

It is noteworthy to mention that, as was previously described, pyrene-4,5-dione is the major product of pyrene oxidation, while pyrene tetraone is the major product of pyrene dione oxidation. This behaviour explains why in figure 3-9, pyrene-4,5-dione concentration is not changing significantly. The increase in the tetraone concentration is actually caused by pyrene-4,5-dione being oxidized to the tetraone derivative. That suggests that RuO_4 only attacks one ring at a time and the simultaneous oxidation of 2 rings is not possible.

The difference in the rate of oxidation between naphthalene and its alkylated counterpart, 2-ethylnaphthalene, was also investigated to establish the contribution of the ethyl group to oxidation rate. The kinetic data is presented in figure 3-10. The rate of disappearance of 2-ethylnaphthalene (0.009) is faster than that of naphthalene (0.007), but the difference in the rate of oxidation is not substantial. This is in agreement with basic chemistry, since the electron donating character of the ethyl group increases the reactivity of the molecule and the possibility of attack from the electrophilic RuO_4.

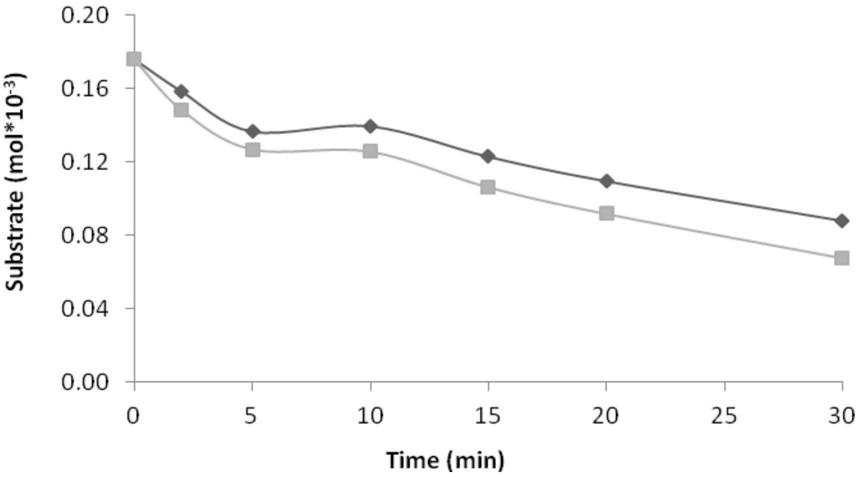


Figure 3–10: Comparison of naphthalene (◆) and 2-ethylnaphthalene (■) oxidation Reaction conditions: Substrate 0.164mmols, $NaIO_4$ 1.312mmols, $RuCl_3$ 0.012mmols, MeCN 20ml, H_2O 10ml, T=22°C, Stirring speed 500rpm

3.6. Oxidation of alkylated aromatics

As previously mentioned, the electron donating character of the aliphatic chain of an alkylated polyaromatic will increase the reactivity of that aromatic ring. This information is very useful for mechanistic investigation as well as for product determination, as it highlights how the presence of aliphatic Hs and Cs contribute towards this chemistry.

3.6.1. Ethylbenzene

Initially, ethylbenzene, being the simplest model compound for alkylated polyaromatic compounds, was used as a model substrate for the RICO reaction. This compound was found not to be very reactive during RICO oxidation and even after 100h of reaction time at 22°C only 27 mol% of acetophenone was obtained. Although the slow rate of ethylbenzene oxidation is not surprising, the alkyl oxidation was less expected as RICO is thought to occur almost exclusively at aromatic carbon atoms. The ethylbenzene rate of reaction was very low using the employed reaction conditions, so it was decided to move to the next highest member of the alkylated aromatic compounds, being 2-ethylnaphthalene.

3.6.2. 2-Ethylnaphthalene

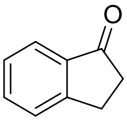
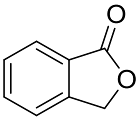
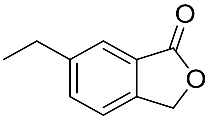
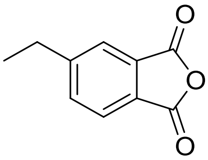
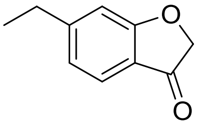
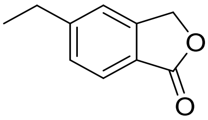
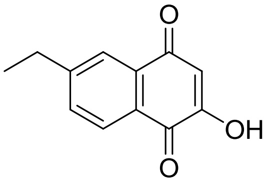
The next analogue, 2-ethylnapththalene was oxidized under standard reaction conditions, similar to the conditions reported in the literature, but in a monophasic solvent system containing acetonitrile and water [12]. Special attention was paid to the differences exhibited between alkyl chain and aromatic ring oxidation.

3.6.2.1. 2-Ethylnaphthalene oxidation - product identification

After reaction, the product mixture was qualitatively analysed by GC-MS to determine the identity of the 2-ethylnaphthalene oxidation products. Based on the mass spectral analyses, the compounds obtained for the oxidation of 2-ethylnaphthalene are listed in Table 3-2. Pure standards of these compounds were analyzed by GC to determine their retention times and to calculate their response factors for quantification purposes. Based on this data, the selectivity for all compounds was calculated under standard reaction conditions (at 22°C, 4 h). From the data presented in Table 3-2, it is evident that 80% of the products have intact alkyl chain attached to an oxidized aromatic ring.

This observation is different from what has been previously reported in the literature, as it is widely thought that when an alkyl aromatic compound is subjected to RICO chemistry, the aliphatic chain attached to the aromatic ring is oxidatively cleaved to form an aliphatic carboxylic acid with CO_2 and water as by-products [15-16]. To confirm these results, the reaction product mixture was analyzed by 2D-^{1}H NMR correlation spectroscopy (COSY), the spectrum of which is given in Figure 3-11.

Table 3-2: Oxidation of 2-ethylnaphthalene in a monophasic solvent system
[a] Compounds identified by GC-MS and GC, [b] at 100% conversion (t=4h); Reaction conditions: Substrate 0.164mmols, $NaIO_4$ 1.312mmols, $RuCl_3$ 0.012mmols, MeCN 20ml, H_2O 10ml, T=22°C, Stirring speed 500rpm

Product[a]		**Molar Selectivity**
Name	**Structure**	**(%)[b]**
2,3-dihydroinden-1-on		0.24
isobenzofuran-1(3H)-one		14.58
6-ethylisobenzofuran-1(3H)-one		13.13
5-ethylisobenzofuran-1,3-dione		20.39
6-ethylbenzofuran-3(2H)-one		17.61
5-ethylisobenzofuran-1(3H)-one		29.55
6-ethyl-2-hydroxynaphthalene-1,4-dione		4.46

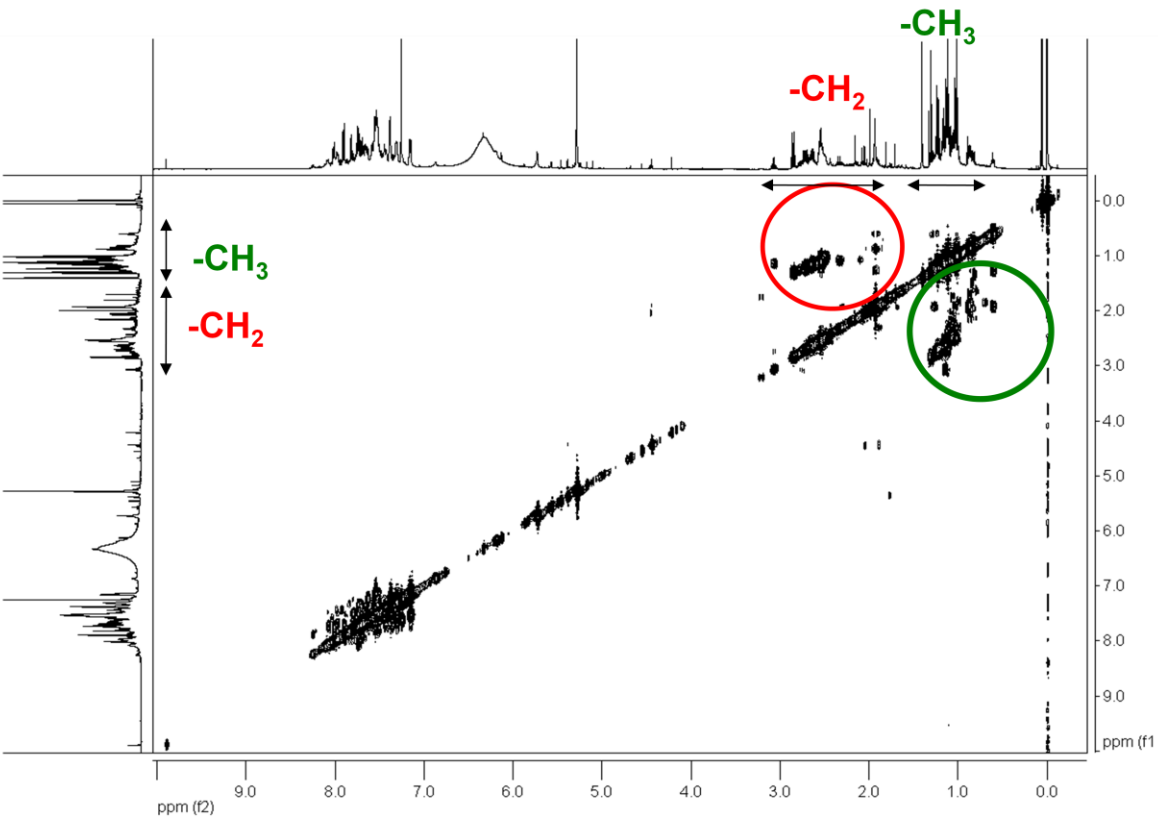


Figure 3–11: COSY spectra of 2-ethylnaphthalene oxidation products
Reaction conditions: Substrate 0.164mmols, $NaIO_4$ 1.312mmols, $RuCl_3$ 0.012mmols, MeCN 20ml, H_2O 10ml, T=22°C, Stirring speed 500rpm, t=4h

COSY NMR identifies ^1H nuclei which are coupled to each other. Here we observed groups of cross peaks below and above the diagonal. The presence of cross peaks indicates that there is a correlation between the signals. This means that protons from $-CH_2$ group are correlating with protons from $-CH_3$ group which in turn indicates that the alkyl chain must be preserved and there are products containing an alkyl chain.

From the above GC, GC-MS and 2D-NMR analyses, it is clear that during the RICO of 2-ethylnaphthalene, aromatic Cs/Hs are more selectively oxidized than their aliphatic counterpart with 80% of the products having the aliphatic chains intact with an oxidized aromatic ring.

3.6.2.2. Aliphatic protons Vs aromatic protons oxidation: ^1H NMR studies

To further understand and substantiate these surprising results, an *in-situ* time online study of this ruthenium ion catalysed oxidation of 2-ethylnaphthalene was performed in an NMR tube as is it described in details in section 2.7.4.1. The ^1H NMR signals of the entire spectra were grouped into four regions; (A) aliphatic region (3.51-0.53 ppm), (B) olefinic region (6.98-6.43 ppm), (C) aromatic region (8.63-7.51 ppm) and (D) carboxylic acid/aldehyde region (10.82-10.63 ppm). The integrated peak areas in the defined regions correspond to the number of protons present in the reaction mixture with that assigned functionality. RICO of 2-ethylnaphthalene was initiated by adding the catalyst to the NMR tube containing the reactants, immediately data collection was commenced with a ^{1}H spectrum collected every 15 min for 9 h as shown in Figure 3-12.

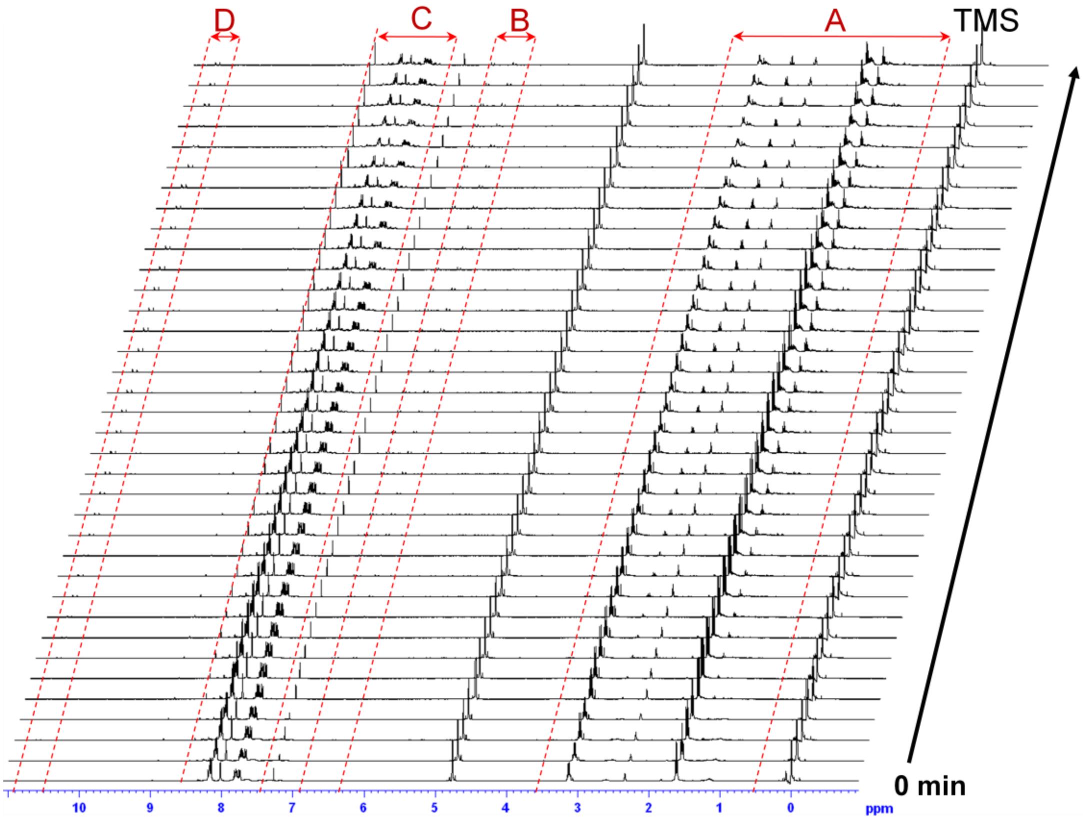


Figure 3–12: Overlaid ^{1}H NMR spectra of 2-ethylnaphthalene oxidation with marked regions of integration

The integrated peak areas from the different regions were normalized against a TMS standard held within the tube. The time-on-line data, expressed as a percentage of the four different regions is presented in Figure 3-13. Sample 0h, without the catalyst was analyzed prior to the addition of the catalyst and gave an ^{1}H integration ratio of aromatic to aliphatic protons as being 1.4, which is correct. After the addition of $RuCl_3$, a change in a ratio between aromatic and aliphatic protons was observed. The data presented in Figure 3-13 shows the quantification results of the relative proportions of protons from the different regions of the reactant and the product molecules. This data does not provide an indication of the total number of protons in the system. To provide such information on the change of the total number of protons, the normalized absolute values were plotted against time, and this data is presented in Figure 3-14.

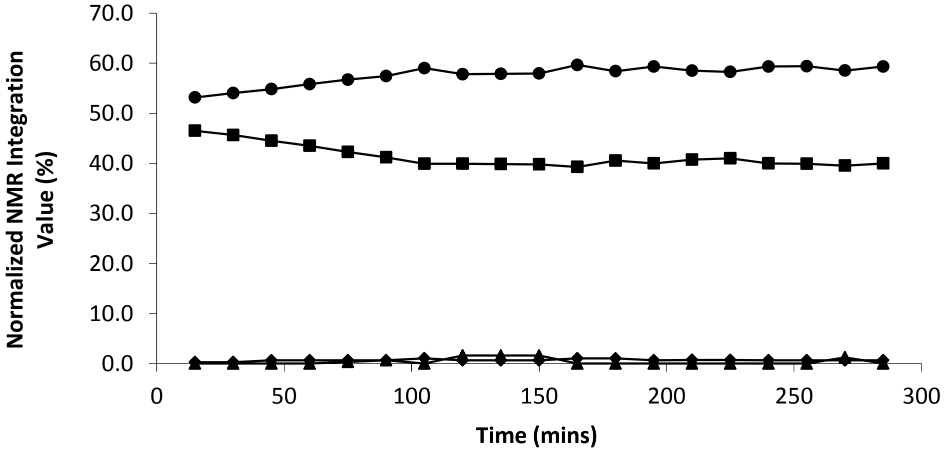


Figure 3–13 Selective oxidation of aromatic hydrogens in the presence of aliphatic hydrogens
2-ethylnaphthalene oxidation, Regions: Acid, Aldehyde (◆), Aromatic Hs(■), Double bond (▲), Aliphatic Hs (●)

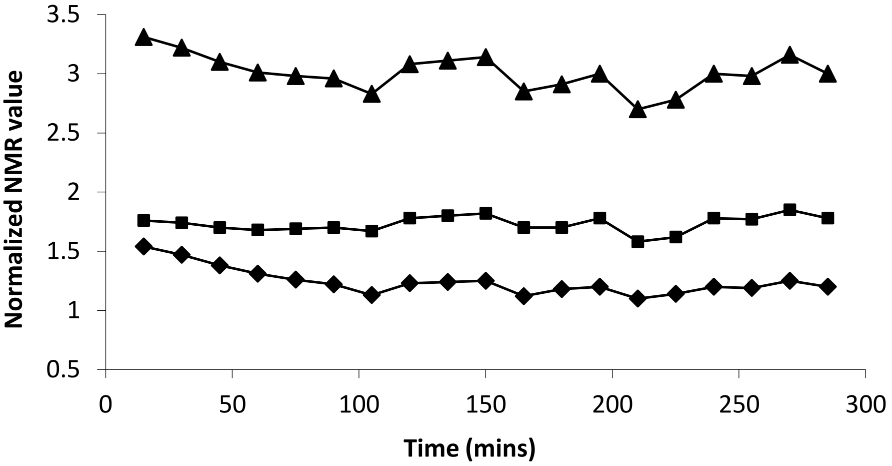


Figure 3–14 Selective oxidation of aromatic hydrogens in the presence of aliphatic hydrogens
Comparison of total (▲), aliphatic (■) and aromatic (◆) normalized protons value

It is clear that there was a reduction in the absolute number of protons, which is expected, yet the reduction is not due to a reduction in the number of aliphatic protons but a reduction in the amount of aromatic protons. The absolute number of aliphatic protons remains unchanged over the whole time period of the experiment. It is important to note that when the aromatic ring loses its aromaticity, the corresponding protons will contribute to the signal from the aliphatic protons. Using this methodology, it is difficult to distinguish between these two types of aliphatic protons. To the best of our knowledge, this is the first ever quantification of the regioselectivity between oxidation of aliphatic and aromatic carbon using an *in situ* ^{1}H NMR technique in the investigation of RICO chemistry. From the data presented above, it is clear that the oxidation of 2-ethylnaphthalene in a monophasic solvent system, leads to the selective oxidation of aromatic carbon, whilst there is little or no oxidation of the aliphatic ethyl side chain. Quantification of the reaction products has revealed that 80% retain an intact ethyl chain.

3.7. Mechanistic investigation into RICO

Studies on mechanism were performed in order to better understand this chemistry and to compare the outcome of experiments with earlier incomplete reports [1]. Previous finding related to RICO mechanism indicates that C-C bond scission is involved in the first step of the reaction. It has been suggested by Plietker that the mechanism may be similar to the oxidative cleavage of double bonds, where RuO_4 adds to the double bond in a way that it forms a ruthenium (VI) compound [1]. This compound, however can undergo an electrocyclic fragmentation to give RuO_2 and products. Frenklin proposed in his theoretical calculations that the formation of ruthenium (VI) goes through [3+2] cycloaddition [17]. This hasn't been confirmed so far as there is no proof from experimental data. Due to this reason, different methods for mechanistic investigation were employed. First, studies with $H_2{}^{18}O$ were performed, then deuterium incorporation from D_2O into the products was investigated for alkylated aromatic compound and finally kinetic studies with D_2O were applied.

3.7.1. Studies using H_2O (^{18}O)

Phenanthrene was used as a model compound for this oxidation reaction. The experiment was scaled down to give a total solvent volume of 3 ml (MeCN 2ml, $H_2{}^{18}O$ 1ml) and the *substrate : oxidant : catalyst* ratio kept constant as previously mentioned in 2.6.1.1. Preliminary studies using GC-MS showed no difference in product distribution between the normal and the scaled down experiment which indicated the data from the scaled down experiment will be reliable (Figure 3-15).

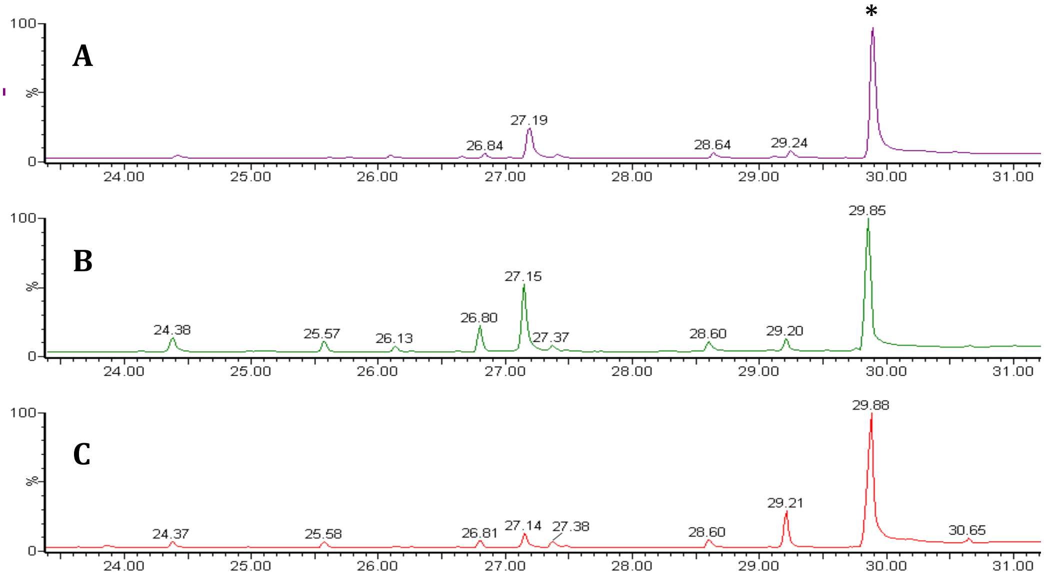


Figure 3–15: Comparison of GC chromatograms from phenanthrene oxidation T=22°C, Stirring speed 500rpm, ***A****: Standard reaction, Phenanthrene 0.164mmols, $NaIO_4$ 1.312mmols, $RuCl_3$ 0.012mmols, MeCN 20ml, H_2O 10ml,* ***B****:Scaled down reaction with labelled H_2O (^{18}O) Phenanthrene 0.0164mmols, $NaIO_4$ 0.1312mmols, $RuCl_3$ 0.0012mmols, MeCN 2ml, $H_2{}^{18}O$ 1ml,* ***C****: Scaled down reaction with H_2O, Phenanthrene 0.0164mmols, $NaIO_4$ 0.1312mmols, $RuCl_3$ 0.0012mmols, MeCN 2ml, H_2O 1ml*

The most abundant peak in the GC chromatogram (Rt=29.88) corresponds to 9,10-phenanthrenequinone and therefore was analyzed in detail. Based on the MS analysis of this peak from reactions run in both H_2O and $H_2{}^{18}O$, a difference in the molecular ion peak was observed, which indicates incorporation of ^{18}O into the product. The intensity of peaks *m/z* 182.05 and *m/z* 212.06 suggests that not only ^{18}O is incorporated into products, but also ^{16}O which can come from $NaIO_4$ source as it is shown in Figure 3-16.

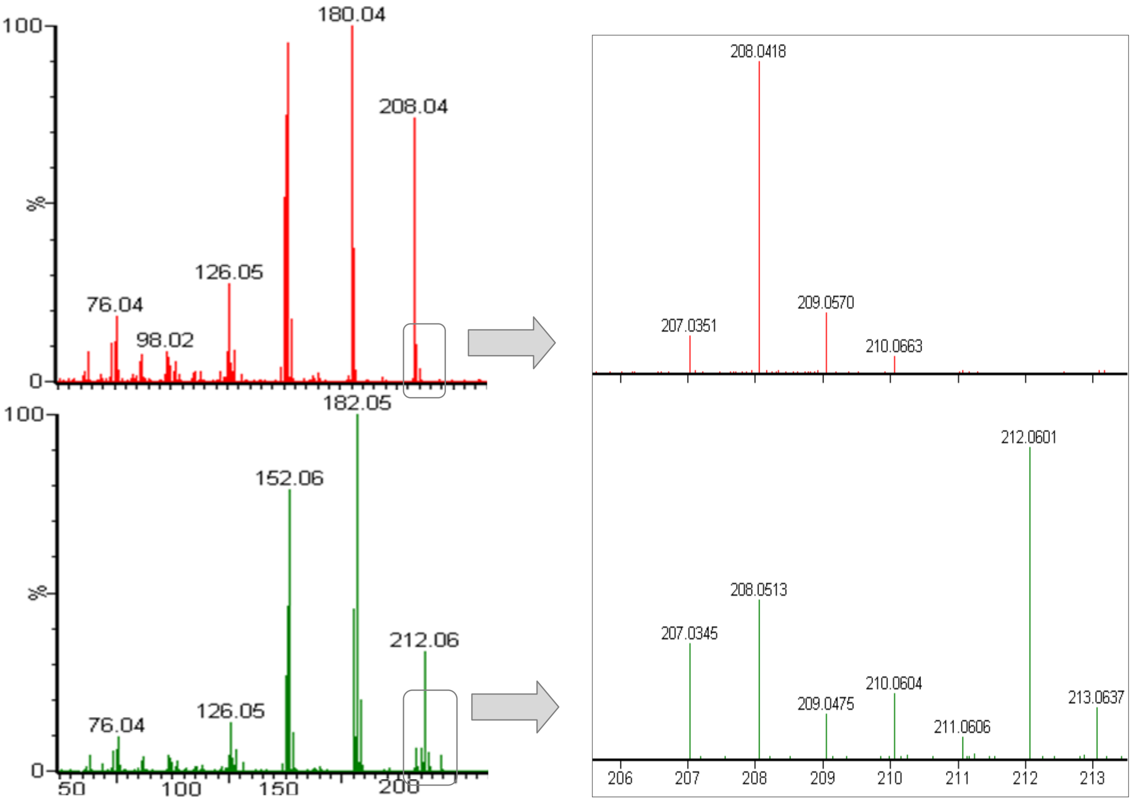


Figure 3–16: MS spectra of 9,10-phenanthrenequinone obtained in the reaction with H_2O (top) and $H_2{}^{18}O$ (bottom) and molecular expansion of peaks

These results emphasize the role of water, and its presence is crucial for reaction to occur. Since $NaIO_4$ is insoluble in MeCN, it is understandable that oxygen from water and from sodium periodate will be in equilibrium, that is why we observed the incorporation of 18 as well as 16 oxygen. In the process of RuO_4 formation 68% of oxygen comes from the oxidant and 32% from water. That is why ^{18}O as well as ^{16}O is being incorporated into oxidation products.

3.7.2. Incorporation of Deuterium into oxidation products

The aim of this experiment was to observe, if ^2D from D_2O is involved in the reaction mechanism and thus be incorporated into the oxidation products. The three compounds used for this experiment were phenanthrene, naphthalene and its alkylated derivative: 2-ethylnaphthalene.

First, the GC chromatograms from each reaction conducted in both H_2O and D_2O were compared (Figure 3-17). No changes in product distribution were observed in the case of all three compounds tested. Using GC-MS, each chromatographic peak from the reaction conducted in H_2O was analyzed by MS and compared with the mass spectrum from each peak generated in D_2O. No change in the mass spectrum was observed when naphthalene and phenanthrene were used as substrates in individual oxidation reactions. Figure 3-17 shows the GC-MS analysis results of phenanthrene oxidation with the predominant peak being 9,10-phenanthrenequinone.

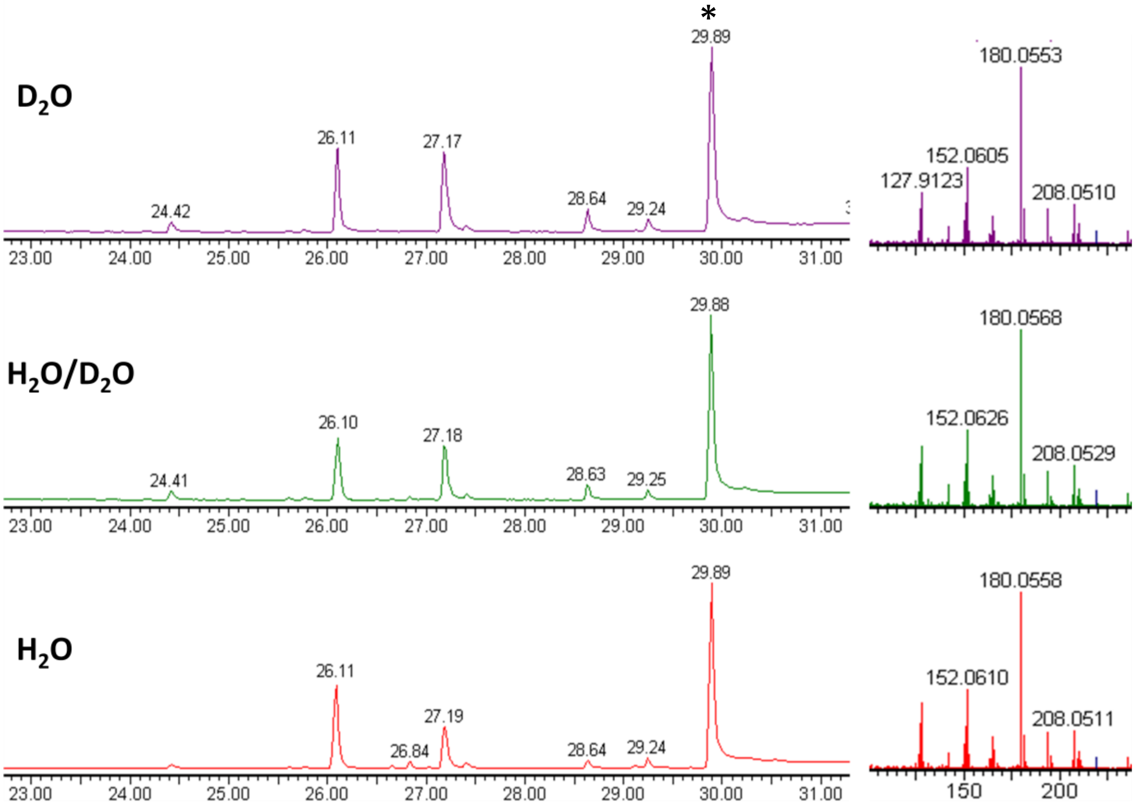


Figure 3–17: Comparison of GC chromatograms from phenanthrene oxidation under different conditions (left) and MS analysis of 9,10 phenanthrenequinone (Rt=29.89) (right) Reaction Conditions: Phenanthrene 0.164mmols, $NaIO_4$ 1.31 mmols, $RuCl_3$ 0.012mmols, MeCN 20ml, D_2O or H_2O/D_2O or H_2O 10ml, T=22°C, Stirring speed 500rpm, t=2h

In the case of reaction run with 2-ethylnaphthalene different data were observed. GC chromatograms from reactions performed in the presence of H_2O and D_2O showed the same peaks (Figure 3-18), but MS analysis of the oxidation products of 2-ethylnaphthalene saw incorporation of deuterium into one of these products (GC-MS Retention time 23.73mins).

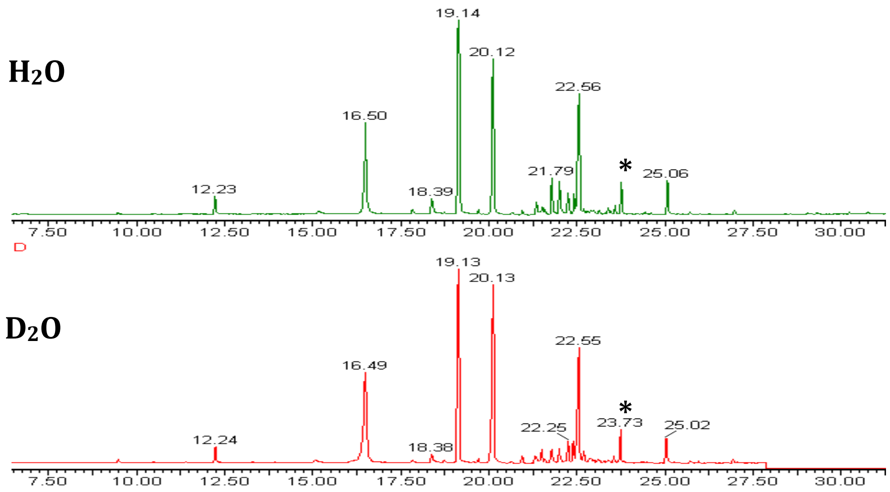


Figure 3–18: GC chromatograms of products from oxidation of 2-ethylnaphthalene in H_2O (top) and D_2O (bottom)
Reaction Conditions: 2-ethylnaphthalene 0.328mmols, $NaIO_4$ 2.62mmols, $RuCl_3$ 0.024mmols, MeCN 20ml, D_2O or H_2O 10ml, T=22°C, Stirring speed 500rpm

MS analysis suggests the incorporation of between 1 to 3 deuterium atoms, which is implied by the presence of peaks at m/z = 203, 204 and 205 (Figure 3-19). The most intensive peak at m/z 204 suggests that the majority of product contains 2 deuterium atoms, when compared to the MS spectrum generated by this product when the reaction is conducted in H_2O.

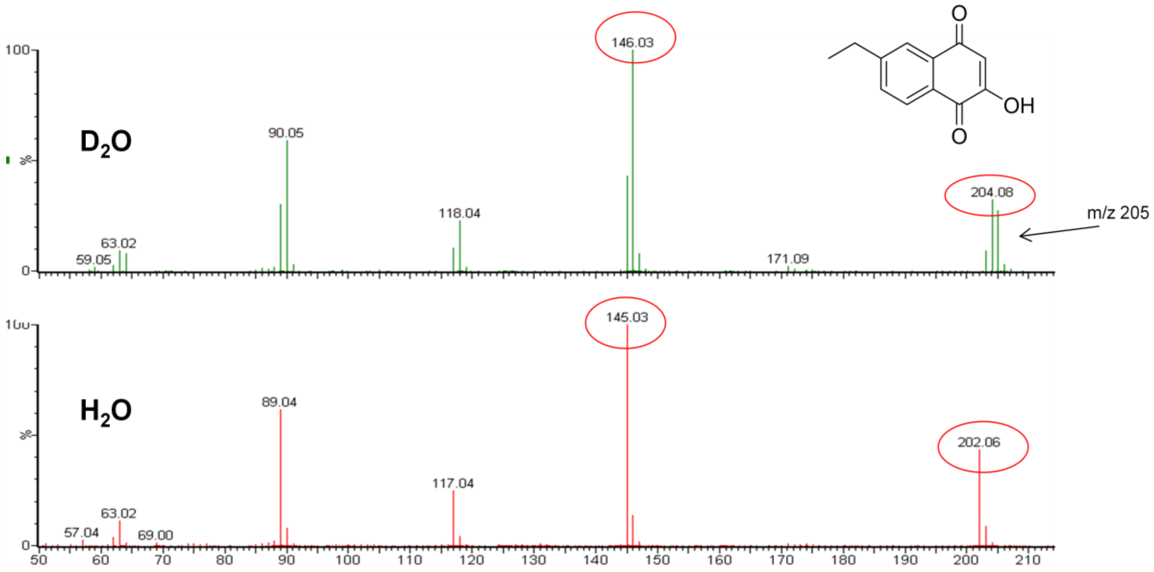


Figure 3–19: Mass Spectrometry analysis of 6-ethyl-2-hydroxynaphthalene-1,4-dione obtained in the reaction with H_2O (bottom) and D_2O (top)

When considering the possible location of the deuterium in the compound, it is highly possible that deuterium is incorporated into the OH group. To find the location of the two other deuterium, ^2H NMR analysis of the dried residue from the reaction with D_2O was performed. ^2H NMR spectra displayed a sharp peak at 3.2ppm, which suggests the presence of D in the α position of the aliphatic chain (Figure 3-20). On the other hand, it is important to remember the possibility of exchange between of H and D between products and D_2O, which could take place here.

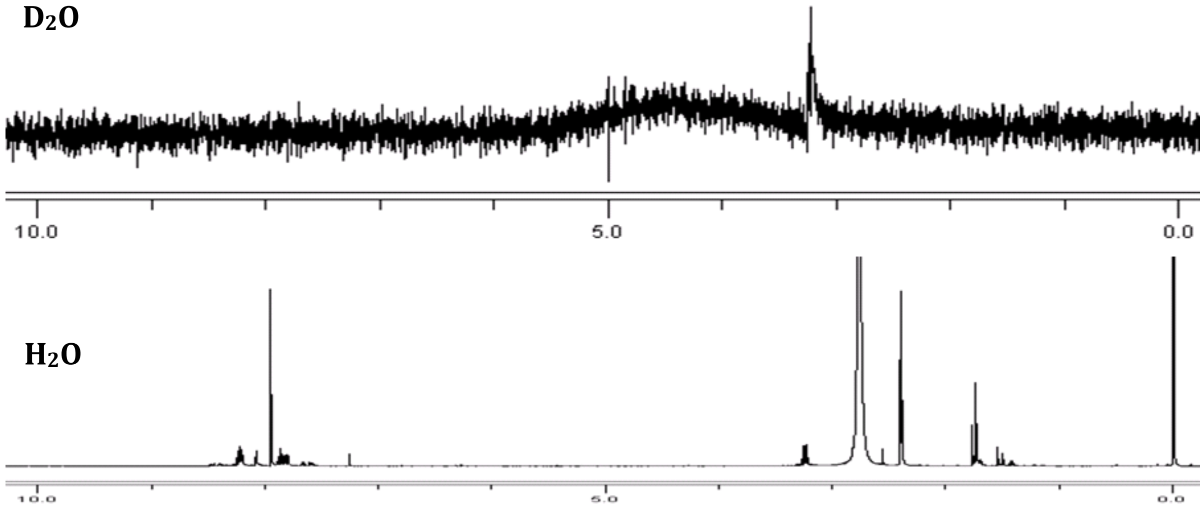


Figure 3–20: NMR analysis of 2-ethylnaphthalene oxidation products at 100% conversion Top figure: 2D NMR, reaction run in D_2O; Bottom figure: ^1H NMR, reaction run in H_2O

3.7.3. Kinetic Studies using D_2O and H_2O

Kinetic studies using H_2O and D_2O were run to determine if there was a Kinetic Isotope Effect (KIE). KIE can be found by comparing the reaction rate between different isotopically labelled compounds in the reaction, in this case H_2O and D_2O.

$$KIE=k_H/k_D \qquad \text{(Equation 3-1)}$$

Where:

k_H =*reaction rate for reaction with* H_2O
k_D =*reaction rate for reaction where* D_2O *was used*

After comparison of the rate of phenanthrene consumed in the reaction conducted in H_2O and secondly in D_2O, it is clear that water is involved in the mechanism (Figure 3-21).

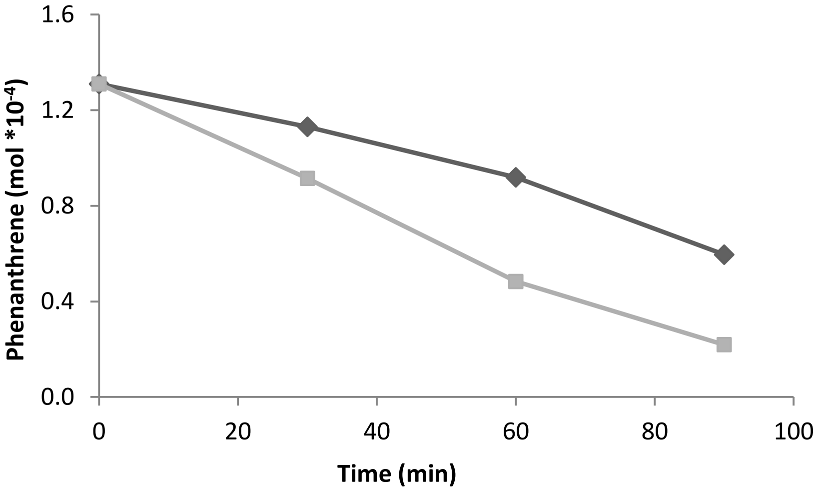


Figure 3–21: Kinetic Studies: Oxidation of phenanthrene
Reaction Conditions: Phenanthrene 0.131mmols, $NaIO_4$ 1.048mmols, $RuCl_3$ 0.010mmols, MeCN 20ml, D_2O(◆)or H_2O(■) 10ml, T=22°C, Stirring speed 500rpm

The calculated KIE value for these reactions was found to be 1.71, which suggests a Primary Kinetic Isotope Effect and the involvement of water in the rate determining step.

Table 3-3: Theoretical and experimental value of Kinetic Isotope Effect

Theoretical value		**Experimental value (Phenanthrene)**
Primary KIE	**Secondary KIE**	
>1.5	<1.2	1.71

The same experiment was performed using 2-ethylnaphthalene (Figure 3-22). Here, the observations are the same as above and the value obtained for the KIE is 1.71 and is exactly the same value as determined for phenanthrene which again, indicates Primary Kinetic Isotope Effect.

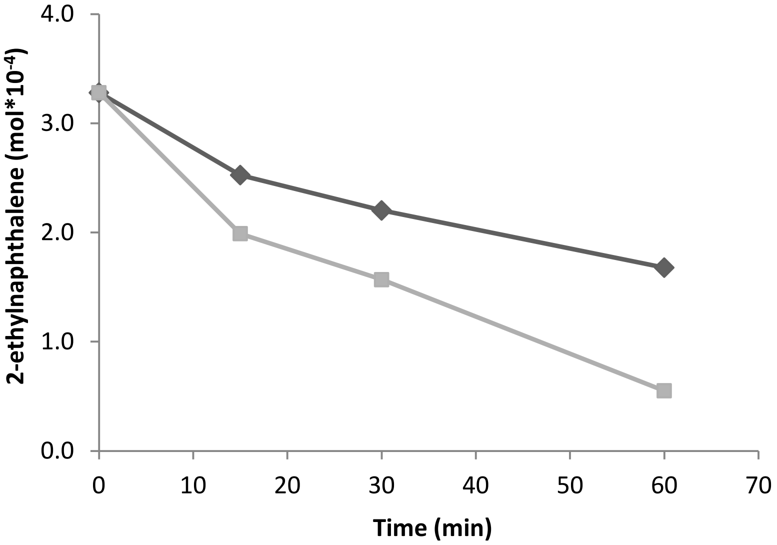


Figure 3–22: Kinetic Studies: Oxidation of 2-ethylnaphthalne
Reaction Conditions: 2-ethylnaphthalene 0.328 mmols, $NaIO_4$ *2.62 mmols,* $RuCl_3$ *0.024 mmols, MeCN 20ml,* D_2O *(◆)or* H_2O*(■) 10 ml, T=22°C, Stirring speed 500rpm*

Identical KIE values obtained for two different substrates prove that the reaction follows the same mechanism, as previously suggested.

3.8. Conclusions

In the work described here, it has been illustrated that minor modification to the RICO system, such as the introduction of a new solvent, can simplify product analysis without affecting the activity of the system. It was presented that Na_2SO_3 can be used as a successful quenching reagent and by its addition to the reaction, the oxidation is stopped, which allows product analysis to be postponed and allow time on line data to be generated. Findings related to mass balance studies showed that via the introduction of a monophasic solvent system it was possible to selectively transform substrates into useful products without the formation of large amounts of CO_2. The introduction of a solvent system has also led to selective oxidation process. In case of all tested substrates it was observed that the products are opened in a one ring at a time fashion, which plays a very important role in case of product valorisation. However, production of aldehydes raises some questions. Firstly, in the case of naphthalene oxidation, the presence of phthalaldehyde is puzzling, since this compound has never been previously observed as a product of naphthalene oxidation using standard RICO chemistry. This oxidation is expected to give acids or alcohols as the major products, however it was reported by Ikunaka that the slightly acidic conditions can selectively oxidize alcohols to aldehydes

[18]. During the course of the RICO reaction, alcohol formation is possible and addition of quenching reagent, Na_2SO_3 may lead to further, mild oxidation to the aldehyde. The presence of CHO group was proven by ^{1}H NMR analysis of the reaction mixture where peak (singlet) was observed at 10.49 ppm (Figure 8-4). Phenanthrene oxidation products identified may again raise questions about reaction selectivity and the possibility of aldehyde formation. Nonetheless, the presence of a singlet in ^{1}H NMR chemical shift at 10.55ppm indicates the existence of biphenyldialdehyde. Similar results were observed for pyrene and pyrene-4,5-dione oxidation. Results show the presence of products with one ring opened, but this has not been reported in the literature before.

In terms of selectivity of aliphatic verses aromatic protons and carbons it was demonstrated that ruthenium chemistry is selective for oxidation of aromatic carbons while leaving aliphatic carbon mainly untouched. From the data presented above, it is clear that RICO of 2-ethylnaphthalene, in a monophasic solvent system, leads to selective oxidation of aromatic carbon, whilst there is little or no oxidation of the aliphatic ethyl side chain. Quantification of the reaction products has revealed that 80% of these products have an intact ethyl chain. Furthermore, no products arising from the oxidative cleavage of the alkyl chain or the aromatic ring were observed.

When comparing this data with that generated via the oxidation of 2-ethylanthracene in a biphasic solvent system, a similar trend was observed, e.g.: products with a preserved ethyl chain were detected [19]. It has also been demonstrated that non substituted aromatic compounds react slower than their counterparts with aliphatic chains, which indicates an electrophilic character of this chemistry.

Studies related to mechanistic investigation helped to reveal and understand the chemistry of aromatic C=C bond cleavage. The presence of aliphatic chains plays a crucial role in terms of deuterium incorporation into the oxidation products. This suggests that if there is an aliphatic chain present in the starting material, a hydrogen atom from water may be involved in the mechanism or H-D exchange took place. On the other hand, the calculated KIE for both molecules, with and without aliphatic chains, had exactly the same value, which would suggest the same mechanism in both reactions. It was also shown that oxygen from water (as solvent) is incorporated to approximately 80% of the products, which suggests the rest of oxygen must be derived from $NaIO_4$.

3.9. References

1. Plietker, B., *Synthesis-Stuttgart*, **2005**(15), 2453
2. Beattie, J.K., *Pure and Applied Chemistry*, **1990**, 62(6), 1145
3. Mills, A. and Holland, C., *Journal of Chemical Research-S*, **1997**(10), 368
4. Carlsen, P.H.J., Katsuki, T., Martin, V.S., and Sharpless, K.B., *Journal of Organic Chemistry*, **1981**, 46(19), 3936
5. Bampenrat, A., Meeyoo, V., Kitiyanan, B., Rangsunvigit, P., and Rirksomboon, T., *Catalysis Communications*, **2008**, 9(14), 2349
6. Zhang, X.W., Shen, S.C., Hidajat, K., Kawi, S., Yu, L.E., and Ng, K.Y.S., *Catalysis Letters*, **2004**, 96(1-2), 87
7. Zhang, X.W., Shen, S.C., Yu, L.E., Kawi, S., Hidajat, K., and Ng, K.Y.S., *Applied Catalysis a-General*, **2003**, 250(2), 341
8. Garcia, T., Solsona, B., Cazorla Amoros, D., LInares Solano, A., and Taylor, S.H., *Applied Catalysis B: Environmental*, **2006**, 62(66-72), 66
9. Lorz, P.M., Towae, F.K., Enke, W., Jckh, R., Bhargava, N., and Hillesheim, W., *Phthalic Acid and Derivatives*. Ullmann's Encyclopedia of Industrial Chemistry **2007**.
10. Bunnett, J.F. and Hauser, C.F., *Journal of the American Chemical Society*, **1965**, 87(10), 2214
11. Tabatabaeian, K., Mamaghani, M., Mahmoodi, N.O., and Khorshidi, A., *Catalysis Communications*, **2008**, 9(3), 416
12. Peng, P., Fu, J.M., Sheng, G.Y., Morales-Izquierdo, A., Lown, E.M., and Strausz, O.P., *Energy & Fuels*, **1999**, 13(2), 266
13. Yurkanis Bruice P., *Organic Chemistry*. 4th ed **2004**, Pearson.
14. Hickey, N. and Willock, D., *Theoretical Calculations*. 2011, Cardiff University.
15. Mojelsky, T.W., Ignasiak, T.M., Frakman, Z., McIntyre, D.D., Lown, E.M., Montgomery, D.S., and Strausz, O.P., *Energy & Fuels*, **1992**, 6(1), 83
16. Singleton, K.E., Cooks, R.G., Wood, K.V., Tse, K.T., and Stock, L., *Analytica Chimica Acta*, **1985**, 174(AUG), 211
17. Frunzke, J., Loschen, C., and Frenking, G., *Journal of the American Chemical Society*, **2004**, 126(11), 3642
18. Yamaoka, H., Moriya, N., and Ikunaka, M., *Organic Process Research & Development*, **2004**, 8(6), 931
19. Mendez, A., Bermejo, J., Santamaria, R., Blanco, C.G., and Menendez, R., *Energy & Fuels*, **2000**, 14(4), 936

4. Ruthenium Ion Catalyzed Oxidation of PAHs in Biphasic Solvent System

4.1. Introduction

The results discussed in this chapter are related to the oxidation of PAHs in a biphasic solvent system. The wide range of substrates studied in these reactions, vary from relatively simple molecules like naphthalene, to heavy, more complex compounds containing long alkyl chains e.g.: 1-octadecylpyrene. The main difference between the reaction systems described here and the one in earlier chapter, is the solvent composition. Here, previously reported literature reaction conditions, especially solvent composition made up of dichloromethane, acetonitrile and water, were applied to the reactions [1]. It is important to emphasize that this solvent combination partitions itself into two layers and oxidation occurs at the solvent interface, therefore product analysis has become more complex [2]. The major aim of the work conducted in this chapter was to compare the reaction kinetics and oxidation products from 2 different solvent systems and therefore understand the solvents role. In addition, the influence of temperature and oxidant concentration on product distribution was studied in detail. What is more, the use of a biphasic solvent system allows reactions to be conducted on more complicated molecules than previously described and to test this system for its ability to remove metals from metalloporphyrins.

4.2. Substrate distribution

For all reactions carried out in biphasic system (DCM, MeCN, H_2O), especially for kinetic reactions, it is crucial to know the relative concentration of substrate present in organic layer. All of the substrates studied were organic molecules and expected to be soluble in non polar solvents, but some of them were sparingly soluble in water. This information was important due to the experiments, where consumption of substrates in competitive reaction was monitored. During the analysis (as described in 2.6.1.2.) it was found that % of substrate present in organic layer is relatively high and it is 99%, 98% and 95% for pyrene, phenanthrene and naphthalene respectively.

4.3. Mass balance and CO_2 analysis

Experiments were performed to quantify any potential loss in mass and any CO_2 formation during the oxidation processes. The first approach was to gravimetrically determine the difference in mass before and after the reaction. Phenanthrene and pyrene were used as model compounds for this study. In a biphasic solvent system, determination of the mass in aqueous as well as in organic layer was possible, thus after reaction the 2 layers were separated, the solvent were evaporated and the mass of the dry residues verified. To clarify the calculation, it is important to mention that $NaIO_4$ and $RuCl_3$ are considered as inorganic compounds, which will be present in the aqueous phase, while the substrate and the major products will be in the organic phase. In the calculations, solvent mass was not taken into account. The obtained % mass was achieved by comparison of the mass before and after the reaction in the separated layers. In the case of phenanthrene oxidation, mass recovery from the aqueous layer (inorganic compounds) was 88%, while in the organic layer it was 77.5% as shown in Table 4-1.

Table 4-1: Mass Balance study performed in biphasic solvent system

	Reaction 1 Phenanthrene		**Reaction 2 Pyrene**	
Layer	**Organic**	**Aqueous**	**Organic**	**Aqueous**
Substrate	0.1g		1.01g	
Oxidant ($NaIO_4$)		0.96g		9.66g
Catalyst ($RuCl_3$)		0.01g		0.095g
Before reaction	0.1g	0.97g	1.01g	9.755g
After reaction	0.0775g	0.854g	0.858g	9.566g
Mass recovery %	77.5%	88%	85%	98%

When a similar experiment was performed using pyrene, the following results were obtained: 98% for aqueous and 85% in organic layer of initial mass was recovered. These results suggest that the possible mass imbalance is the result of CO_2 formation, so quantification of CO_2 was carried out for one of the substrates. Pyrene was chosen for this reaction. By connecting a gas-bag to the Parr autoclave outlet, it was possible to collect the gas and analyze it post reaction using GC-FID fitted with a methanizer. Prior to the commencement of the reaction, the reactor was firstly purged with He, and after

2 hours reaction, the system was cooled down to -3°C and a sample was collected. Firstly, a blank reaction without oxidant and catalyst was run and this yielded 108 ppm of CO_2 (n=3.5x10^{-9}mol). In the standard pyrene oxidation in the presence of $RuCl_3$ and $NaIO_4$, the concentration of CO_2 produced was 293.5ppm (n=9.58x10^{-9}mol). However, taking into account the number of moles of pyrene used in the reaction (n=1.28x10^{-4} mol) and the number of moles of pyrene converted to CO_2, it is apparent that only 0.00475% of pyrene was converted to CO_2. These results were quite encouraging and suggest very low CO_2 formation. However, the outcome of the experiment is not compatible with the mass balance study where we observed a 15% loss in mass, which could be caused by experimental error. Nevertheless, the obtained results still put RICO chemistry in the range of reactions with relatively low level of over oxidation to undesirable products.

4.4. Product identification of non alkylated aromatics

4.4.1. Naphthalene

After analyzing samples from both, aqueous and organic layer using GC and GC-MS, peaks corresponding to phthaldialdehyde (5A), phthalic acid (identified as phthalic anhydride) (5B) and isobenzofuran 1(3H)-one (phthalide) (5C) were identified as shown in figure 4-1 and scheme 4-1.

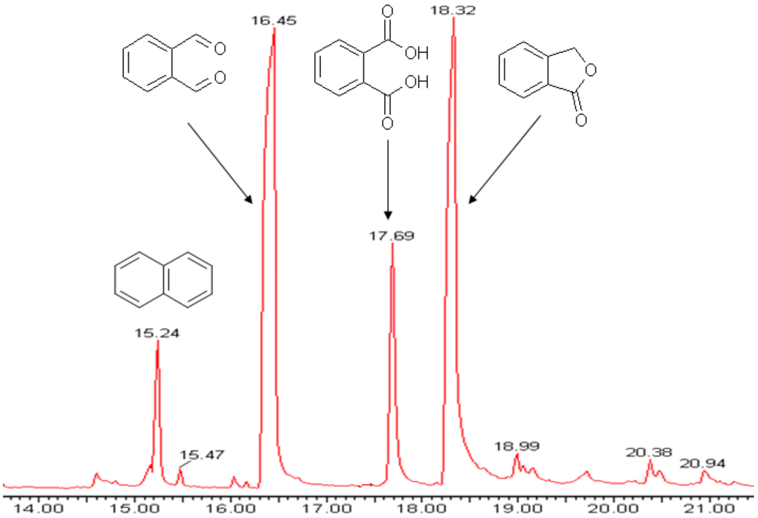
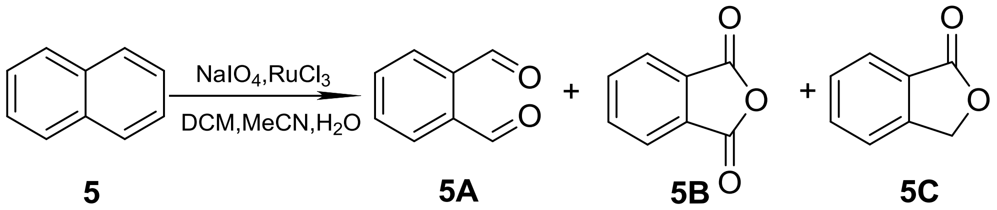


Figure 4–1: Naphthalene oxidation: GC-MS analysis



Scheme 4-1: Products of naphthalene oxidation in biphasic solvent system
Reaction conditions: Phenanthrene 0.131mmols, $NaIO_4$ 1.048mmols, $RuCl_3$ 0.01mmols, DCM 16ml, MeCN 7ml, H_2O 7ml, T=22°C, Stirring speed 500rpm, t=4h

Also ^{1}H NMR spectra confirmed occurrence of the above mentioned products. A sharp singlet at 10.5ppm in the ^{1}H NMR suggests the presence of an aldehyde group and can be assigned to phthaldialdehyde as shown below (Figure 4-2).

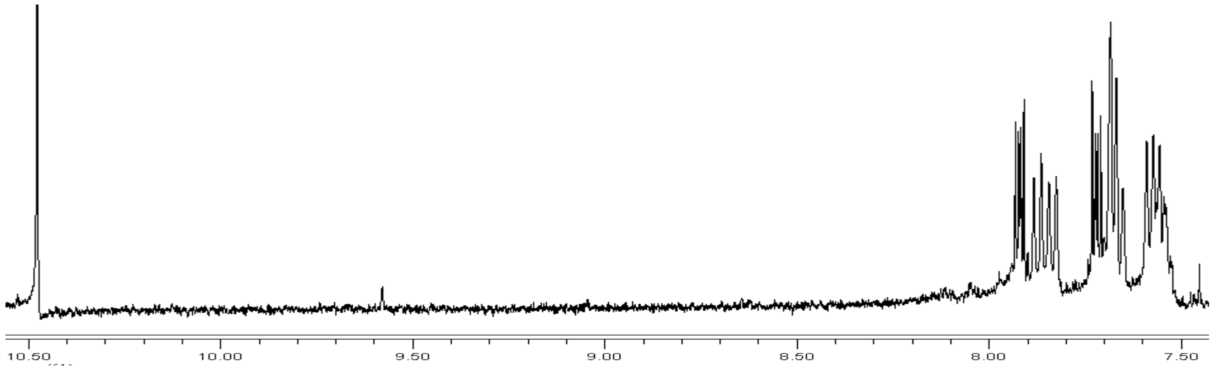


Figure 4–2: Naphthalene oxidation in biphasic system: ^{1}H NMR analysis

It is worth mentioning that phthalic acid and phthalic anhydride have the same retention time in the GC, probably due to the dehydration of the acid and its transformation into the anhydride. However, phthalic acid seems to be the major product, which is in agreement with the results reported in the literature [3]. Spitzer and Lee observed 70% selectivity to phthalic acid even when acetonitrile was not present in the reaction mixture [4]. However, comparing the products obtained in the oxidation of naphthalene in a biphasic solvent system with products from the oxidation performed in a monophasic solvent system, it is observed that naphthalene is transformed into exactly the same products and the change of solvent composition does not play a role in product selectivity (Scheme 3-1).

4.4.2. Phenanthrene

Regarding oxidation of phenanthrene, the major product identified by GC and ^{1}H NMR analysis, in the organic layer was phenanthrene-9,10-dione (6A) and diphenic anhydride (6B) as shown in figure below.

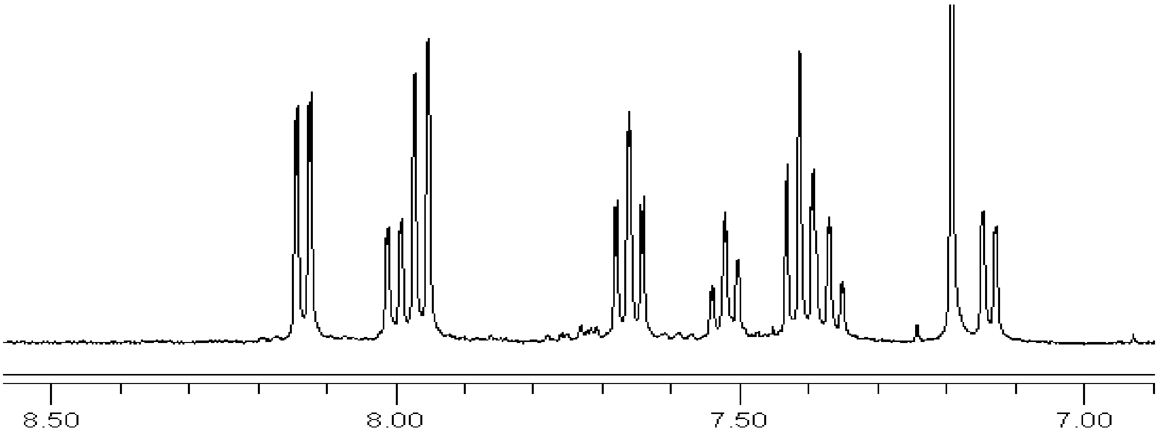
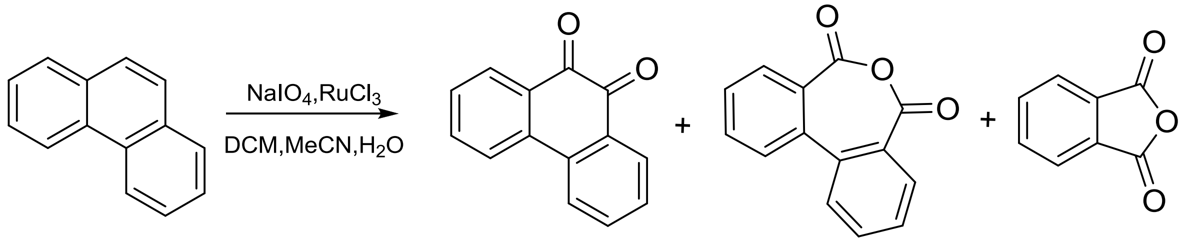


Figure 4–3: Phenanthrene oxidation: ^{1}H NMR analysis of product in organic layer (Phenanthrene 9,10-dione: δ 8.15 (dd, 2H), 7.95 (dd, 2H), 7.65 (t,2H), 7.41 (t, 2H); Diphenic anhydride: δ 8.05 (dd, 2H),7.51(t, 2H),7.38 (t,2H),7.12 (dd,2H))

Phthalic acid (6C), however was detected in the aqueous layer. Obtained product are presented in the scheme below (Scheme 4-2). These findings are different from those previously reported by Menendez, who observed 8 products. However, Stock in his publication reported the presence of the same products [5]. In both cases diphenic acid was detected, with Stock reporting 91% selectivity towards diphenic acid, while Menendez only mentioned the presence of this product [6]. Kasai and Ziffer, in addition to Djerassi pointed out that phenanthrene 9,10-quinone is the major product in this oxidation [7-8]. However, it must be taken into account that the reaction conditions applied to the oxidation of phenanthrene varied from paper to paper. Here, the product distribution differs from those products obtained in a monophasic solvent system, where compounds with one open ring were observed. In the biphasic solvent system, the presence of phthalic acid suggests that the oxidation proceeded further to yield this acid.



6 6A 6B 6C

Scheme 4-2: Products of phenanthrene oxidation in biphasic solvent system
Reaction conditions: Phenanthrene 0.131mmols, $NaIO_4$ 1.048mmols, $RuCl_3$ 0.01mmols, DCM 16ml, MeCN 7ml, H_2O 7ml, T=22°C, Stirring speed 500rpm, t=4h

4.4.3. Pyrene

Pyrene oxidation was performed in a biphasic solvent system with the objective to understand the differences in product distribution as a result of a change in the solvent systems and reaction conditions. Different analysis methods were used: ^{1}H NMR, HR-MS, LC-MS and HPLC. From previous studies it is known that the carbon position 4,5 and 9,10 in the pyrene molecule are more susceptible to RuO_4 attack than any other [9], therefore the mass and identity of all the possible oxidation products at these positions was calculated and presented in table 4-2, below. It is worth emphasizing that the location of ketone, aldehyde or acid group in possible product may change between position 4,5,9,10. Here, compounds listed below were used as models.

Table 4-2: List of possible products obtained during pyrene oxidation using RICO

Compound	**Empirical formula**	**Molecular weight (g/mol)**
Pyrene -4,5- dione	$C_{16}H_8O_2$	232
Pyrene-4,5,9,10-tetraone	$C_{16}H_6O_4$	262
Pyrene-4,5-Dialdehyde Pyrene-4,5-Diol	$C_{16}H_{10}O_2$	234
Pyrene-4,5-Dialdehyde-9,10-Dione	$C_{16}H_8O_4$	264
Pyrene-4,5,9,10-Tetraaldehyde	$C_{16}H_{10}O_4$	266
Pyrene-4-Monoaldehyde-5,9,10- Triacid	$C_{16}H_{10}O_7$	314
Pyrene-4,5-Dialdehyde-9,10-Diacid	$C_{16}H_{10}O_6$	298
Pyrene-4,5,9-Trialdehyde-10-Monoacid	$C_{16}H_{10}O_5$	282
Pyrene-4,5,9,10-Tetraacid	$C_{16}H_{10}O_8$	330
Pyrene-4-Monoacid-5-Monoaldehyde -9,10-Dione	$C_{16}H_8O_5$	280
Pyrene-4,5-Diacid-9,10-Dione	$C_{16}H_8O_6$	296

4.4.4. Effect of temperature on product distribution

Firstly, pyrene oxidation was carried out under standard reaction conditions, at 22°C (section 2.6.1.2.). After analyzing the reaction mixture using ^1H NMR, signals corresponding to pyrene-4,5-dione were recognized in the organic layer. Moreover, the number of signals in the aromatic region as well as signals indicating the presence of CHO species, which suggests the presence of additional products were found as seen in Figure 4-4.

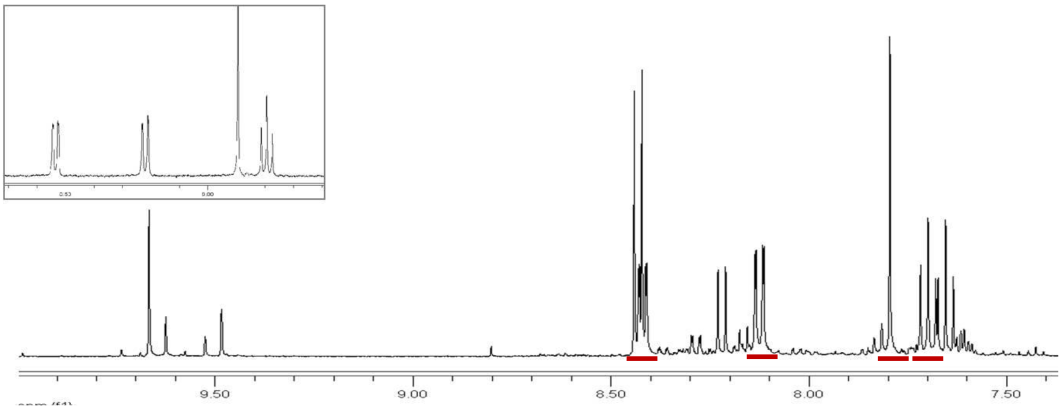


Figure 4–4: ^{1}H NMR spectra of pyrene oxidation products in organic layer
Marked signals from pyrene-4,5-dione; above a spectra of standard pyrene-4,5-dione. Reaction conditions: Pyrene 0.131mmols, $NaIO_4$ 1.048mmols, $RuCl_3$ 0.01mmol, DCM 16ml, MeCN 7ml, H_2O 7ml, Stirring speed 500rpm, T=22°C

However, ^{1}H NMR analysis of the aqueous layer shows the presence of a product giving a doublet at 8.1ppm and triplet at 7.55ppm, which is specific to products of pyrene oxidized in the 4,5,9,10 position. What is more, the presence of aldehyde or acid group was also observed. This finding definitely suggests that carbons in the positions 4,5,9,10 were oxidized to ketones, aldehydes or acids. In order to determine unknown products, HRMS analysis were performed as shown below (Figure 4-5).

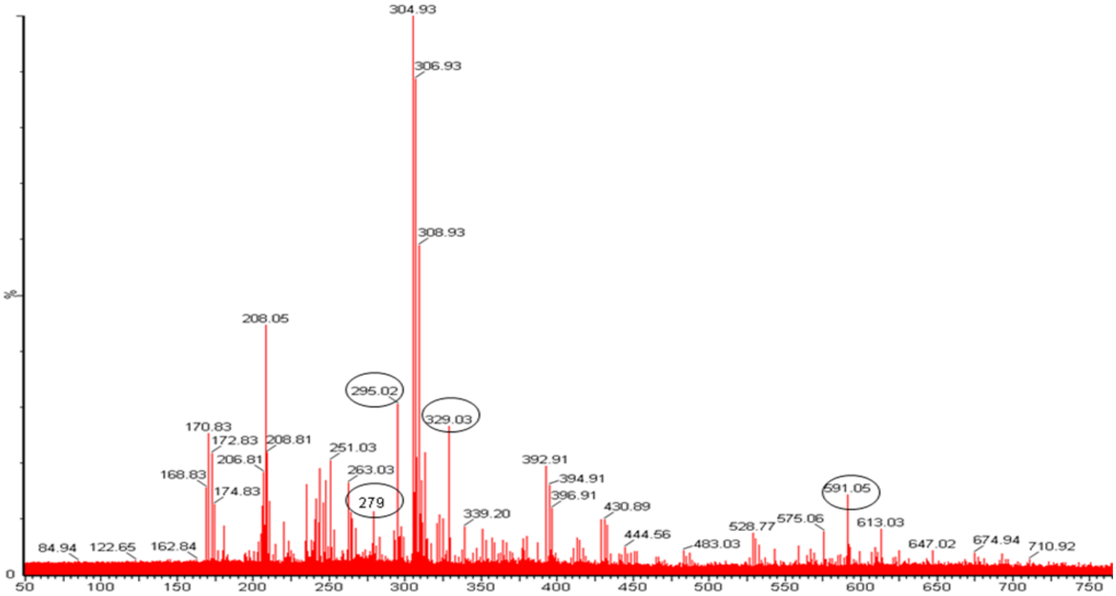
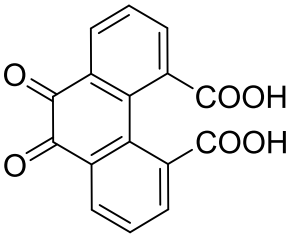
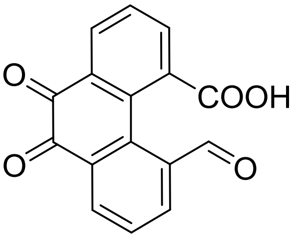
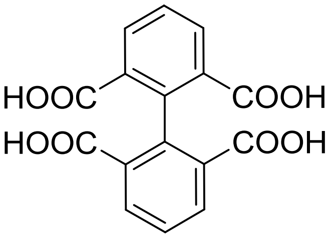


Figure 4–5: Pyrene oxidation: MS analysis of organic layer; m/z ions corresponding to possible products are marked

Using Electrospray Negative technique in High Resolution Mass Spectrometry for analyzing a sample from the aqueous layer, it was possible to observe ions corresponding to the following products as shown in the table below (Table 4-3).

Table 4-3: HR-MS (Electrospray Negative) analysis of pyrene oxidation products, aqueous layer

Ions observed m/z	**Possible product**	**Possible product structure**	**Molecular weight (g/mol)**
M-H$^+$ 295 2M-H$^+$ 591	Pyrene Dione, Diacid		296
M-H$^+$ 279	Pyrene Monoacid, Monoaldehyde, Dione		280
M-H$^+$ 329	Pyrene Tetraacid		330

In the case of analyzing the sample from organic layer using Electrospray Positive technique, the following ions: M+H$^+$ 233, M+Na$^+$ 271, M+MeCNNa$^+$ 296, 2M+Na$^+$487 were detected and associated with pyrene-4,5-dione (Figure 4-6).

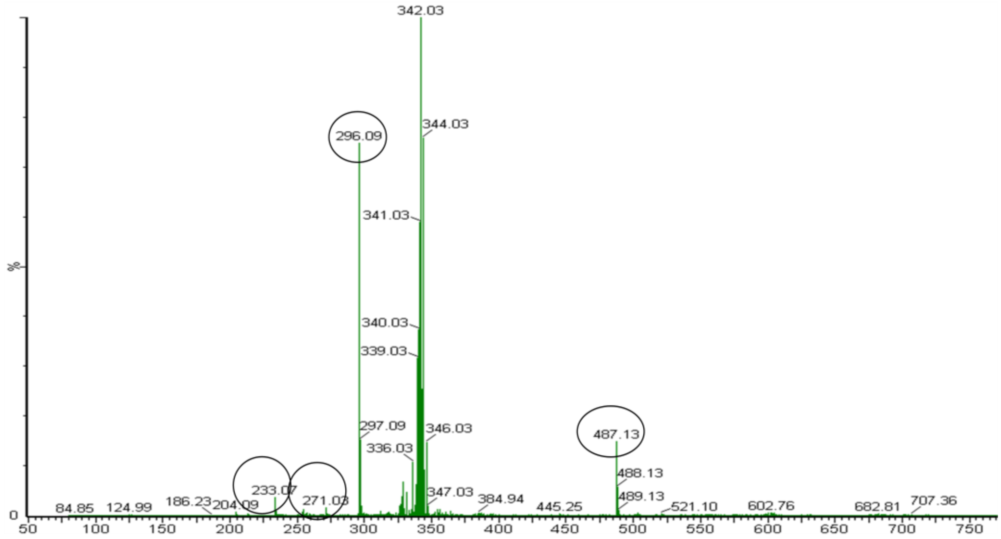


Figure 4–6: MS spectra(ES+) of pyrene oxidation products: organic layer; M/z signals corresponding to pyrene-4,5-dione

No other peaks were observed for the sample from organic layer even while using Electrospray Negative technique. The incompatibility between results from MS and NMR analysis for the organic layer was a reason for further investigation using an HPLC technique coupled with MS. Here, HPLC-MS (UV diode array) of 30, 60, 90, 120, 180, 240 minutes samples from organic layer showed a number of peaks, with the major one corresponding to pyrene-4,5-dione (Rt=9.45) as it is shown on figure 4-7.

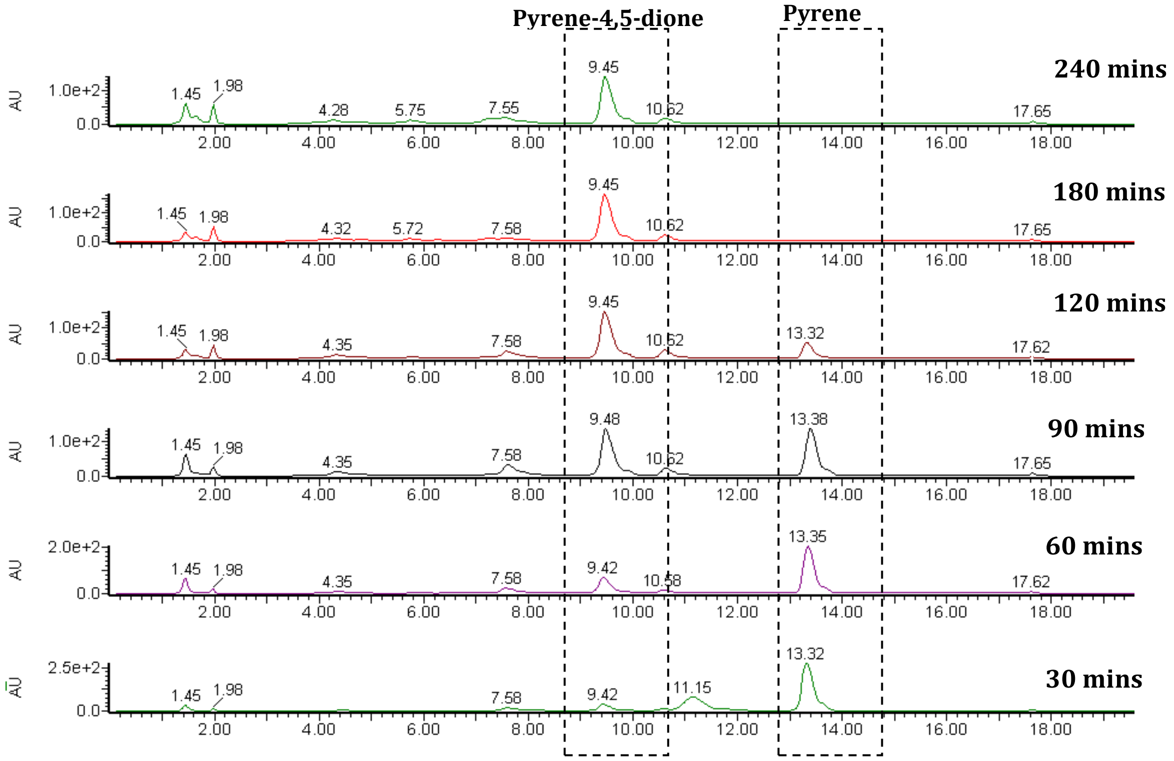


Figure 4–7: Oxidation of pyrene at 22°C, HPLC-MS analysis of organic layer
Reaction conditions: Pyrene 0.131mmols, $NaIO_4$ 1.048mmols, $RuCl_3$ 0.01mmol, DCM 16ml, MeCN 7ml, H_2O 7ml, Stirring speed 500rpm

Mass spectral analysis of the peak with Rt 7.58 min gave a molecular mass ion at m/z 263 (ES-) which can be associated with either pyrene dione dialdehyde or pyrene dione dialcohol. The molecular mass ion of peaks with Rt=4.35 and 5.72 mins did not match with the mass of any expected oxidation product. IR analysis of the sample withdrawn from the organic layer after 60min reaction did not show any stretching characteristic of an OH group in region 3100-3500nm, therefore presence of pyrene dione dialcohol was excluded from further consideration.

HPLC-MS analysis did not show any significant peaks in the aqueous layer apart from the peak corresponding to pyrene-4,5,9,10-tetraacid. This incompatibility with findings from HRMS analysis, where 2 more products in addition to pyrene-4,5,9,10-tetraccid were obtained, is believed to be a result of the lower sensitivity while using the LC-MS technique.

To achieve significant oxidative ring opening, the RICO was carried out at a slightly elevated temperature 35°C and the resultant reaction mixture was analysed as previously described, using HPLC coupled with MS. Compared to when the reaction was conducted at 22°C, here reaction showed 4 products detected by LC-MS in the organic layer and these components were identified as pyrene-4,5-dione (7A), pyrene dione dialdehyde (7B), pyrene monoacid trialdehyde (7C) and pyrene diacid dialdehyde (7D) (Figure 4-8).

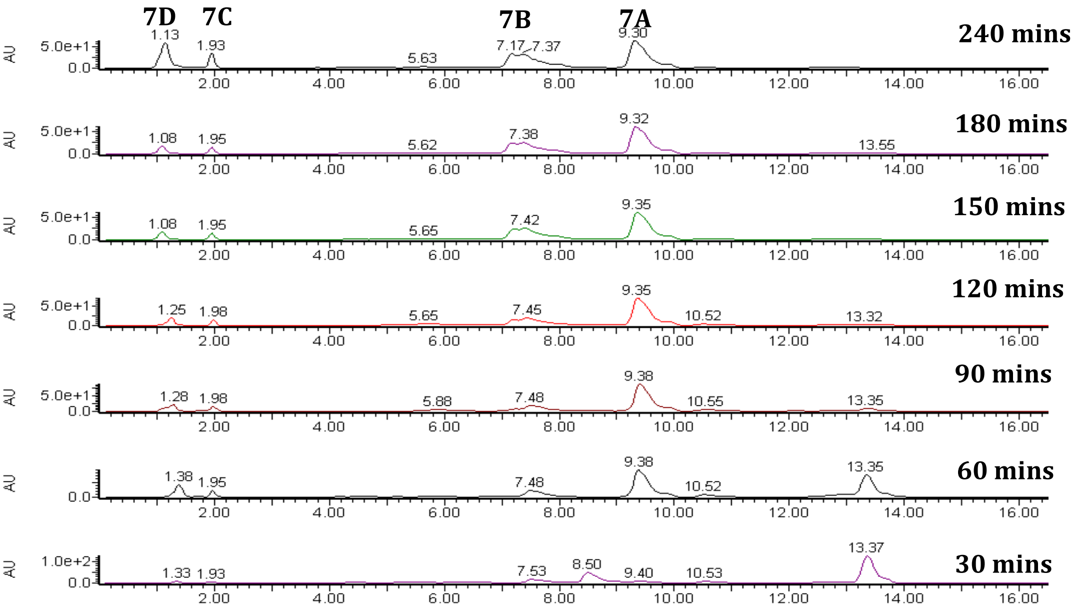


Figure 4–8: Oxidation of pyrene at 35°C, HPLC-MS analysis of organic layer
Reaction conditions: Pyrene 0.131mmols, $NaIO_4$ 1.048mmols, $RuCl_3$ 0.01mmols, DCM 16ml, MeCN 7ml, H_2O 7ml, Stirring speed 500rpm

Firstly time on line sampling of the aqueous layer did not show any pyrene oxidation products, however after 180 min of reaction 3 products were detected as shown in figure 4-9. The products were identified as pyrene tetraacid (7F), pyrene monoaldehyde triacid (7E) and pyrene dialdehyde diacid (7D).

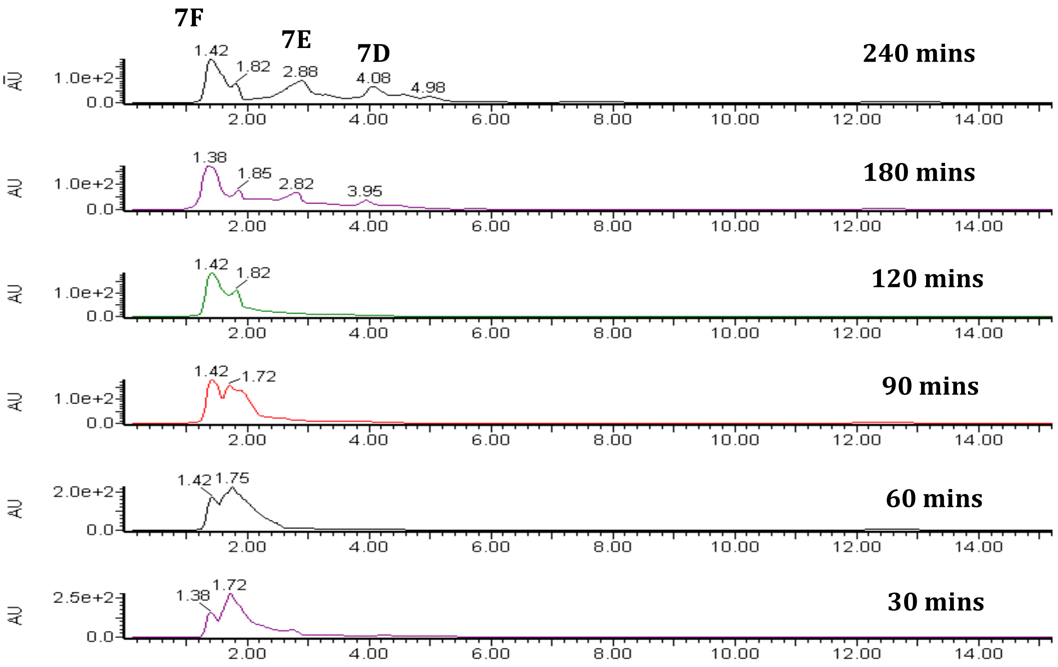
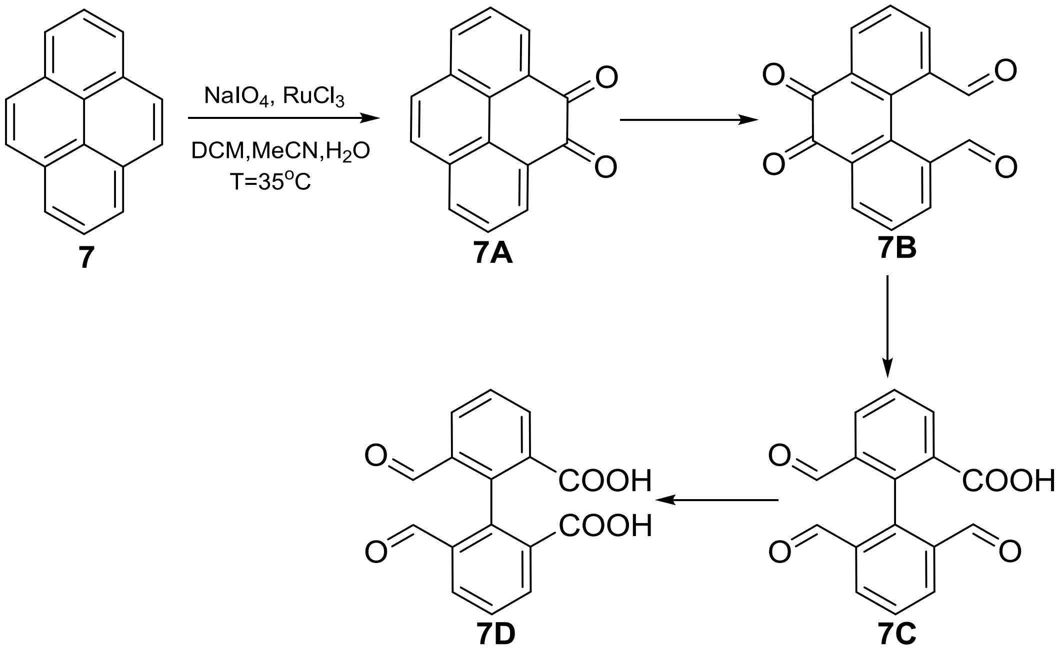


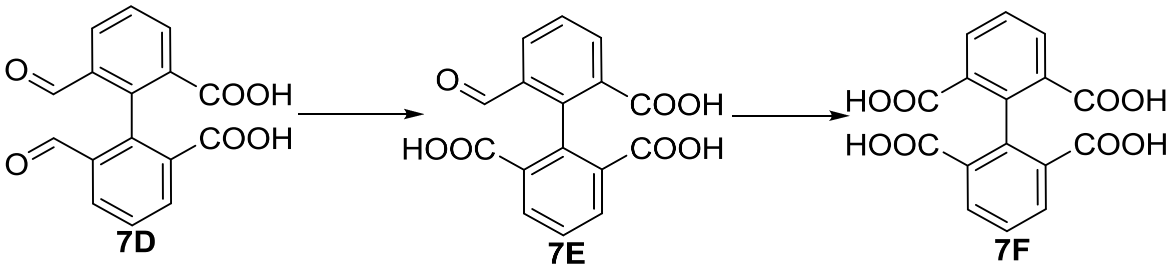
Figure 4–9: HPLC-MS analysis: Oxidation of pyrene in 308K in biphasic solvent system, Aqueous layer; Reaction conditions: Pyrene 0.131mmols, $NaIO_4$ 1.048mmols, $RuCl_3$ 0.01mmol, DCM 16ml, MeCN 7ml, H_2O 7ml, Stirring speed 500 rpm

The appearance of products in the aqueous layer, late on in the reaction (180mins) suggests that these are products formed in the latter stages of an oxidation, formed by a series of consecutive reactions, where the products from the initial reactions are detected only in the organic layer. In other words, products which are held in the organic phase, undergo further oxidation forming more polar compounds, thus migrating to the water phase. The presence of pyrene dialdehyde diacid in both layers only after 180 minutes of reaction seems to prove this theory. A schematic representation of the reaction and a proposed routes for the formation of all the observed products is given in Scheme 4-3 for those product detected in the organic phase and in scheme 4-4 for products detected in the aqueous phase.

All the products in the scheme given are detected and the sequence of oxidation is believed to be: pyrene oxidizes to pyrene-4,5-dione which then oxidizes to pyrene tetraone before the one ring opens up to form dialdehyde or oxidation to dialdehyde may proceed directly from pyrene and independently from dione formation. Ketone can be oxidize further to aldehyde and acid, which is the final step in this reaction. On the contrary to the literature reports, here we do not detect any mass which could correspond to pyrene tetraone under our reaction conditions. Only when samples were analyzed using HPLC with a different column, peak from pyrene-4,5,9,10-tetraone was detected and appeared only after 300mins of the reaction.



Scheme 4-3: Pyrene Oxidation: Sequence of oxidation based on HPLC-MS studies in organic layer



Scheme 4-4: Pyrene oxidation: Product determined in aqueous layer based on HPLC-MS analysis

Comparing the ^{1}H NMR spectra from the aqueous layer when the reaction was run at 22°C and 35°C, no significant difference between the spectra were observed. Taking into account the fact, that ^{1}H NMR spectra would have very similar pattern for pyrene 4,5,9,10-tetracacid and pyrene diacid, dione, it is clear that ^{1}H NMR should be an extra method of analysis, not the major one. The most visible difference between ^{1}H NMR spectra from both reactions is the intense of signals, which suggest higher concentration of pyrene 4,5,9,10-tetracid for reaction conducted at 35°C.

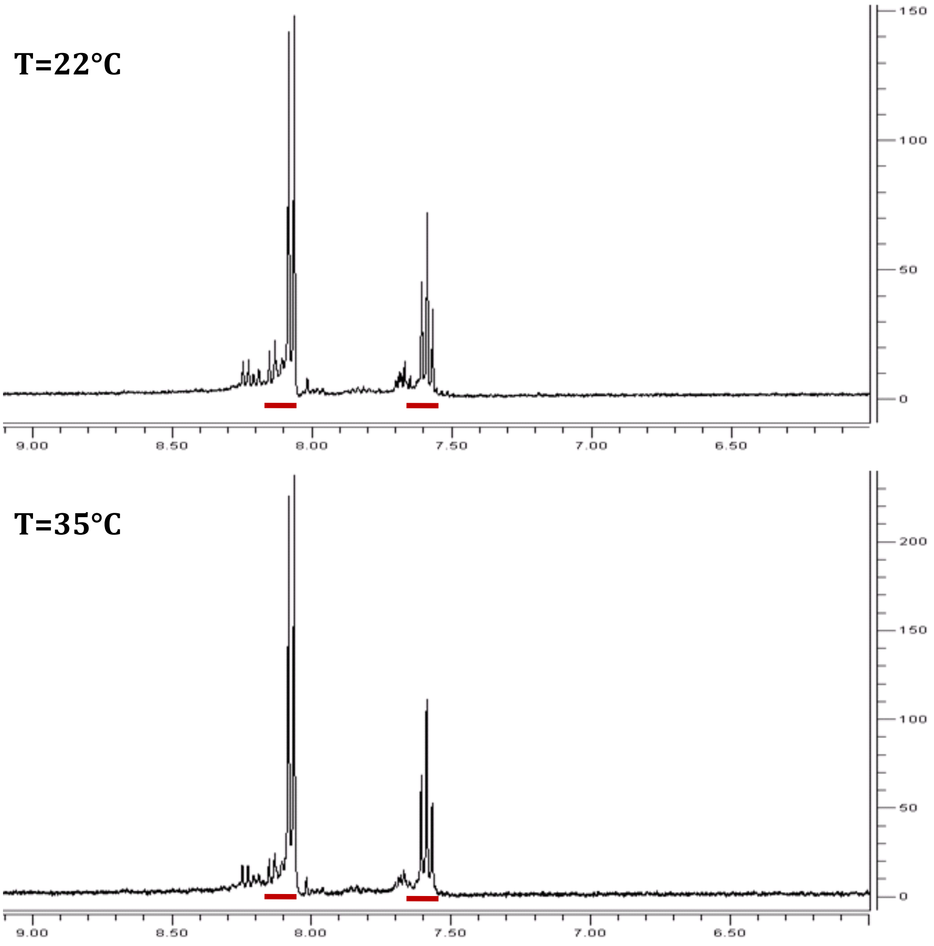


Figure 4–10: ^{1}H NMR Spectra of pyrene oxidation products in aqueous layer
Top: reaction performed in 22°C, Bottom: T=35°C; Reaction Conditions: Reaction conditions: Pyrene 0.131mmols, $NaIO_4$ 1.048mmols, $RuCl_3$ 0.01mmol, DCM 16ml, MeCN 7ml, H_2O 7ml, Stirring speed 500 rpm

However, looking at MS analysis of aqueous layer from reaction performed at 22°C and 35°C, it is clear that reaction performed at higher temperature resulted in opening of 2 aromatic rings, while in lower temperature products with one ring opened were observed. ^{1}H NMR analysis of the organic layer at 35°C suggests the presence of pyrene-4,5,9,10-tetraone as a major product when ^{1}H NMR analysis were performed for samples after 15h reaction.

4.4.4.1. Influence of *substrate : oxidant* ratio on product distribution

A similar experiment investigating the product distribution after using ratio *substrate : oxidant* 1:16 was performed. After analysing the organic layers using ^{1}H NMR, it was found that the major product was pyrene-4,5,9,10–tetraone. Signals indicating products with a CHO group were not found.

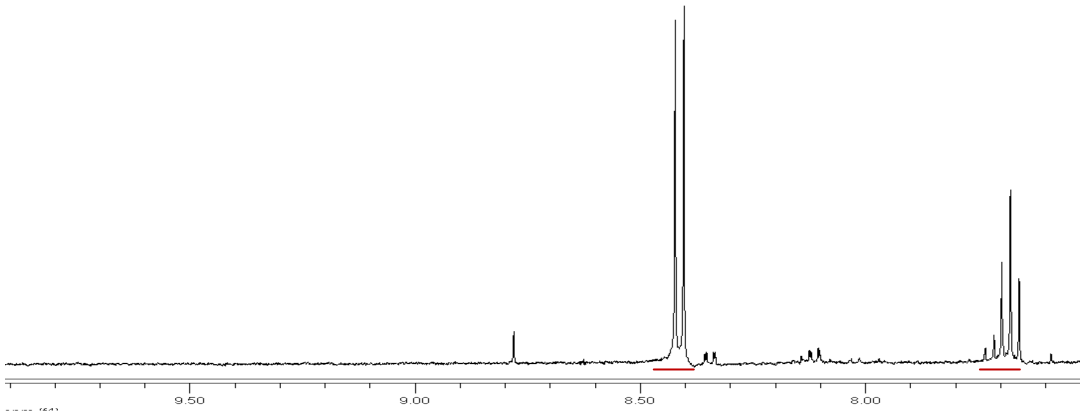


Figure 4–11:^{1}H NMR spectrum of pyrene oxidation products: organic layer
Reaction conditions: Pyrene 0.131mmols, $NaIO_4$ 2.096mmols, $RuCl_3$ 0.096mmol, DCM 16ml, MeCN 7ml, H_2O 7ml, Stirring speed 500 rpm, T=22°C

In the aqueous layer signals indicating oxidation of carbon at positions 4,5,9,10 were detected. These results suggest that the greater the concentration of oxidant present in the system, the more products with 2 rings opened are observed. Most probably all pyrene-4,5-dione was converted to pyrene-4,5,9,10-tetraone and all intermediate products observed in the reaction with ratio 1:8 were oxidized to pyrene-4,5,9,10-tetraacid.

4.4.4.2. Discussion on pyrene oxidation products

The presence of pyrene-4,5-dione in addition to pyrene-4,5,9,10-tetraone in the reaction has been previously reported and it is well known that the selectivity of this reaction is dependent on temperature and substrate : oxidant ratio [10]. However, Harris *et al.* did not focus on determining all the products, they just mentioned the presence of several additional by-products as indicated by TLC. In the experiments reported here, which were performed at 35°C (ratio 1:8), TLC chromatography also showed the presence of 4 compounds in the organic layer. In a similar publication, Dixon *et al.* tested RuO_2 and $NaIO_4$ in a acetone-water solution for the oxidation of pyrene [11]. They were able to isolate 2 products: pyrene-4,5-dione and lactol of 4-formylphenanthrene-5-carboxylic acid. The selectivity to these products changed with the substrate : oxidant ratio used. When a molar ratio of 1:2 was applied, selectivity towards the dione was 10% and to the lactol 13%. With a molar ratio of 1:5 selectivity to the dione was 23% and to the lactol 24%. The second product is of special interest, as the data reported is not in agreement with Dixon's observations. The reason may be attributed to the different solvent system used in this study. On the other hand when OsO_4, a reagent similar to RuO_4 was used, selectivity towards pyrene-4,5-dione was only 7%. In our studies attention was paid to the products with one open ring, therefore identification of all the products was needed. What is more, to our knowledge, this is the first complete and detailed determination of pyrene oxidation products using RICO chemistry.

4.4.5. Oxidation of pyrene-4,5-dione

The major challenge in the oxidation of pyrene-4,5,-dione was the selective opening of the activated ring by reducing the amount of oxidant. Considering previous results, where increasing the amount of oxidant saw more products with an open ring, it was suggested that by limiting the amount of oxidant and controlling the reaction temperature it would be possible to oxidize pyrene-4,5,-dione to phenanthrene-4,5-dialdehyde or diacid. Two reactions, where the *substrate : oxidant* ratio was kept at 1:1 were performed at 22°C and 35°C. Products obtained in the reactions were analyzed using HPLC-MS. The chromatograms suggests the presence of the same products as observed in the oxidation of pyrene, i.e.: pyrene dione dialdehyde (7B), pyrene monoacid trialdehyde (7C) and pyrene diacid dialdehyde (7D) as it can be seen in figure 4-12. There was no change in product distribution between the reactions carried out at 22 and 35°C as illustrated in figure 4-12. It is worth mentioning that the presence of pyrene-4,5,9,10-tetraone was detected after 300 mins of reaction.

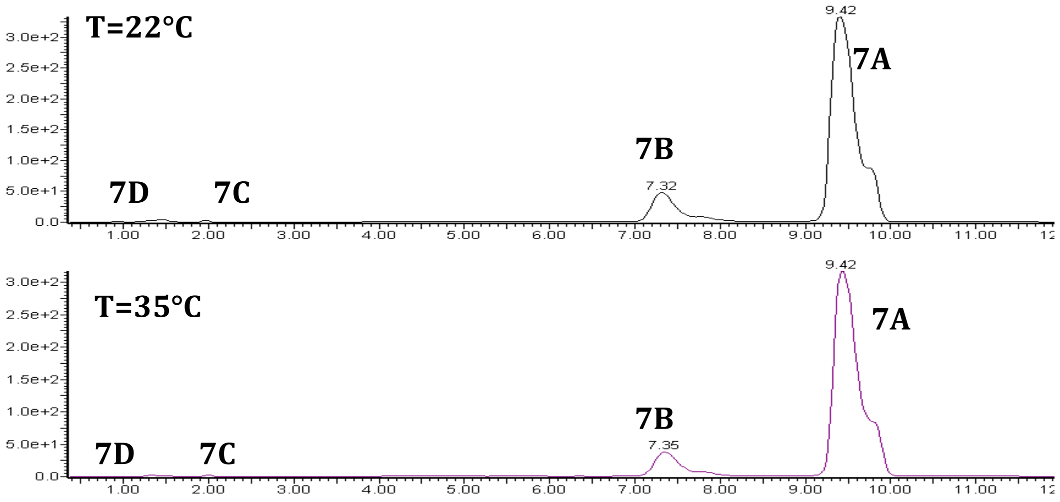


Figure 4–12: HPLC-MS analysis: Oxidation of pyrene-4,5-dione at 22°C (top) and 35°C (bottom), organic layer

Reaction conditions: Pyrene-4,5-dione 0.131mmols, $NaIO_4$ 0.131mmols, $RuCl_3$ 0.006mmols, DCM 16ml, MeCN 7ml, H_2O 7ml, stirring speed 500rpm

4.5. Mechanistic investigation

Similarly as for reactions run in the monophasic solvent system, experiments related to mechanistic studies were performed. As previously shown (section 3.4 and 4.4), solvent composition affects the product distribution and this may suggest that different mechanisms are involved. To investigate this phenomenon, studies with D_2O were performed.

4.5.1. Deuterium incorporation into products

Studies using D_2O in a monophasic solvent system, showed that deuterium was not incorporated into the reaction product in phenanthrene oxidation. Assuming that the oxidation mechanism is the same in mono as well as in a biphasic solvent system, no deuterium incorporation should be observed in the products when the reaction is carried out in a DCM/MeCN/D_2O solvent system. To confirm this, an oxidation reaction of phenanthrene in a biphasic solvent system was firstly run. The GC chromatograms from this reaction run in DCM/MeCN/H_2O, DCM/MeCN/H_2O/D_2O mixture and DCM/MeCN/D_2O were compared. GC chromatograms and mass spectra for product found in organic (Figure 4-13) and aqueous (Figure 4-14) layers are given below. No changes in product distribution were detected either in organic or aqueous layer. Using GC-MS, each chromatogram peak from the reaction run in DCM/MeCN/H_2O was analyzed by MS and compared with the products MS spectra of the reaction conducted in DCM/MeCN/D_2O. No change in the mass was observed in both layers. As an example, mass spectra of diphenic anhydride is given below. This data suggest the same reaction mechanism for the reaction in biphasic as well as in monophasic solvent system.

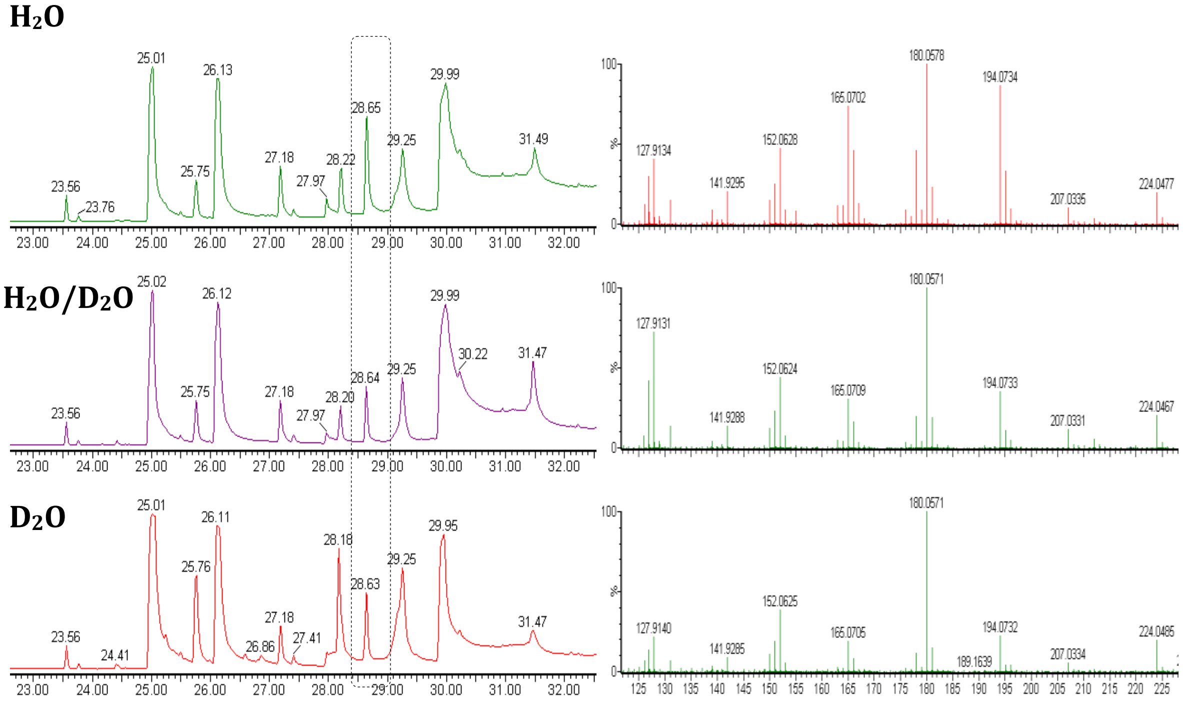


Figure 4–13: Comparison of GC chromatograms from phenanthrene oxidation (organic layer) using H_2O, H_2O/D_2O and D_2O(left) and MS analysis of product with Rt=28.64, diphenic anhydride (right) Reaction Conditions: Phenanthrene 0.131mmols, $NaIO_4$ 1.048mmols, $RuCl_3$ 0.01mmols, DCM 16ml, MeCN 7ml, H_2O or H_2O/D_2O or D_2O 7ml, T=22°C, Stirring speed 500rpm, t=4h

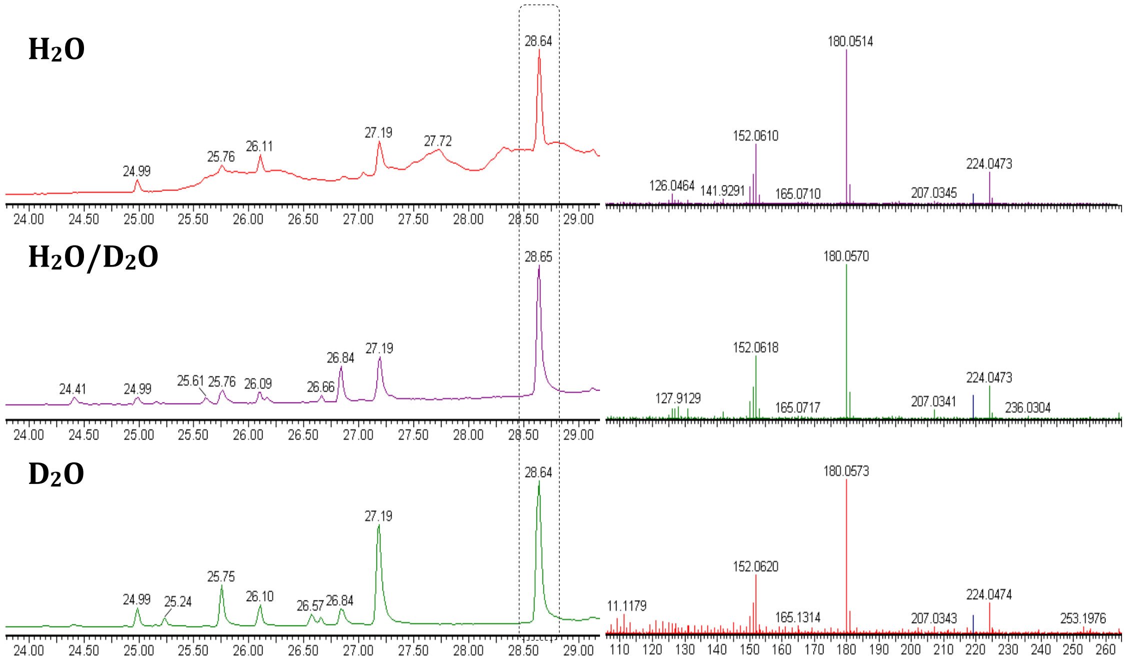


Figure 4–14: Comparison of GC and MS chromatograms from phenanthrene oxidation (aqueous layer)

MS of Product with Rt=28.64 (right), Reaction Conditions: Phenanthrene 0.131mmols, $NaIO_4$ 1.048mmols, $RuCl_3$ 0.01mmols, DCM 16ml, MeCN 7ml, H_2O or H_2O/D_2O or D_2O 7ml, T=22°C, Stirring speed 500rpm, t=4h

4.5.2. Kinetic studies using D_2O

To prove that the mechanism in both solvent systems is the same, kinetic studies using H_2O and D_2O were run, to determine if there was any Kinetic Isotope Effect. The same substrate, phenanthrene, was used for the experiment. The figure displaying the consumption of phenanthrene in the reaction run in the presence of H_2O and D_2O is given below (Figure 4-15). Here, the calculated KIE value for phenanthrene oxidation was found to be 1.54 which suggests a primary kinetic isotope effect. Taking into account the fact that in both solvent systems no deuterium incorporation was observed during phenanthrene oxidation, it can be concluded that the mechanism of reaction is the same in the monophasic and in biphasic solvent system, therefore similar KIE value should be observed. Previously calculated KIE numbers for reactions performed in the monophasic solvent system (KIE = 1.71, 1.70) (section 3.7.3.), were clear-cut to confirm primary KIE. Here, KIE value 1.54 suggests primary KIE, so it can be said that mechanism in monophasic and biphasic solvent system is the same.

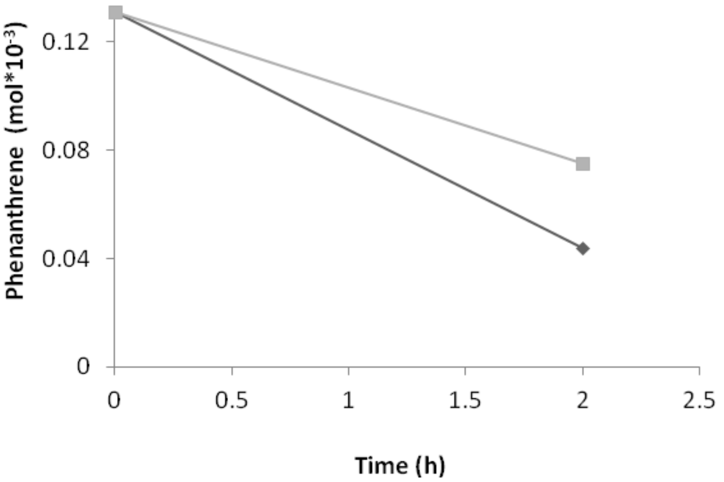


Figure 4–15: Kinetic Studies: Oxidation of phenanthrene using H_2O and D_2O in biphasic solvent system
Reaction Conditions: Phenanthrene 0.131mmols, $NaIO_4$ 1.048mmols, $RuCl_3$ 0.01mmols, H_2O(◆)/D_2O(■) 7 ml, DCM 16ml, MeCN 7ml, Stirring speed 500rpm, T=22°C

4.6. Kinetic studies

Kinetic studies were performed in order to investigate, if the modification of reaction environment, a change from monophasic to biphasic solvent system will affect the rate of reaction. It was highly possible that the use of a two phase system, where oxidation occurs on the aqueous and organic layer interface, will have an influence on reaction kinetics. Thus appropriate experiments were performed and compared with results obtained in chapter 3, where oxidation in monophasic system was reported.

4.6.1. Kinetic studies of non alkylated PAHs

The results presented in chapter 3 show the difference in the rate of reaction between naphthalene, phenanthrene and pyrene. Due to the solubility limitations of the monophasic solvent system only individual reactions of those substrates were performed, while here it was possible to run not only individual, but also competitive reactions using those 3 substrates.

4.6.1.1. Individual reactions

By running individual oxidations of naphthalene, phenanthrene and pyrene in a biphasic solvent system, it was possible to compare the data with that previously reported (chapter 3) when a monophasic solvent system was used and observe how the solvent composition affects the rate of reaction. The consumption of substrates in individual oxidation reactions is presented in figure 4-16 (below).

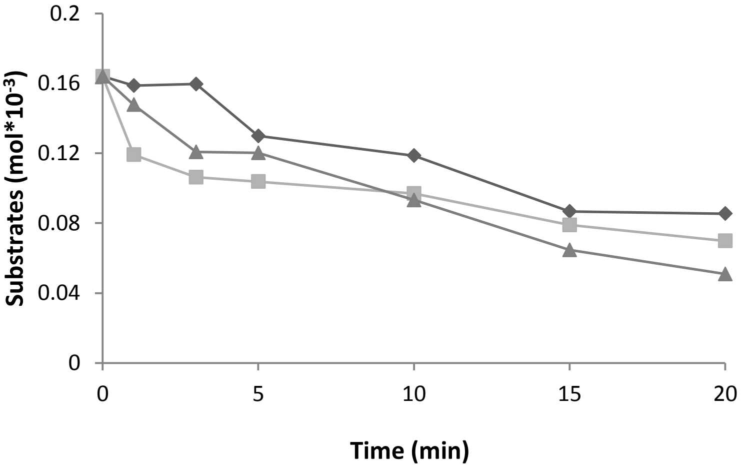


Figure 4–16 Substrate consumption in individual reactions: Biphase solvent system (◆:Naphthalene;, ■:Phenanthrene; ▲:Pyrene) Reaction Conditions: Substrate 0.164mmols, $NaIO_4$ 1.312mmols, $RuCl_3$ 0.012mmols, DCM 16ml, MeCN 7ml, H_2O 7ml, T=22°C, stirring speed 500rpm

It can be seen that the initial rate of oxidation is similar for all three molecules. This observation is different from reaction run in the monophasic solvent system. Moreover if comparing the initial reaction rates for the first 5 minutes of the reaction (Table 4-4), it is observed that when the oxidation in conducted in a biphasic solvent system phenanthrene reacts slightly faster than pyrene. However, for all molecules the rate of reaction in a homogeneous solvent system is higher. The reason for the reaction rate increase can be explained by homogeneity of the reaction environment. In a biphasic solvent system the reaction takes place at the interface between the aqueous and organic layers, thus mass transfer plays a crucial role, while in a monophasic solvent system the reaction occurs in the whole volume of the reaction mixture.

Table 4-4: Reaction rate for individual substrates oxidation in monophasic and biphasic solvent system measured during first 5 minutes of reaction

Substrate	**Reaction rate [mmols min^{-1}]**	
	Monophasic	**Biphasic**
Naphthalene	0.005	0.006
Phenanthrene	0.009	0.010
Pyrene	0.027	0.009

The difference in the reaction rate of pyrene between the two systems is quite intriguing. While naphthalene and phenathrene increased reaction rate only by 0.001 mmol/min in the biphasic solvent system, pyrene reacted 3 times faster in a monophasic system than in a biphasic system. The possible explanation for this behaviour can be based on the differences of product distribution. In the monophasic system pyrene is transformed to two products, then pyrene-4,5-dione is oxidized further to the stable molecule, pyrene-4,5,9,10-tetraone. This is related to the attack of RuO_4 on only two carbons at a time, so only 2 positions are oxidized. In the biphasic solvent system the number of products is higher and it is related to the reaction cascade and thus following oxidation of carbons in position 9,10 prior to the oxidation in position 4 and 5.

As it was said earlier, the use of the biphasic solvent system allows us to study more complicated molecules and performed reactions without facing the solubility problem. Here, five different substrates were studied under individual oxidation conditions (Figure 4-17). This graph shows clearly that bigger molecules react faster than smaller molecules even when the access to the oxidant is equal for all substrates. Perylene was consumed faster than pyrene. Chrysene and phenanthrene reacted with similar reaction rates, and naphthalene as the smallest molecule was converted into product with the slowest rate.

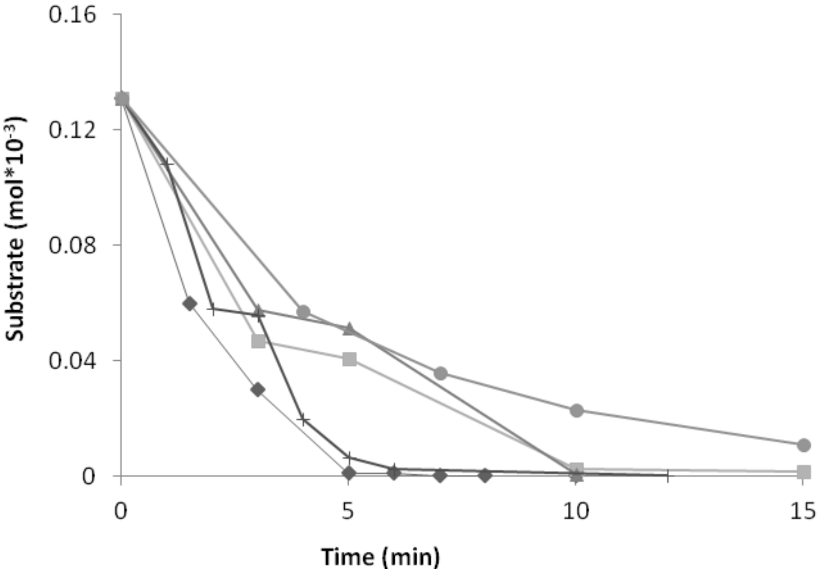


Figure 4–17: Comparison of substrate disappearance in biphase solvent system based on GC analysis in individual reactions
(●:Naphthalene; ◆:Perylene; +:Pyrene; ■Chrysene; ▲Phenanthrene) Reaction conditions: Substrate 0.131mmols, $NaIO_4$ 5.24mmols, $RuCl_3$ 0.04mmols, DCM 16ml, MeCN 7ml, H_2O 7ml, T=22°C, stirring speed 500rpm

4.6.1.2. Competitive oxidation

Pyrene is a four ring system, the next higher PAH is the five ring system perylene, which is insoluble in acetonitrile and hence a comparison between monophasic and biphasic solvent systems could not be performed, thus for substrates with more than 4 aromatic rings RICO chemistry was investigated in biphasic systems only.

For this study, compounds containing a different number of aromatic rings were used. Initially, the *substrate : oxidant* molar ratio was kept at 1:5. Firstly, naphthalene, phenanthrene, pyrene and perylene were tested together to study the effect of competitive oxidation. Figure 4-18 illustrates the oxidation rate for the molecules with different number of fused aromatic rings in each compound. Here, as illustrated in figure 4-17, the rate of substrate disappearance follows the trend 5R > 4R > 3R > 2R (R=number of fused aromatic rings).

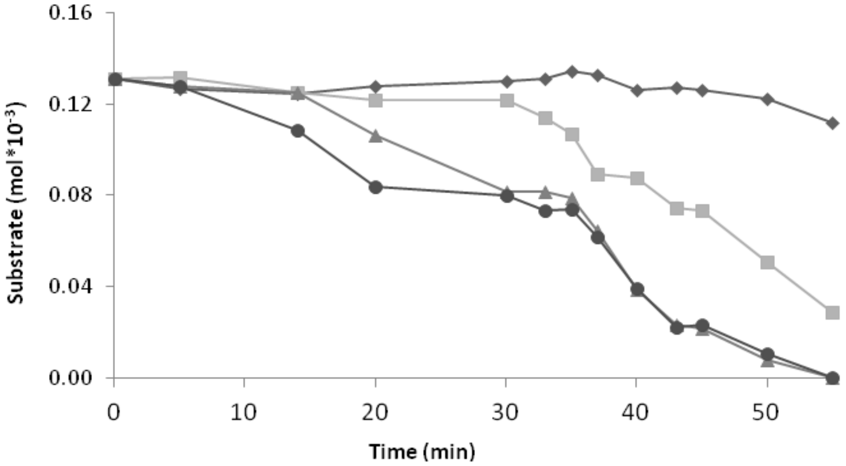


Figure 4–18: Comparison of the rate of substrate disappearance in a biphasic solvent system based on GC analysis
(◆:Naphthalene; ■:Phenanthrene; ▲:Pyrene; ●:Perylene) Reaction conditions: Substrate 0.131mmols, $NaIO_4$ 2.8mmols, $RuCl_3$ 0.024mmols, DCM 16ml, MeCN 7ml, H_2O 7ml, T=22°C, stirring speed 500rpm

In next experiment, pyrene was replaced by another 4 ring system, chrysene and competitive reaction between naphthalene, phenanthrene, chrysene and perylene was performed (Figure 4-19).

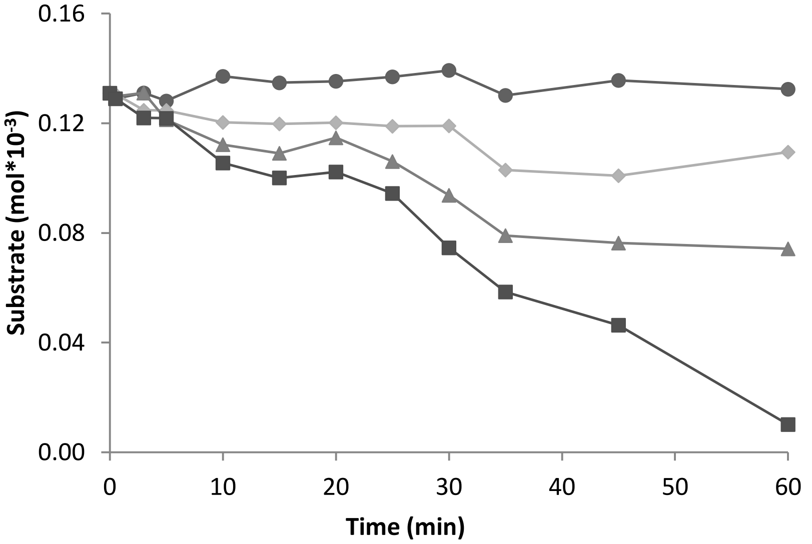


Figure 4–19: Comparison of the rate of substrate disappearance in a biphasic solvent system based on GC analysis
(●:Naphthalene; ◆:Phenanthrene; ▲:Chrysene; ■: Perylene) Reaction Conditions: Substrate 0.131mmols, $NaIO_4$ 2.8mmols, $RuCl_3$ 0.024mmols, DCM 16ml, MeCN 7ml, H_2O 7ml, T=22°C, stirring speed 500rpm

This experiment show that pyrene seemed to react faster than chrysene, what most probably is a result of molecule structure and energy of RuO_4 adduct formation which is lower for pyrene [12].

In the next part of the study, the substrate : oxidant ratio was kept at 1:8. Figure 4-20, shows the competitive reaction between phenanthrene, chrysene, pyrene and perylene. Here, pyrene and chrysene contain the same number of aromatic rings, although the size of molecule is the same, the observed reaction rate is different. This result confirmed that molecule aromaticity plays an important role, pyrene is more condensed, so in electrophilic substitution reaction it is expected to be more reactive. Perylene however, has 5 aromatic rings and reacts at a similar rate to pyrene, but faster than chrysene.

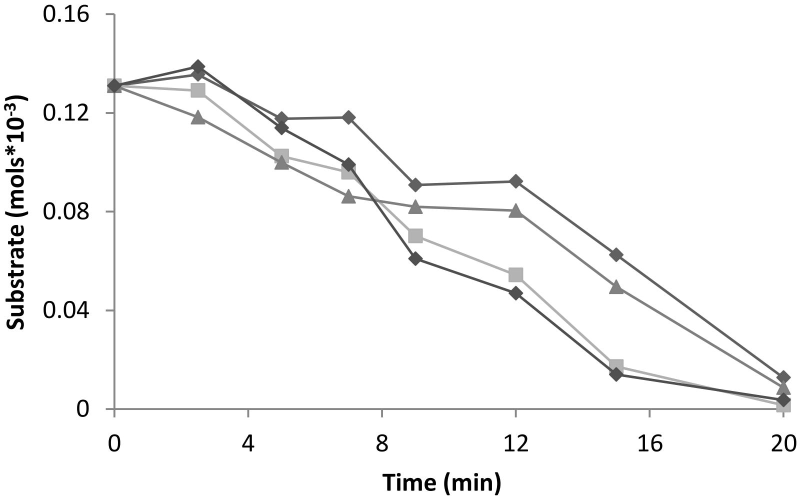


Figure 4–20: Comparison of substrate disappearance in biphase solvent system based on GC analysis (◆:Phenanthrene; ■:Pyrene; ▲:Chrysene; ◆:Perylene)
Reaction conditions: Substrate 0.131mmols, $NaIO_4$ 4.215mmols, $RuCl_3$ 0.035mmols, DCM 16ml, MeCN 7ml, H_2O 7ml, T=22°C, stirring speed 500rpm

Another interesting observation was when naphthalene, phenanthrene chrysene and perylene were studied in the competitive oxidation (Figure 4-21). Firstly, the complete oxidation of perylene and chrysene was achieved. Chrysene was much more reactive than in the reaction when pyrene was present in the system.

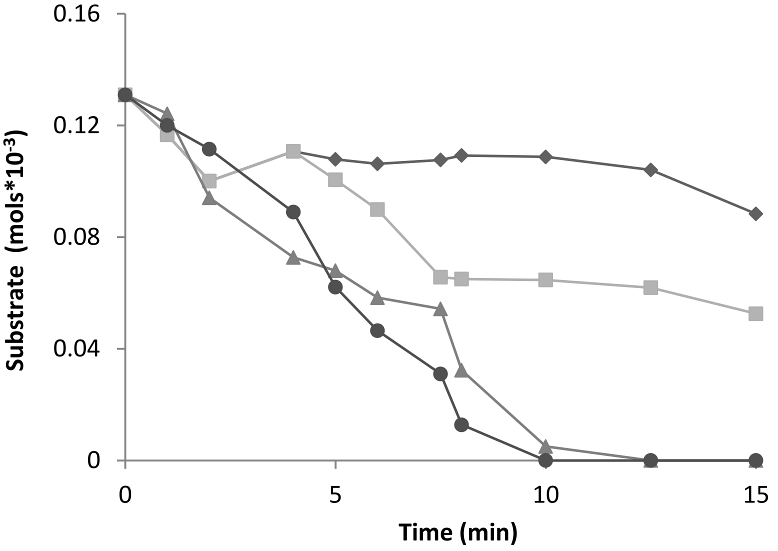


Figure 4–21: Comparison of substrate disappearance in biphase solvent system based on GC analysis (◆:Naphthalene; ■:Phenanthrene; ▲:Chrysene; ●:Perylene)
Reaction conditions: Substrate 0.131mmols, $NaIO_4$ 4.215mmols, $RuCl_3$ 0.035mmols DCM 16ml, MeCN 7ml, H_2O 7ml, T=22°C, stirring speed 500rpm

It has also been proven that the rate of oxidation depends on the number of fused aromatic rings and the rate of substrate reactivity follows the trend 5R > 4R > 3R > 2R (R=number of fused aromatic rings). Although different molar ratio substrate: oxidant was used in the reaction the trend of substrate reactivity remains unchanged.

4.6.2. Kinetic studies of alkylated PAHs

Valorisation of crude oil residues requires bigger molecules to react faster than smaller ones. As has been previously shown, RICO chemistry fulfils this condition. However the question remains if this trend is observed for compounds containing aliphatic chains attached to the aromatic ring. It is preferable to direct the selectivity of the reaction towards oxidation of aromatic protons and carbons, rather than aliphatic. Appropriate experiments were run to answer these questions.

4.6.2.1. Alkylated vs non alkylated compounds

Naphthalene and 1-Decylnaphthalene were used to determine selectivity in the oxidative competitive reactions. As it can be seen (Figure 4-22), the alkylated aromatic reacts faster than the aromatic without alkyl groups, however the difference is minor. This behaviour is rather expected due to the electron donating character of the aliphatic chain attached to the ring [4, 13]. Oxidation occurs at the ring which does not bear the decyl group therefore favouring the oxidation of aromatic carbon over that of aliphatic.

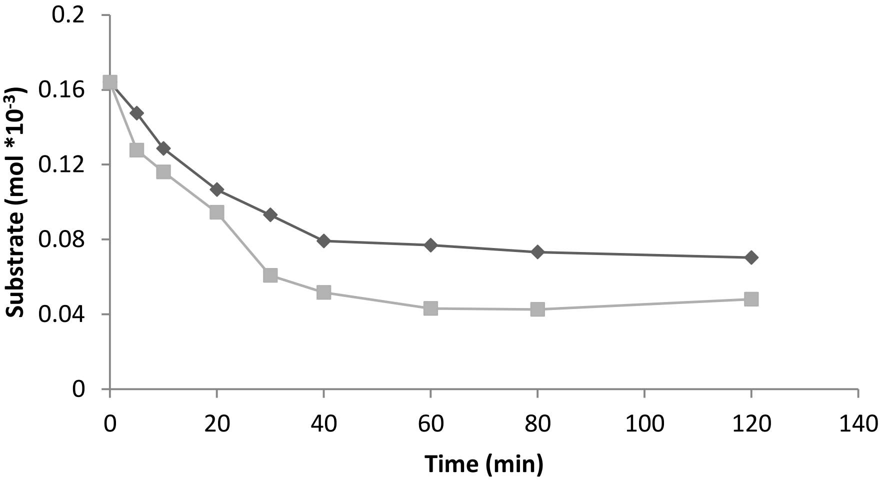


Figure 4–22: Competitive oxidation of Naphthalene and 1-Decylnaphthalene (◆:Naphthalene, ■:1-Decylnaphthalene), Reaction Conditions: Substrate 0.164mmols, ratio 1:1, $NaIO_4$ 2.624mmols, $RuCl_3$ 0.024mmols, DCM 16ml, MeCN 7ml, H_2O 7ml, T=22°C, stirring speed 500rpm

4.6.2.2. Competitive reaction between alkylated PAHs

To test the selectivity in this reaction, 1-decylnaphthalene, 2-nonylphenanthrene and 1-octadecylpyrene were oxidized. Competitive reaction between those 3 substrates is illustrated in figure 4-23. Quicker consumption of 1-octadecylpyrene than 2-nonylphenanthrene and 1-decylnaphthalene indicates that the selectivity for ring number is the same as observed in the reaction with standard PAHs. Therefore it can be suggested that rate in this reaction depends on number of aromatic rings. Here, by using compounds with different lengths of alkyl chain, it was partially possible to investigate the influence of aliphatic chain on selectivity. Comparing 1-decylnaphthalene and 2-nonylphenanthrene it can be seen that the rate of reaction is higher for substituted phenanthrene and the difference in reactivity is significant. It is important to emphasize than phenanthrene in competitive reaction with naphthalene in a biphasic solvent system reacted faster as well. Only kinetic studies of aromatics with equal length of alkyl chain would answer the question about the real role of aliphatic carbons during the oxidation reaction. However, due to the shortage of substrate, this experiment was not performed.

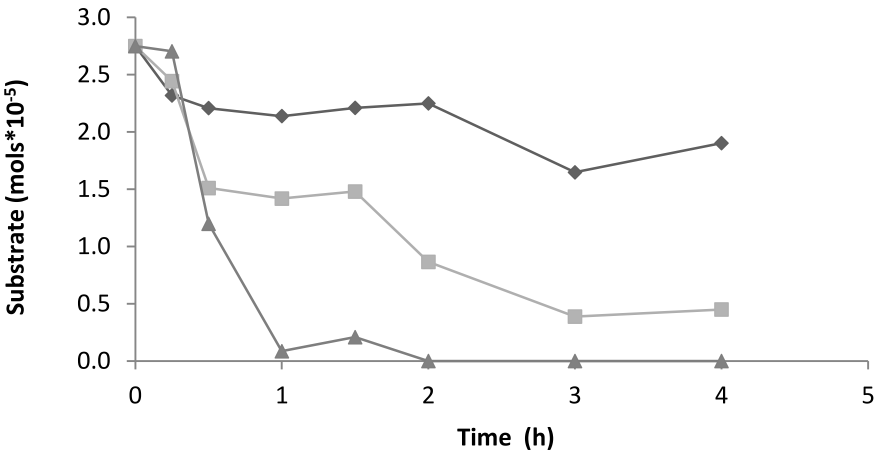


Figure 4–23: Oxidation of alkylated aromatics (◆:1-Decylnaphthalene, ■:2-Nonylphenanthrene, ▲:1-Octadecylpyrene), Reaction Conditions: Substrates: 0.0825mmols (molar ratio 1:1:1), $NaIO_4$ 0.7mmols, $RuCl_3$ 0.006mmols, DCM 16ml, MeCN 7ml, H_2O 7ml, T=22°C, stirring speed 500rpm

4.7. Oxidation of Alkylated Aromatics

One of the main requirements for chemical upgrading of heavy oils, resids and bitumens are to tailor the reaction conditions to selectively oxidise aromatic carbon and not aliphatic carbon. Based on simple model molecules, like naphthalene and 2-ethylnaphthalene, it was presented in the previous chapter that ruthenium chemistry appeared to have the potential to deliver the required selectivity. It targeted aromatic carbon and the cationic nature of the chemistry suggested that aromatic cores with more fused rings may oxidize faster. Nevertheless, control of this chemistry and investigation into its selectivity for bigger model compounds with long alkyl chains (>C9) needs to be studied.

4.7.1. Mass balance study

It was important to know how the presence of an aliphatic chain will affect the loss in mass. 1-Decylnaphthalene was used as a model compound for this study. Following previous methodology of gravimetric analysis in biphasic solvent system described in section 4.3., it was found that mass recovery in the organic layer was 145% and in aqueous 84% as shown in table 4-5. Here, the aim was also to calculate how much substrate was converted to CO_2. If consider that the missing mass in aqueous layer comes from oxygen loss, which was transferred to the organic layer and contributed to the mass increase, then the calculation is possible. In terms of oxygen it was calculated that 0.00775mols of O_2 is missing in the aqueous layer, but only 0.00404mols O_2 was transferred to the organic layer. Therefore 0.003076mols of O_2 is missing and could be converted to CO_2. If we consider this option, then 0.003076mols of O_2 can only give 0.001853mol of CO_2, which would suggest that a maximum of 16.8% of substrate was converted to CO_2. On the other hand, it is important to take into account experimental error, sample drying and purely theoretical calculation for CO_2.

Table 4-5: Mass Balance study performed for oxidation of 1-decylnaphthalene

	Reaction (1-decylnaphthalene)	
Layer	**Organic**	**Aqueous**
Substrate	0.141g	
Oxidant $NaIO_4$		0.8432g
Catalyst $RuCl_3$		0.0081g
Before reaction	0.141g	0.8513g
After reaction	0.2057g	0.7192g
Mass recovery	145%	84%
Number of moles of oxygen	Transferred from $NaIO_4$: 0.00404mols	Used: 0.00775mols
Difference	**0.003706mols**	

4.7.2. Quantification using ^{13}C NMR

The simplest and the most reliable technique in the detection of aliphatic and aromatic C is ^{13}C NMR. Using ^{13}C NMR it is possible to quantify the number of aromatic and aliphatic carbons before and after reaction and investigate its selectivity (Figure 4-24). The chemical shift of aliphatic carbons is in the range 5-40ppm, while aromatic carbons have a chemical shift in the range of 115-150ppm. However, only highly concentrated samples may be analyze and quantified using this method, because of poor ^{13}C NMR sensitivity. Thus the experiment was scaled up. This analysis also requires the addition of a paramagnetic compound to the solution so as to decrease the relaxation time of the

^{13}C nuclei, which take a very long time to relax back to equilibrium. $Cr(acac)_3$ was found to be an effective relaxation agent for quantitative studies using ^{13}C NMR.

Firstly, a test analysis was performed on 1-decylnaphthalene, dissolved in $CDCl_3$, followed by the addition of 0.6g of $Cr(acac)_3$ prior to NMR analysis. Peaks in the aromatic and aliphatic region were integrated versus TMS and the experimental integration value was compared to the theoretical value. The expected ratio between aromatic and aliphatic carbons was 1:1, while the ratio obtained in the analysis was 1:1.5. Unfortunately, integration of aromatic carbons versus aliphatic carbons gave unreliable results, so was of no use for further analysis.

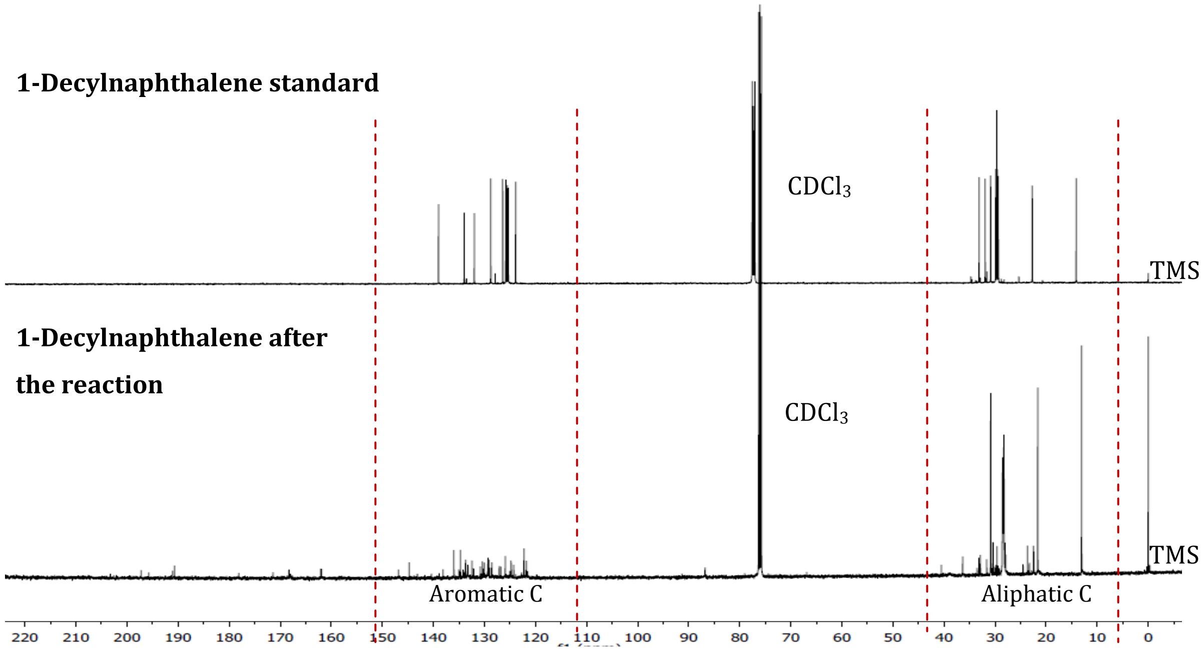


Figure 4–24: Methodology of ^{13}CNMR quantification
Reaction conditions: Substrate 0.51mmol, $NaIO_4$ 4.1mmol, $RuCl_3$ 0.040mmol, MeCN 7ml, DCM 16ml, H_2O 7ml, Stirring speed 500rpm

4.7.3. ^1H NMR studies: aliphatic Hs Vs aromatic Hs

As previously described, quantitative ^{13}C NMR analysis did not provide reliable results, thus ^1H NMR was used in the studies with 1-decylnaphthalene and 2-decylphenanthrene oxidation. A similar methodology, based on comparison between integrated peaks from the aromatic and aliphatic regions, described in section 3.6.2.2. was employed. The ^1H NMR signals of the entire spectra were grouped into 5 regions, 4 region of aliphatic protons: (A) α-CH_2- (3.4-2.9 ppm), (B) ß-CH_2-(2.0-1.9 ppm), (c) -CH_2-

(1.8-1.1 ppm), (D) terminal protons -CH_3-(1.10-0.80 ppm) and one region for aromatic protons (8.80-7.10 ppm)as presented in table 4-6 and figure 4-25.

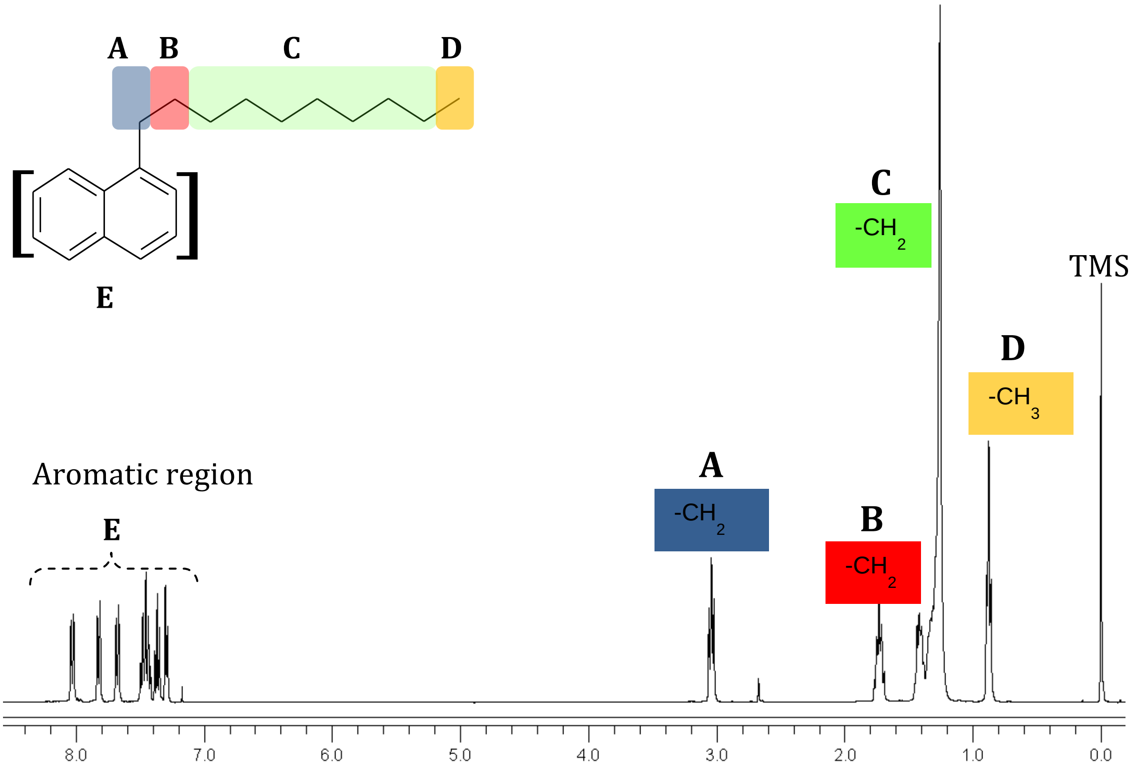


Figure 4–25: ^1H NMR of 1-decylnaphthalene in $CDCl_3$

After integration, the values obtained from protons from the aromatic and the aliphatic regions were presented as a ratio. The data presented in table 4-6 shows quantification of the relative proportions of protons from the different regions of the reactant and the product molecules. By comparing the ratios for sample 0 and sample 20h it is clear that there is a steady increase in the number of aliphatic protons formed at the expense of aromatic protons.

Table 4-6: Oxidation of 1-decylnaphthalene and 2-decylphenanthrene in a biphasic solvent system

Integration values (against TMS), Molar ratio substrate : oxidant 1:2, Reaction conditions: Substrate 0.0264mmols, $NaIO_4$ 0.052mmols, $RuCl_3$ 0.0006mmols, $CDCl_3$ 2.4ml, CD_3CN 1ml, H_2O 1ml, T=22°C, stirring speed 500rpm

Substrate	**Sample (h)**	**Aromatic Region (Integral values)**	**Aliphatic Region (Integral values)**				**Integral Ratio Aromatic Vs Aliphatic**	**Integral Ratio Aromatic Vs Aliphatic (%)**
			A	**B**	**C**	**D**		
1-Decylnaphthalene	0	3.58	1.13	1.09	7.37	1.55	1:2.9	26% : 74%
	20	4.01	1.28	1.12	8.60	1.83	1 : 3.1	24% : 76%
2-Decylphenanthrene	0	4.55	1.04	1.04	7.3	1.55	1:2.4	29% : 71%
	20	4.02	1.07	0.96	6.62	1.46	1:2.51	28.5%: 71.5%

It was speculated that the preservation of the alkyl chain could be the result of the relatively low concentration of oxidant used in the reaction. A similar experiment, where the molar ratio of *substrate : oxidant* was increased to 1:8 was performed for the oxidation of 1-octadecylpyrene. Also the effect of reaction time was investigated. As it is presented in table 4-7, after 20 hours reaction the ratio between aromatic and aliphatic protons is similar to the ratio obtained after 4 h reaction, so the oxidation of substrate did not proceed further and there was no consecutive oxidation. However, this experiment proves that the oxidation selectivity in the reaction is directed toward aromatic protons.

Table 4-7: Oxidation of 1-octadecylpyrene

Molar ratio substrate : oxidant 1:8, Reaction conditions: Substrate 0.0264mmols, $NaIO_4$ 0.206mmols, $RuCl_3$ 0.0024mmols, $CDCl_3$ 2.4ml, CD_3CN 1ml, H_2O 1ml, T=22°C, stirring speed 500rpm

Sample (h)	**Aromatic Region (Integral values)**	**Aliphatic Region (Integral values)**				**Integral Ratio Aromatic Vs Aliphatic**	**Integral Ratio Aromatic Vs Aliphatic (%)**
		A	B	C	D		
0	0.98	0.21	0.21	1.02	0.31	1 : 3.8	21% : 79%
4	0.83	0.39	0.12	2.99	0.31	1 : 4.6	18% : 82%
0	1.88	0.41	0.41	6.24	0.65	1 : 4.0	20% : 80%
20	1.52	0.24	0.43	5.91	0.76	1:4.8	17% : 83%

4.7.4. ^{1}H NMR studies into the preservation of aliphatic chain in wider range of PAHs

Once the region selectivity of the RICO reactions in a biphasic solvent system was determined, there was still the question regarding the amount of products with preserved or unreacted alkyl chain. This quantification was essential to test the assumption that the aliphatic chain is unaffected by RICO chemistry irrespective of the substrate structure. The electronic environment of carbon in the terminal CH_3 group in a long chain of alkylated aromatics is not susceptible to oxidation. This is because the potential point of attack, which is the aromatic carbon or aliphatic carbon attached to the aromatic ring, is far removed from the terminal proton of the aliphatic chain. Consequently, the terminal proton can be use as an internal standard for the quantification of the RICO of alkyl aromatics in a biphasic solvent system using ^{1}H NMR. Conversely, the methylene protons of the aliphatic carbon, which are attached to the aromatic ring, will produce a triplet and this signal is highly susceptible to any reactivity at the point of attachment of the aliphatic chain to the aromatic ring. Therefore, this triplet signal was used for the quantification of the oxidation products in which the aliphatic chain remained intact. What is more, using GC-MS analysis for 1-decylnaphthalene oxidation, no signs of alkyl chain fragments were detected, which confirmed that the methodology is valid and can be used for quantification of products with preserved alkyl chain.

To explain this methodology in detail, RICO of 1-decylnaphthalene was used as a standard. Figure 4-26 shows the ^{1}H NMR spectra of 1-decylnaphthalene before and after the RICO oxidation for 4.5 h. The singlet at 0.9 to 0.7 ppm (region D in Figure 4-26) is assigned to the protons of the terminal methyl group which will be used as an internal standard. The triplet at 3.1-2.9 ppm (region A in Figure 4-26) is used for quantifying the amount of products with aliphatic chain intact after RICO.

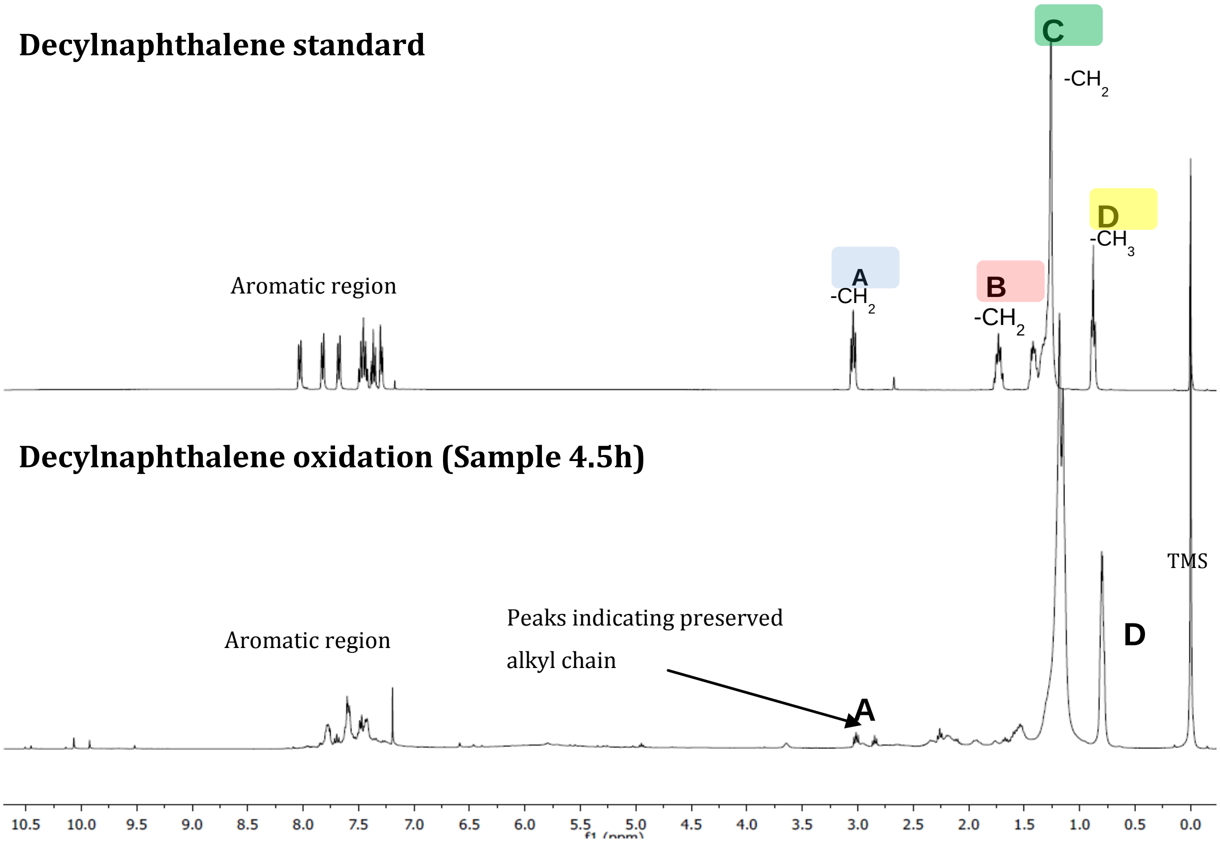


Figure 4–26: ^{1}H NMR spectra of 1-decylnaphthalene before and after RICO reaction

The areas of these two peaks, for the 0h and 4.5h samples, were calculated and normalized against TMS and are given in Table 4-8. The ratio of peak areas for protons A and D between the 0h and 4.5h samples provided a measure of the % of products in which the aliphatic chain remains intact and it is attached to the aromatic ring. This calculation is represented in the form of the equation below.

$$p_a(\%) = (r_x/r_{0h}) \times 100\% \qquad \text{(Equation 4-1)}$$

where r_x denotes the area ratio between region A and region D for the x^{th} hour sample, while p_a(%) is the % of products with intact aliphatic chain attached to the aromatic ring.

For 1-decylnaphthalene oxidation it was found that 60% of the products still had the aliphatic chain attached, whilst the remaining 40% of the products no longer had an aliphatic chain attached, or the carbon in the α position underwent oxidation to a carbonyl group, therefore the peaks will be shifted in the NMR spectra and will appear beyond the integration region. This is in sharp contrast to the well known assumption that RICO oxidation of an alkyl aromatic which results in the complete oxidation of the aromatic system leaving the aliphatic chain as a carboxylic acid. To the best of our knowledge, this is the first ever quantification of the products generated in the RICO oxidation of alkyl aromatics.

Table 4-8: Oxidation of 1-decylnaphthalene in a biphasic solvent system; integration values (against TMS)

Sample (h)	**Area A**	**Area D**	**Area Ratio A/D**	**p_a (%)**
0	0.28	0.43	0.65	100
4.5	0.17	0.43	0.39	60

Having successfully demonstrated a quantification methodology for the RICO oxidation of alkyl aromatics using ^{1}H NMR, our next objective was to understand the effect of the size of the aromatic ring moiety, the aliphatic chain length and its point of attachment on selectivity. For this purpose, six substrates, in addition to 1-decylnaphthalene with different aliphatic chain lengths and different numbers of aromatic rings were chosen for investigation using RICO. These substrates were 1-octadecylnaphthalene, 2-nonylphenanthrene, 9-nonylphenantrene, 1-butylpyrene 1-decylpyrene and 1-octadecylpyrene. The ^{1}H NMR spectra of all these substrates were measured independently before and after reaction and the peaks were grouped as before; 8.80-7.10 ppm (Aromatic protons), 3.40-2.90 ppm (α Hs, CH_2) of the aliphatic chain, 2.00-1.90 ppm (βCH_2) of the aliphatic chain, 1.81-1.10 ppm (CH_2) and 1.10-0.80 pm (terminal CH_3 group). Using the proven methodology the % of alkylated polyaromatics in which the alkyl chain remained attached after 4.5 h as well as 6 and 10h (1-decylnaphthalene) of reaction was calculated and the results are summarized in Table 4-9.

Table 4-9: Effect of chain length and ring number on the activity and selectivity
*Reaction Conditions: T=22°C, t=4h, stirring speed: 500 rpm, substrate 0.0276 mmols, $NaIO_4$ 0.2065 mmols, $RuCl_3·xH_2O$ (2µmols) *after 6h reaction, **after 10h reaction with addition of extra 0.2065 mmols $NaIO_4$*

No.	Substrate	Conversion (%)	Preserved aliphatic Hs (%)
1.	1-Decylnaphthalene	42	60
		46*	59*
		99**	4**
2.	1-Octadecylnaphthalene	76	87
3.	2-Nonylphenanthrene	73	69
4.	9-Octadecylphenanthrene	62	46
5.	1-Butylpyrene	80	68
6.	1-Decylpyrene	90	86
7.	1-Octadecylpyrene	81	83

It is clear that the amount of products with intact alkyl chain after RICO oxidation ranged from 4% for 1-decylnaphthalene to 87% for 1-octadecylnaphthalene. This clearly suggests that the reactivity of the alkyl chain in the RICO of alkyl aromatics is alkyl chain length dependent as opposed to the general belief that is irrespective for aromatic ring leaving the aliphatics as a carboxylic acid. Comparison of results from 1-decylnaphthalene and 1-octadecylnaphthalene shows that the longer the length of the alkyl chain the more the chain is preserved after oxidation. This observation is further substantiated from the results for the RICO oxidation of 1-octadecylpyrene and 1-butylpyrene. In this case, the reactivity for both pyrenes was very similar, yet there was an increase in the preservation of alkyl chain as the chain length increased.

Conversely, if we compare the conversion data of reaction for all molecules it seems that the length of alkyl chain also contributes to the reactivity. By comparing conversion data for naphthalene and pyrene derivatives, a clear trend was observed, where conversion was higher for molecules with longer alkyl chain.

Another intriguing observation came when comparing substrates with similar alkyl chain length but a different number of aromatic rings: 1-decylnaphthalene, 2-nonylphenanthrene and 1-decylpyrene. It is clear that conversion and the % of preserved alkyl chain increased with number of fused rings. Therefore we can assume that, the bigger the molecule the less probable oxidation will occur at the α CH_2 position. Taking into account reactions analyzed after 4.5h, it is evident that the amount of products with unoxidized alkyl chain was not 100%, as has been previously assumed. Probably the conversion and the concentration of oxidant used plays a crucial role. Thus by allowing the reaction to go to completion, using 1-decylnaphthalene as a model, we observed that by increasing the amount of oxidant and catalyst, the % of product with preserved alkyl chain was only 4%, which is in agreement with previously published literature. However, we believe, that this selectivity is highly dependent on the aliphatic chain length and the number of fused aromatic rings present in the substrate. What is more, the 1-decylnaphthalene molecule is of special interest, because alkyl chain location plays an important role and naphthalene has few positions which are the most susceptible for RuO_4 attack. It is possible that products of 1-decylnaphthalene oxidation will still have attached, but oxidized alkyl chain, which α protons in ^1H NMR spectra will give a signals in region beyond integration. This is a very important observation, because in the characterization of coal and asphaltenes, it has always been assumed that all of the alkyl chains end up as aliphatic acids. This assumption seems to be wrong, as we demonstrated that aromatics with long as well as short alkyl chain are transformed into products with preserved alkyl chain.

On the other hand, it has been shown that the point of attachment of the alkyl chain to the aromatic ring system also contributes to the selectivity of the reaction. Alkyl chain in the case of 9-octadecylphenanthrene is attached to the position which is most likely to be attacked by RuO_4, due to the lowest energy of carbons located there, being the most susceptible for attack. If we compare the % of preserved α protons with conversion in this reaction, it is obvious that only un-reacted substrate contributes to the obtained p_a

number. Nevertheless it has been found that the product from oxidation still contains a preserved alkyl chain oxidized in the α position, proven by MS analysis. From the above results it is clear that the amount of alkyl chain that is un-reacted (preserved) under RICO condition depends on the ring size, the length of the alkyl chain and where it is attached to the aromatic ring system.

To conclude, it can be said that one major trend has been observed: the bigger the molecule with longer alkyl chain, the higher the conversion and the greater % of preserved alkyl chain observed.

4.7.5. Products identification: 1-decylnaphthalene oxidation

Using the methodology previously described in section 4.7.4., it was possible to determine the amount of products with preserved alkyl chain in the oxidation of alkyl group containing PAHs. However, it is important to prove the presence of those products by qualitative analysis of at least one substrate. Here, 1-decylnaphthalene was used as a model compound. To determine the products, a sample from the aqueous and organic layer were withdrawn after 2, 8 and 18 hours time and analyzed using GC and GC-MS. The first interesting observation was made in the GC-MS chromatogram generated from the sample withdrawn from organic layer (figure 4-27). GC-MS analysis detected several compounds where the calculated molecular formula indicated the preservation of the alkyl chain. Moreover, it was also observed that the peaks did not disappear during the course of the reaction, suggesting no consecutive oxidation.

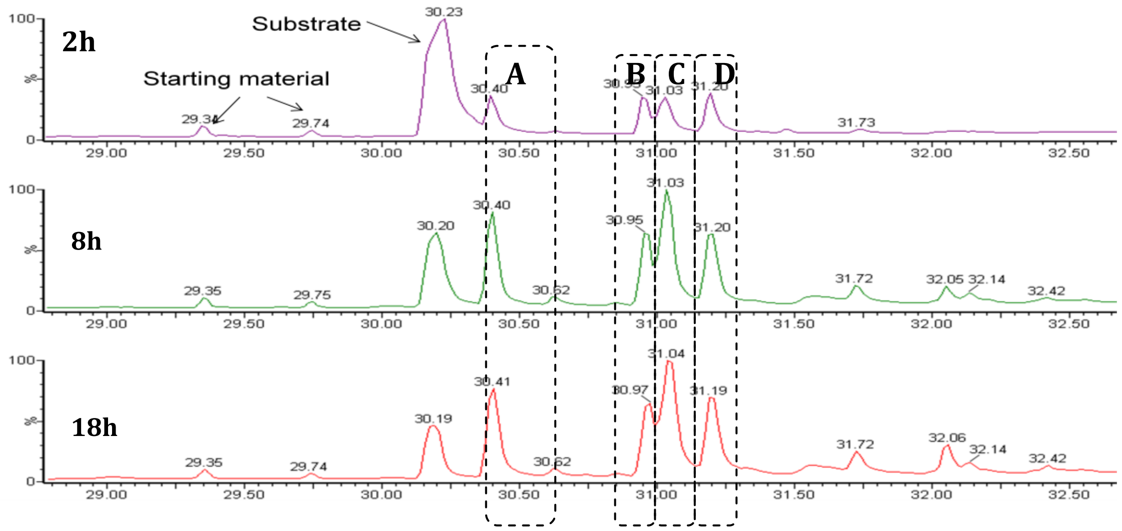
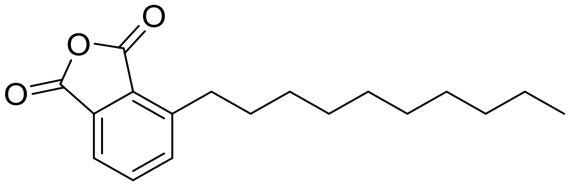
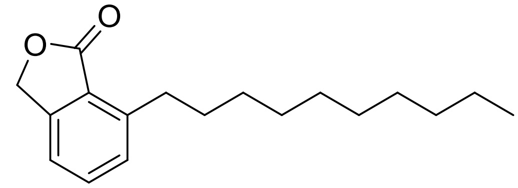
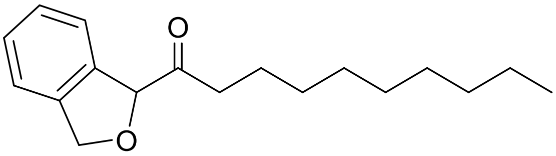
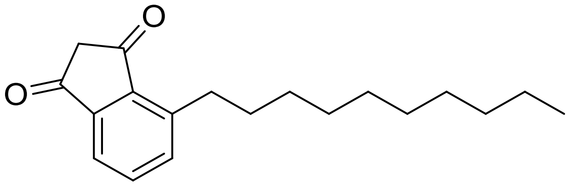
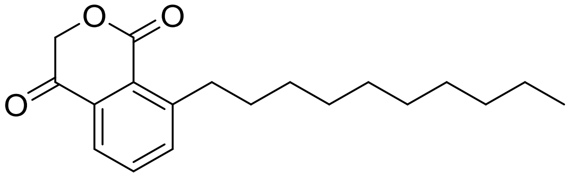
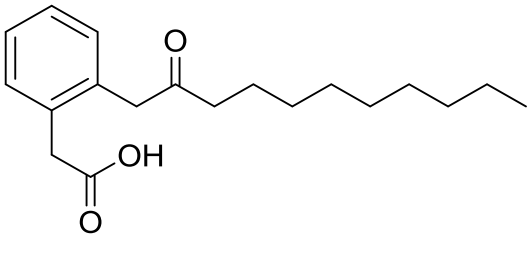


Figure 4–27: GC-MS analysis of samples from organic layer
Reaction Conditions: 1-decylnaphthalene 0.0276mmols, $NaIO_4$ 0.2065mmols, $RuCl_3$ 0.0024mmols, MeCN 1ml, DCM 2.4ml, H_2O 1ml, stirring speed 500rpm

Based on the molecular formula information, obtained by GC-MS analysis, a list of possible oxidation products was prepared (Table 4-10).

Table 4-10: Possible products obtained in the oxidation of 1-decylnaphthalene

Symbol	Molecular Formula	Molecular Weight	Possible structure
A	$C_{18}H_{24}O_3$	288	
B	$C_{18}H_{26}O_2$	274	 
C	$C_{19}H_{26}O_2$	286	
D	$C_{19}H_{26}O_3$	304	 

Here, two molecules are of special interest. Molecules with preserved, but oxidized carbon in position α, confirmed that the methodology developed for quantification of preserved aliphatic Hs is valid. That is why the number describing % of preserved aliphatic Hs is related to the unreacted substrate. In those two molecules, protons in position α (in substrate), during the course of reaction disappeared and cannot be seen anymore.

In the aqueous layer, decanoic acid and phthalic acid were also detected. It is believed that these products are obtained after C-C bond cleavage between the aromatic ring carbon and the α C of the alkyl chain. However the concentration of these product was minor in comparison to products found in the organic layer.

4.5.1. Product Identification: 9-octadecylphenanthrene oxidation

Identification of the products derived from the oxidation of 9-octadecylphenanthrene was crucial due to the location of the alkyl chain in the substrate. The aliphatic chain is attached at the 9 position in phenanthrene, which is the most likely to be attacked by RuO_4. Therefore cleavage of the bond between $C_{aromatic}$ - $C_{aliphatic}$ should be more probable than in the case of 2-nonylphenanthrene. GC-MS and MS analysis of the reaction mixture were performed and products with open ring and preserved alkyl chain were detected. The GC-MS trace is presented in figure 4-28.

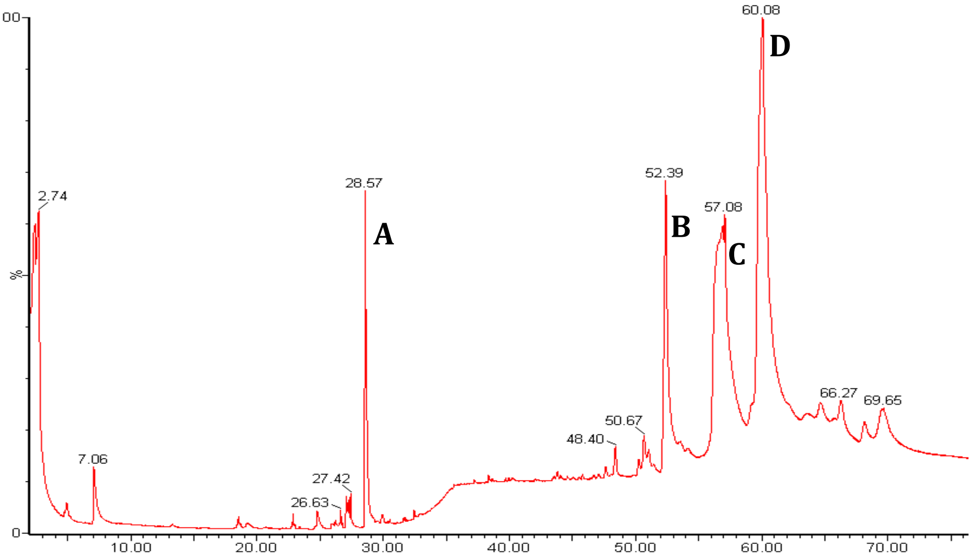
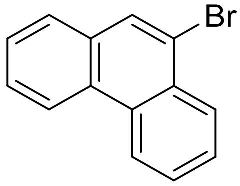
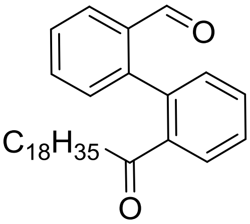
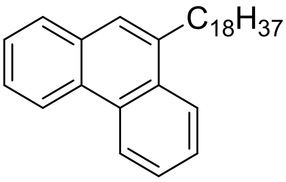
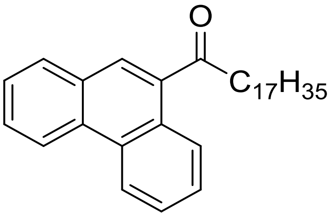


Figure 4–28: Oxidation of 9-octadecylphenanthrene, GC-MS analysis

The reaction mixture was also analyzed using a MS (ES+, EI) technique and structures of possible products were drawn and are shown below (Table 4-11).

*Table 4-11: Possible products of 9-octadecylphenanthrene oxidation and contamination**

Symbol used in GC-MS chromatogram	**Possible Structure**	**Mass detected (EI data)**
A*		256
B		462
C		430
D		444

Using the EI method a molecular ion peak at m/z 462 was detected and assigned to structure B. Moreover a strong peak from unreacted substrate was detected (structure C). Using Electrospray positive analysis peaks at m/z 463 and m/z 445 were determined which can be assigned to structures B and D, respectively. 9-Bromophenanthrene (structure A*) was found even in the starting material and it is probably a substrate from 9-octadecylphenanthrene synthesis. This data suggests that there are only 2 products obtained in this reaction. Using the developed NMR methodology it was only possible to quantify unreacted substrate, because the signals from products corresponding to the α Hs are not present anymore. On the other side ß-Hs, which now became α Hs are significantly shifted in the NMR spectra due to the presence of the C=O group and are outside the integration region. Those findings demonstrate the deviations in using the methodology and limit its use.

4.8. Oxidation of Porphyrins

Refining processes are being continuously called upon to increase efficiency. This can be obtained by improving demetallation process during catalytic thermal cracking. The reason why it is necessary to introduce a demetallation process are metalloporphyrins, a major source of metal contamination and therefore catalyst deactivation [14]. Several approaches for metal removal were investigated, however, most of the methods require a high expenditure of energy and more environmentally friendly methods of demetallation are needed [15]. Knowing the chemistry of RICO reaction and its high reactivity, it was suggested to apply this chemistry to porphyrins oxidation and the simultaneous removal of metal. Two model compounds were investigated: vanadyl tetraphenylporphyrin (VOTPP) and nickel tetraphenylporphyrin (NiTPP). A number of analytical techniques e.g. GC, MS, UV-Vis were employed to monitor the oxidation progress and determine the amount of metal present in the oxidized product. The most popular and reliable method for the direct determination of metalloporhyrins concentration is spectrometry [16-17]. Using this technique, the level of oxidation of porphyrins was monitored via changes in the intensity of the band at a wavelength of 526nm for NiTPP and 548nm for VOTPP. The breakdown of NiTPP, VOTPP was monitored by the MS analysis and compared with the MS spectra of the non-metal containing porphyrin, 5,10,15,20-Tetraphenyl-21H, 23H-porphine (TPP). The model compound structures and TPP are presented below (Figure 4-29).

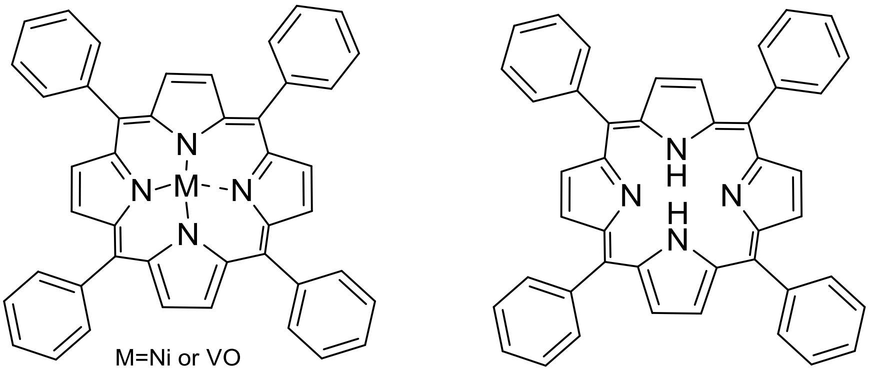


Figure 4–29: Structure of NiTPP, VOTPP(left) and TPP (right)

4.8.1. Nickel (II) tetraphenylporphyrin

Three reactions with different *substrate : oxidant* ratio were performed using the biphasic solvent system. A detailed description of the experimental protocol can be found in section 2.6.1.3. It is worth repeating that NiTPP is soluble only in organic solvents, thus the organic layer was monitored during the analysis in order to investigate the conversion level. When the reaction was carried out with a use of oxidant at concentration C=0.00187M and 0.0002g $RuCl_3$, no colour change was observed even after 20h reaction. When an oxidant at concentration C=0.187 M was employed, it resulted in the significant peak reduction of the λ band at 526nm even after just 2 h of reaction as it is shown in figure 4-30. When the concentration of oxidant was changed to C=0.0187M, the same results were observed and total oxidation of porphyrine was achieved in a reaction time of 16h (Table 4-12).

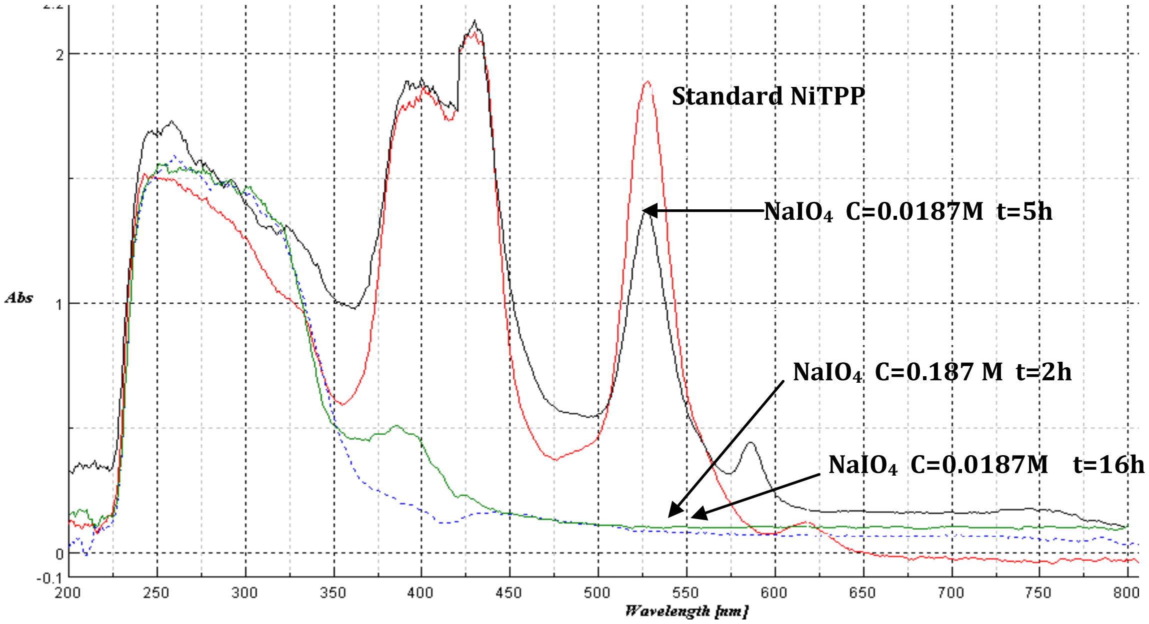


Figure 4–30: Oxidation of NiTPP using different substrate : oxidant ratio
*Reaction conditions: Substrate: C= 1.19 *10^{-4} M, DCM 12 ml, H_2O 5ml 1)$NaIO_4$ 0.2g, $RuCl_3$ 0.002g, 2)$NaIO_4$ 0.02g, $RuCl_3$ 0.0002*

Table 4-12: Absorbance and concentration value obtained during NiTPP oxidation

Sample Number	Description	Absorbance	Concentration (mol/dm^{-3} * 10^{-4})
1	Standard NiTPP	1.86	1.03
2	$NaIO_4$ C=0.0187M $RuCl_3$ 0.0002g; t=5h	1.34	0.74
3	$NaIO_4$ C=0.187M $RuCl_3$ 0.002g; t=2h	0.20	0.11
4	$NaIO_4$ C=0.0187M $RuCl_3$ 0.0002g; t=16h	0.18	0.10

It was postulated that during the oxidation of NiTPP, a metal is set free and it is transferred to the aqueous layer, thus analysis of aqueous phase were performed.

Nickel determination was performed using AAS and ICP-MS. Using AAS no nickel was detected in the organic layer with 90% of total mass of nickel determined in the aqueous layer. However, due to the low AAS Ni lamp resolution, the sample was further analyzed using ICP-MS. ICP-MS analysis showed that 99.6% of the total Ni was transferred from the organic to the aqueous phase, indicating the breakdown of the Ni porphyrin. The hypothesis was confirmed by MS analysis, where a wide range of peaks implies high molecule fragmentation, which may be the result of metal removal. Contrary to the oxidation of NiTPP, the oxidation of TPP occurs in a different way, as suggested by the MS data, shown in figure 4-31, which suggests that the presence of a metal plays an important role during the oxidation.

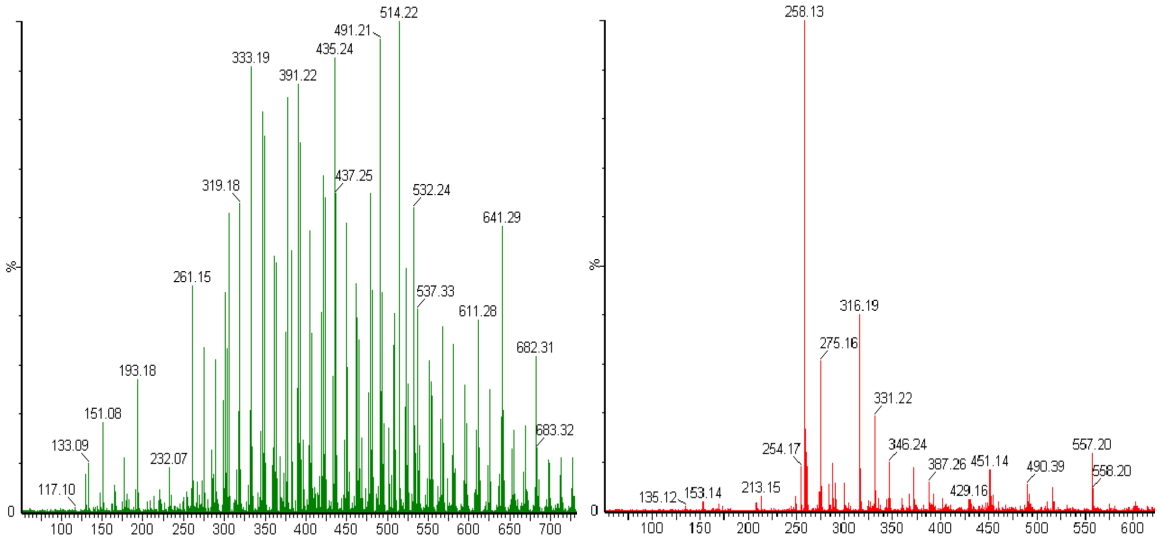


Figure 4–31: MS analysis: Comparison of NiTPP and TPP oxidation
*Reaction conditions: t=16h, Substrate: NiTPP (left) (Mw=671.41 gmol^{-1}), TPP (right) (Mw=614.75gmol^{-1}) C= 1.19*10^{-4} M, $NaIO_4$ 0.02g, $RuCl_3$ 0.0002g, DCM 12 ml, H_2O 5ml*

4.8.2. Vanadyl tetraphenylporphyrin

Oxidation of vanadyl tetraphenylporphyrin, the second model compound was investigated using the optimum oxidation conditions found for NiTPP and force the removal of the metal from the metalloporphyrin ($NaIO_4$ 0.02g, $RuCl_3$ 0.0002g). The end of this reaction was indicated when the colour of the solution changed from red to colourless. As illustrated in figure 4-32, the UV-Vis spectrum of the reaction mixture after 15h of reaction shows no absorbance peak at 548nm, which indicates the disappearance of the substrate.

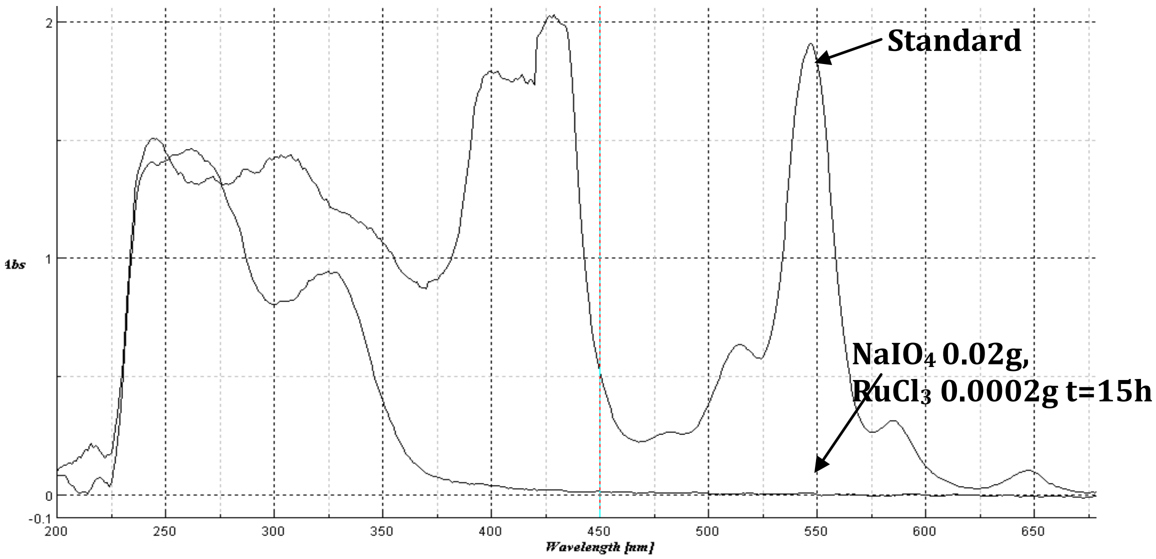


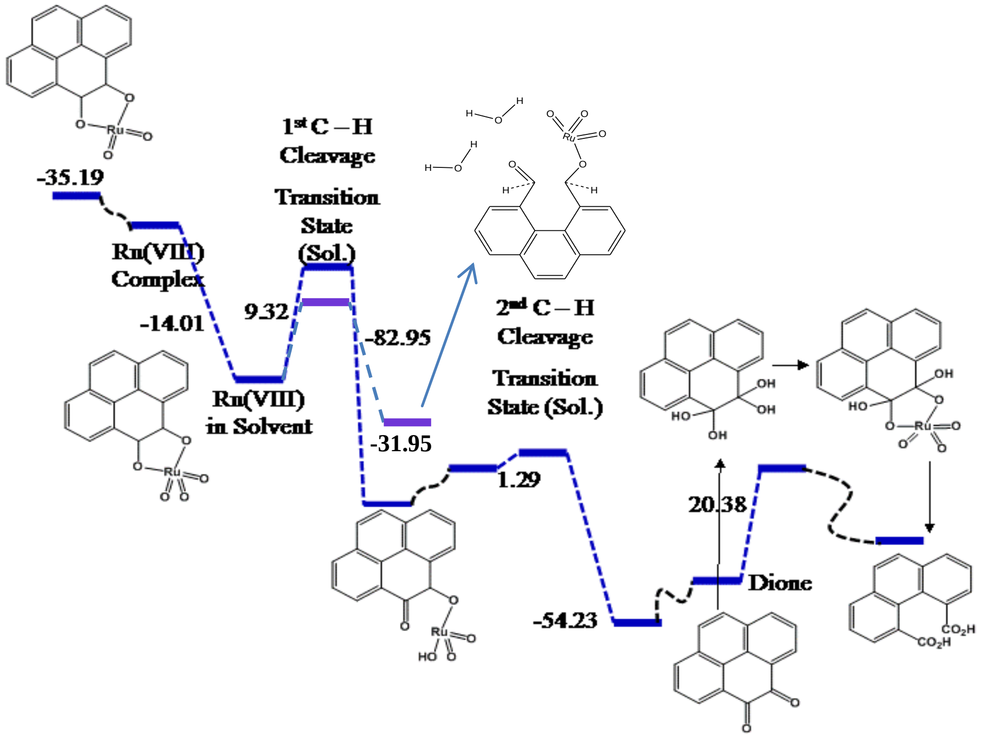
Figure 4–32: UV-Vis analysis: Oxidation of VOTPP
*Reaction conditions: Substrate: C= 1.19 *10^{-4} M, $NaIO_4$ 0.02g, $RuCl_3$ 0.0002g, DCM 12 ml, H_2O 5ml*

ICP analysis of the aqueous layer determined that amount of vanadium detected was 99% of that present in starting material. This data indicates that RICO chemistry can be successfully used to oxidatively breakdown the porphyrins and remove the central metal from the framework. Moreover, metal does not undergo oxidation as was deduced from the XPS analysis.

4.9. Further discussion and conclusions

Data presented in this chapter illustrates that oxidation of PAHs using Ruthenium Ion Catalyzed Oxidation chemistry is a very selective method of oxidation and by optimizing reaction conditions it can be tailored to yield the desired products. It has been shown, that a change in the solvent system results in a different product distribution. Naphthalene, which has 2 aromatic rings, was oxidized to the same products both in a monophasic and in a biphasic solvent system. Oxidation of phenanthrene resulted in a different product profile. Pyrene yielded very different oxidation products when the reaction conditions were changed from a monophasic to a biphasic system. It is believed, that in a monophasic solvent system, the oxidation is milder and therefore more selective, giving products with one ring opened. Based on the results obtained for naphthalene, phenanthrene and pyrene, it was demonstrated that the size of molecule plays a crucial role during this electrophilic oxidation.

Taking into account the data from mechanistic investigations, it is suggested that the oxidation mechanism is the same in both solvent systems. Considering the solvent role as a controlling factor in selectivity towards products with one open ring, it can be stated that products observed when the oxidation was conducted in a monophasic solvent system must be the intermediates to those products obtained in a biphasic system. The second possibility here is the parallel formation of products with one open ring and diones. Selectivity in RICO may also depend on pH [18]. Mechanism of this oxidation, based on theoretical calculations and the observed product profile, assume that the formation of phenanthrene-4,5-dialdehyde and pyrene-4,5-dione is simultaneous [12]. What is more, until now, there was no concrete evidence for the mechanism of this oxidation, however, there was some speculation that C=C scission could be involved in the first step of the reaction [19-20]. The highest energy barrier and so the expected rate determining step in the production of the pyrene-4,5-dione product is the first C-H bond cleavage step. This process is only competitive with C-C bond cleavage (forming dialdehyde) in the presence of water which indicates a proton shuttle that aids the removal of the H atom from the PAH with a barrier of 9.3 kcal mol^{-1}. However, with water present the C-C bond cleavage barrier to form dialdehyde is still lower (6.4 kcal mol^{-1}) than the C-H cleavage barrier but now by only 3 kcal mol^{-1} and so we conclude that the two processes are competitive as it can be seen on scheme 4-5 [12].



Scheme 4-5: Reaction mechanism for Ru catalyzed PAH oxidation from modelling studies [12]

As previously stated in this chapter, molecule size plays a crucial role during the oxidation process. Bigger compounds react faster than smaller compounds and reactivity follows the trend: 5R>4R>3R>2R>>1R and it is not solvent dependent. The most important factor which determines the rate of oxidation is the number of delocalized electrons in the PAHs, in this electrophilic reaction. A similar observation was made for the competitive reaction between alkylated aromatics with different ring sizes. It has been shown that the aliphatic chain attached to the aromatic molecule acts as a electron donating group, so increasing the probability of attack by the RuO_4. Conversely, the number of aromatic rings in the PAH determines the kinetics of the reaction. Additional, interesting data presented in this chapter is related to the % of preserved aliphatic protons in the RICO reaction. This value is of special interest because of the residues valorisation approach. It was also described, that the bigger the molecule and the longer the alkyl chain, the higher the observed conversion and % of preserved alkyl chain.

What is more, the proof that RICO chemistry can be a successful method for the removal of metal from metalloporphyrins and can contribute to the energetic improvement in the refining processes was also given in this chapter.

4.10. References

1. Peng, P., Fu, J.M., Sheng, G.Y., Morales-Izquierdo, A., Lown, E.M., and Strausz, O.P., *Energy & Fuels*, **1999**, 13(2), 266
2. Carlsen, P.H.J., Katsuki, T., Martin, V.S., and Sharpless, K.B., *Journal of Organic Chemistry*, **1981**, 46(19), 3936
3. Teixeira, M.A.G., Gonçalves, M.L.A., and Pereira, R.C.L., *Fuel Chemistry Division Preprints*, **2002**, 47(1), 183
4. Spitzer, U.A. and Lee, D.G., *Journal of Organic Chemistry*, **1974**, 39(16), 2468
5. Mendez, A., Bermejo, J., Santamaria, R., Blanco, C.G., and Menendez, R., *Energy & Fuels*, **2000**, 14(4), 936
6. Stock, L.M. and Kwok-tuen, T., *Fuel*, **1983**, 62, 974
7. Kasai, M. and Ziffer, H., *Journal of Organic Chemistry*, **1983**, 48(14), 2346
8. Djerassi, C. and Engle, R.R., *Journal of Organic Chemistry*, **1953**, 75, 3838
9. Bailey, P.S., *Chemistry & Industry*, **1957**(34), 1148
10. Hu, J., Zhang, D., and Harris, F.W., *Journal of Organic Chemistry*, **2005**, 70(2), 707
11. Oberender, F.G. and Dixon, J.A., *Journal of Organic Chemistry*, **1959**, 24(9), 1226
12. Hickey, N. and Willock, D., *Theoretical Calculations*. 2011, Cardiff University.
13. Lee, D.G. and Spitzer, U.A., *Canadian Journal of Chemistry*, **1971**, 49(17), 2763
14. Speight, J.G., *The Desulfurization of Heavy Olis and Residua*. **1981**, New York, Marcel Dekker.
15. Eisner, U. and Harding, M.J.C., *Journal of the Chemical Society (Resumed)*, **1964**, 4089
16. Shcherbakova, N.P., *Chemistry and Technology of Fuels and Oils*, **1994**, 30, 42
17. Galimov, R.A. and Krivonozhkina L.V., *Khimiya i Tekhnologiya Topliv i Masel*, **1993**, 6, 27
18. Yamaoka, H., Moriya, N., and Ikunaka, M., *Organic Process Research & Development*, **2004**, 8(6), 931
19. Lee, D.G., Chang, V.S., and Helliwell, S., *Journal of Organic Chemistry*, **1976**, 41(22), 3644
20. Strassner, T. and Drees, M., *Journal of Molecular Structure-Theochem*, **2004**, 671(1-3), 197

5. Oxidation of PAHs using H_2O_2/H_2WO_4 system

5.1. Introduction

The results presented in this chapter were obtained using tungsten chemistry which utilizes H_2WO_4 as a catalyst, a phosphorus based acid as co-catalyst, a quaternary ammonium salt as a phase transfer catalyst and H_2O_2 as the oxidant. This reaction system is very attractive, because tungsten catalysts are physiologically harmless and do not cause unproductive H_2O_2 decomposition [1-2]. What is more, H_2WO_4 is more available and less expensive than those catalysts described in chapter 3 and 4 and H_2O_2 is a cheaper alternative to the $NaIO_4$ oxidant, used in the RICO chemistry. Comparing the two systems, it is clear that ruthenium and tungsten chemistry both use homogenous catalysts which are dissolved in an aqueous phase along with the oxidant. Here, the aqueous phase containing the H_2WO_4 and the H_2O_2 is in contact with toluene or another organic solvent at a solvent interface, containing a model compound or petroleum resids. The reaction occurs at 70°C or at higher temperatures over several hours and does not require the addition of reagent e.g. Na_2SO_3 to quench the reaction which is needed in RICO chemistry. Taking into account all the positive attributes of tungsten chemistry, it was decided to study the effect of different solvents to find their influence on the catalytic activity and product distribution. Moreover, the selectivity of tungsten chemistry on aromatics with long alkyl chain was studied extensively. Attempts have been made to investigate the reaction kinetics of different heteroaromatics, whilst also to characterize the oxidation products of desulfurization and denitrogenation. Finally, in the last section of this chapter, results related to oxidative metal removal from metalloporphyrins using tungsten chemistry are discussed.

5.2. Studies of solvent effect on product distribution

Experiments began with reactions of H_2WO_4 and H_2O_2 in chlorobenzene as outlined in the literature reference [3]. Toluene and a number of different solvents were used to establish their influence on product distribution.

5.2.1. Chlorobenzene

Chlorobenzene was used as a solvent during the oxidation of 4 compounds: naphthalene, phenanthrene, pyrene and 2-ethylnaphthalene. Products from the oxidation were characterized by GC-MS, MS, ^{1}H NMR and ^{13}C NMR.

5.2.1.1. Naphthalene

After 6 hours of reaction, naphthalene-1,4-dione (8A) and phthalic anhydride (8B) were detected in the reaction mixture in ratio 1:1.25 as shown in figure 5-1. Apart from the products, unreacted substrate was also detected due to the low conversion level, which was only 10%.

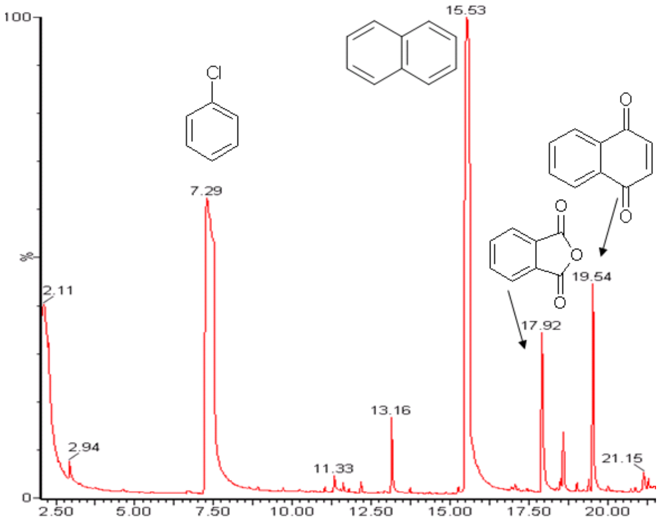
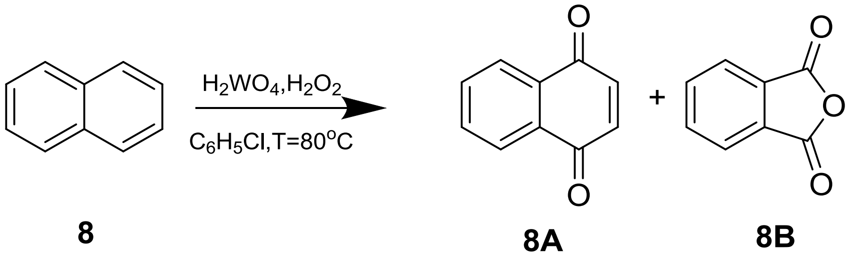


Figure 5–1: Naphthalene oxidation: GC-MS analysis

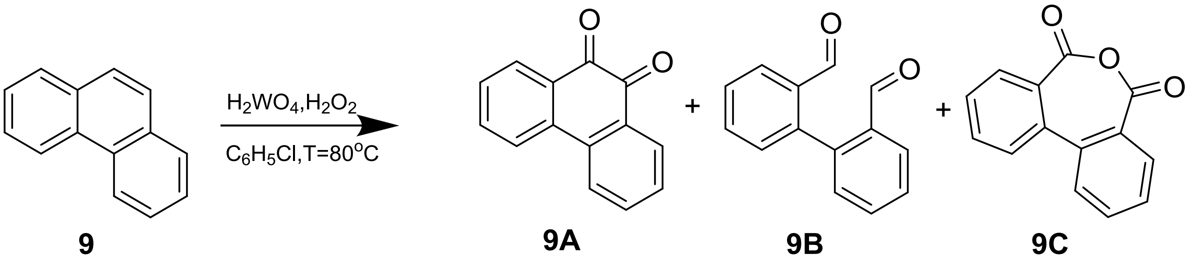
Here, as previously observed in chapter 3 and 4, the presence of phthalic anhydride is a consequence of the dehydration of phthalic acid. However this result was very promising because product with one opened ring was detected.



Scheme 5-1: Products of naphthalene oxidation
Reaction Conditions: Substrate 18.8 mmol, H_2WO_4 0.153g (0.614mmol), H_2O_2 35% 12ml, Aliquat 336 0.24ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, T=80°C, t=6h

5.2.1.2. Phenanthrene

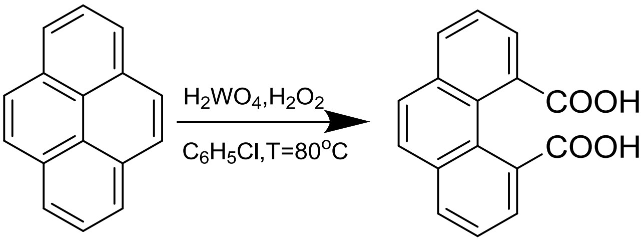
Phenanthrene was oxidized with higher conversion than naphthalene, which was calculated at the level of 32%. Products identified in this reaction were: phenanthrene 9,10-dione (9A), biphenyl-2,2'-dicarbaldehyde (9B) and biphenyl anhydride (9C) (selectivity around 80%) as shown in scheme below (Scheme 5-2). The anhydride is considered to be a dehydration product of the biphenyl-2,2'-dicarboxylic acid. Moreover, GC-MS analysis suggests a number of products at low concentration whose structures could not be deduced from the empirical formulas generated by GC-MS ($C_{13}H_8O_2$ and $C_{15}H_4O_2$). These results are slightly different from that reported by Saito *et al.*, who mainly observed biphenyl-2,2'-dicarboxylic acid at selectivity of 90% [4].



Scheme 5-2: Products of phenanthrene oxidation
Reaction Conditions: Substrate 18.8 mmol, H_2WO_4 0.153g (0.614mmol), H_2O_2 35% 12ml, Aliquat 336 0.24ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, T=80°C, t=6h

5.2.1.3. Pyrene

Oxidation of pyrene was carried out using similar conditions as previously described in the literature resulting in one product, phenanthrene-4,5-dicarboxylic acid (10A) [3]. The isolated solid material was dissolved in 1.25M NaOH (200ml), decolorized with activated charcoal and neutralized with glacial acetic acid to yield a reddish brown precipitate. The resultant compound had a melting point of 238°C (lit. 248-250°C). ^1H NMR spectrum: (400MHz, DMSO-d_6) δ 8.11(d, 2H), 7.98 (d, 2H), 7.91 (s, 2H), 7.67(t, 2H).



10 **10A**

Scheme 5-3: Product of pyrene oxidation
Reaction Conditions: Substrate 18.8 mmol, H_2WO_4 0.153g (0.614mmol), H_2O_2 35% 12ml, Aliquat 336 0.24ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, T=80°C, t=6h

Pyrene was transformed to phenanthrene 4,5-diacid at a conversion of 79% and illustrates that this reaction is very selective toward acids. ^{1}H NMR spectra shows signals from phenanthrene 4,5-diacid which partially masks signals from pyrene (Figure 5-2).

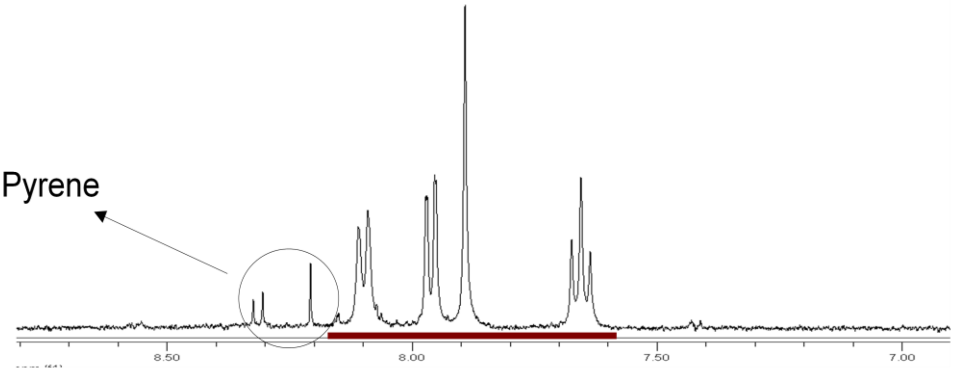


Figure 5–2: Pyrene Oxidation: ^{1}H NMR analysis with marked signals from pyrene and phenanthrene 4,5-diacid (400MHz, δ 8.10(d, 2H, J=7.7Hz), δ 7.97(d, 2H, J=7.3Hz), δ 7.89(s, 2H), δ 7.65(t, 2H, J=7.7Hz))

What is more, it proved that molecules with higher number of fused rings reacts quicker and selectivity to acid also increases with molecule size. By comparison of this result with that reported in literature, it can be seen that Saito *et al*. did not report 100% selectivity, while in our reaction, no other product was detected. Saito investigated the selectivity towards acids by changing reaction conditions, mainly pH. It was reported that selectivity changed from 71.3% to 98.9% which shows that reaction conditions and the type of reactants used have an influence on the products of oxidation [4].

It is worth mentioning that in reactions which use H_2WO_4/H_2O_2, temperature also plays an important role. When reaction with pyrene was performed at a temperature of 40°C, the only oxidation product was pyrene-4,5-dione. This observation was verified by ^{1}H NMR and MS analysis. MS analysis detected a strong peak m/z 233.07, which indicates presence of pyrene-4,5-dione as it can be seen on figure 5-3. This suggests that when chlorobenzene is used as a solvent, carbons in position 4,5 are attacked, but it is reaction temperature which is a crucial factor in deciding the extent of oxidation.

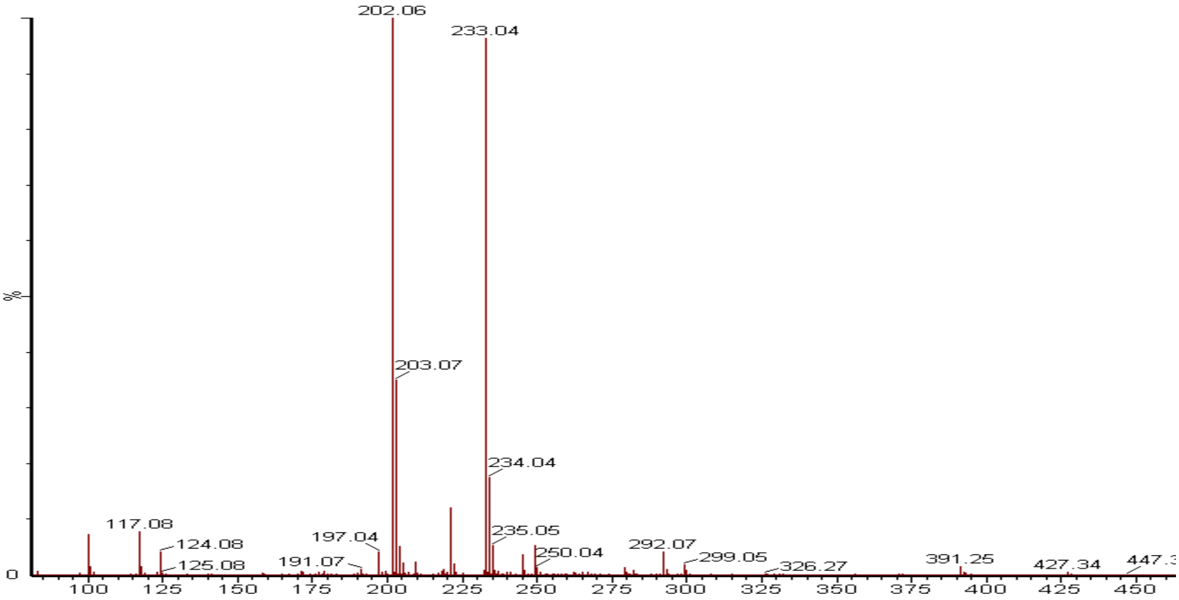


Figure 5–3: MS analysis (ES+) of reaction mixture from pyrene oxidation
Reaction Conditions: Substrate 18.8 mmol, H_2WO_4 0.153g (0.614mmol), H_2O_2 35% 12ml, Aliquat 336 0.24ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, T=40°C, t=20h

5.2.1.4. 2-Ethylnaphthalene

Since it has been observed that the H_2WO_4/H_2O_2 system is very selective towards products with one opened ring, it was necessary to perform the same reaction with alkylated aromatics to examine the selectivity between aromatic and aliphatic carbons. 2-Ethylnaphthalene was used in this reaction as a model substrate. After GC-MS and ^{1}H NMR analysis it was apparent that the major product of the oxidation is acetonaphthone (11B). 5-ethyl phthalic acid (11A) and compound with elemental composition $C_{12}H_{10}O_3$ were also detected but in lower concentration (Figure 5-4).

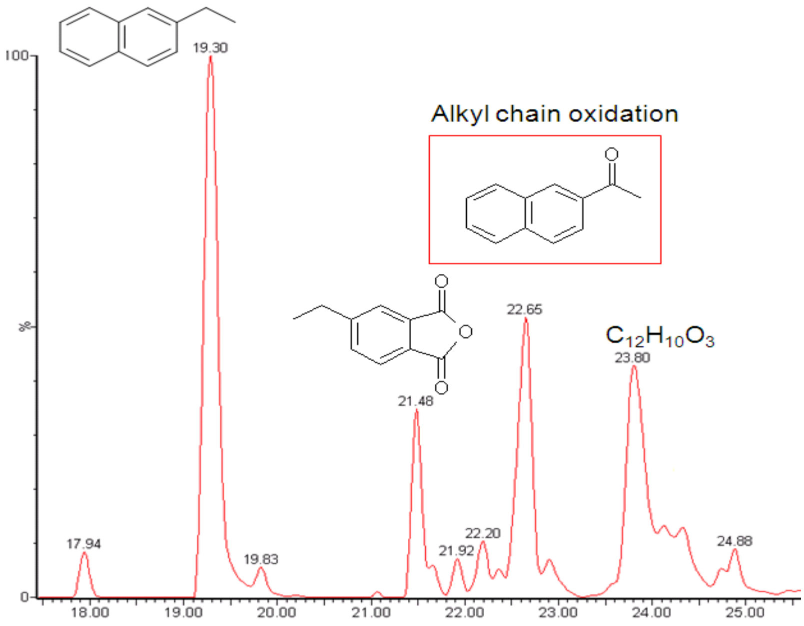
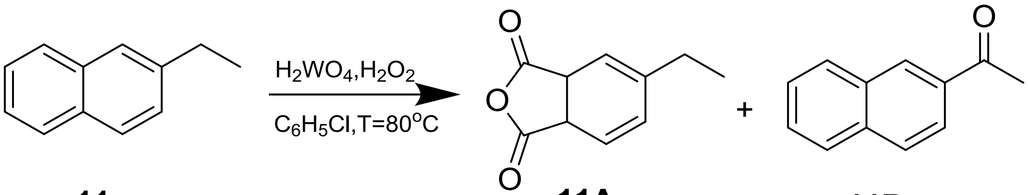


Figure 5–4: 2-Ethylnaphthalene oxidation performed in chlorobenzene: GC-MS analysis



11 **11A** **11B**

Scheme 5-4: Identified products of 2-ethylnaphthalene oxidation
Reaction conditions: Substrate 18.8mmol, H_2WO_4 0.153g (0.614mmol), H_2O_2 35% 12ml, Aliquat 336 0.24ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, T=80°C, t=6h

This data shows that when the oxidation was performed in chlorobenzene, it was selective in the oxidation of aliphatic hydrogen and carbon. However, the outcome of this experiment did not meet the requirements set out in the project outline. As previously described in chapter 3 and 4, a change in solvent in the RICO chemistry improved oxidation selectivity. Based on this observation, it was decided to test different solvents in the system and examine how they influence reactions in the presence of H_2WO_4 and H_2O_2.

2-Ethylnaphthalene is a molecule, which can be used as a model compound for investigation of the oxidation selectivity, due to one simple reason. Regarding 2-ethylnaphthalene, the carbon which is the most susceptible for oxidation in aliphatic chain is the α carbon, thus the product of oxidation would be 2-acetonaphtone. Analysis of oxidation product, with special attention paid to the presence of 2-acetonaphthone can answer the question about selectivity.

5.2.2. 2-Chlorobutane as a reaction solvent

Chlorobenzene provided good conversion in the reaction; however selectivity was directed towards aliphatic carbons. Because chlorinated aliphatic hydrocarbons provide high solubility for PAHs, it was decided to use 2-chlorobutane as a solvent in the oxidation of 2-ethylnaphthalene. When 2-chlorobutane was used as a reaction solvent, 2-acetonaphthone was one of the major products of 2-ethylnaphthalene oxidation as shown in figure 5-5. What is more, the reactivity was lower compared to when the reaction was carried out in chlorobenzene.

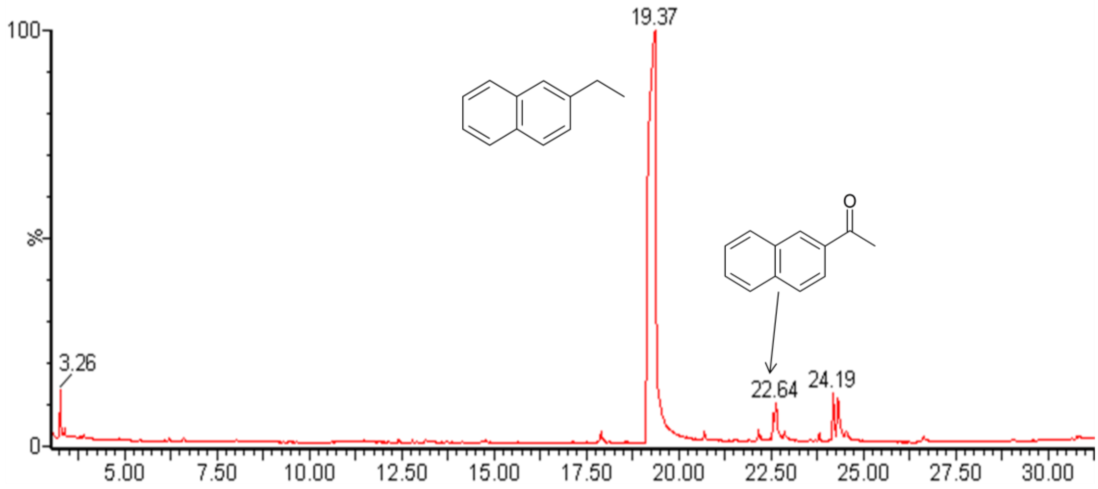


Figure 5–5: GC-MS analysis: 2-ethylnaphthalene oxidation
Reaction conditions: Substrate 18.8mmol, H_2WO_4 *0.153g (0.614mmol),* H_2O_2 *35% 12ml, Aliquat 336 0.24ml,* H_3PO_4 *10% 0.14ml,* C_4H_9Cl *8ml, T=65°C, t=6h*

5.2.3. Toluene

Toluene was chosen as a next reaction solvent, because of its relatively high boiling point, similarity to petroleum and its ability to dissolve the model aromatic compounds as well as heavy oils, resids and bitumens. Unfortunately the reaction selectivity observed with toluene, was as expected. At least one product of 2-ethylnaphthlene oxidation contained an oxidized alkyl chain. This product, 2-acetonaphthone (12A) was detected using GC-MS analysis. The GC chromatograph showed a sharp peak at retention time 22.63 mins (Figure 5-6) and generated a molecular ion at m/z 170.07.

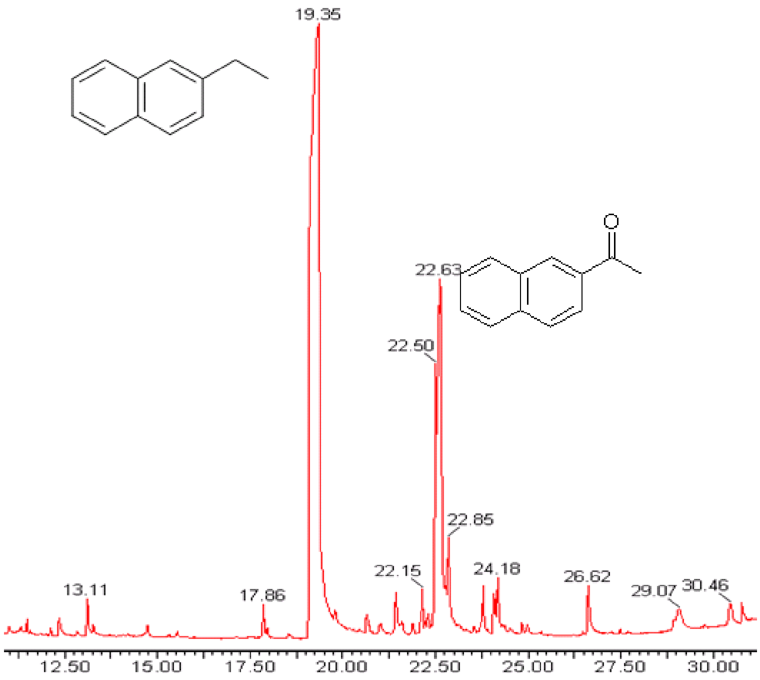
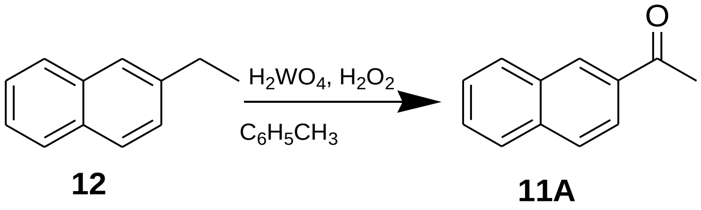


Figure 5–6: 2-Ethylnaphthalene oxidation: GC-MS analysis

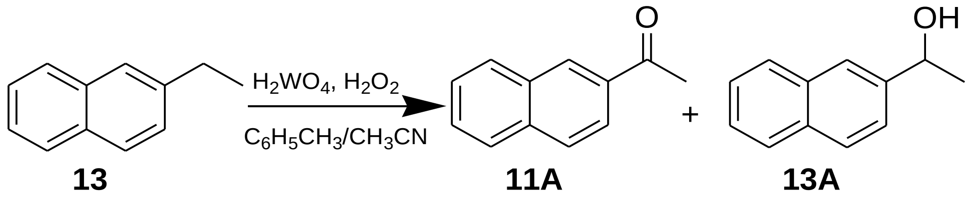
The mass spectrum was compared with one generated from commercially available standard of 2-acetonaphthone and where seen to be identical, proving the presence of product with an oxidized alkyl chain.



Scheme 5-5: Product of 2-ethylnaphthalene oxidation
Reaction conditions: Substrate 18.8mmol, H_2WO_4 0.153g (0.614mmol), H_2O_2 35% 12ml, Aliquat 336 0.24ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, T=80°C, t=6h

5.2.4. Toluene solvents mixture

Since toluene did not fulfil the requirement of reaction selectivity, it was decided to use a mixture of toluene and acetonitrile. Toluene provided the high solubility, while the use of acetonitrile in the RICO reaction turned out to be a solvent which increased the efficiency of the reaction. This solvent combination was used in the oxidation of 2-ethylnaphthalene in a ratio of 1:1, the total volume was 8ml. However, product analysis of the 2-ethylnaphthalene oxidation reaction, analyzed by GC-MS, showed products with preserved, as well as oxidized aliphatic chain, mainly 2-acetonaphthone (1-(naphthalene-2-yl)ethanon))(13A) and also 1-(naphthalene-2-yl)ethanol (13B).



Scheme 5-6: Products of 2-ethylnaphthalene oxidation with oxidized aliphatic chain
Reaction conditions: Substrate 18.8mmol, H_2WO_4 0.153g (0.614mmol), H_2O_2 35% 12ml, Aliquat 336 0.24ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, T=75°C, t=6h

The undesirable selectivity observed in this reaction and the relatively low reaction temperature employed (75°C) led to the conclusion that acetonitrile should be replaced by its homologue, propionitrile, which has a higher boiling point.

The reaction with toluene/propionitrile as a solvent was performed at 90°C. Based on GC-MS analysis, it was found that 2-ethylnaphthalene oxidation resulted in the production of mainly 2-acetonaphthone. When pyrene was tested under these conditions, the only product of oxidation was pyrene-4,5,-dione. MS analysis (ES+) showed intense peaks at m/z 202.07 from pyrene and m/z=233 suggesting the presence of pyrene 4,5,-dione as shown in figure 5-7.

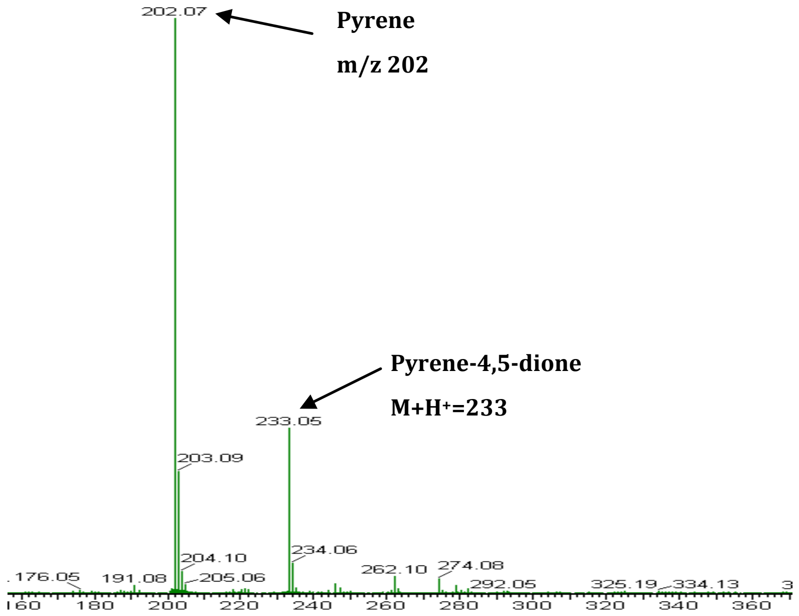


Figure 5–7: MS (ES+) analysis of reaction mixture from pyrene oxidation
Substrate 18.8mmol, H_2WO_4 0.153g (0.614mmol), H_2O_2 35% 12ml, Aliquat 336 0.24ml, H_3PO_4 10% 0.14ml, $C_6H_5CH_3$:C_2H_5CN ratio 1:1 8ml, T=90°C, t=6h

In the case of both toluene solvent mixtures selectivity of the reaction was directed towards aliphatic carbons, which eliminated this solvent system from further study. The oxidation of pyrene with this system showed that carbons in positions 4,5 were oxidized, however, the oxidation was not strong enough to cleave the C-C bond and lead to the formation of pyrene-4,5-dione.

5.2.5. Propionitrile

The use of propionitrile as a solvent was proposed for two reasons. Firstly, because of its similarity to acetonitrile, the best performing solvent in the reaction and secondly, because it has a higher boiling point than CH_3CN, which allows the reaction to be performed at a higher temperature. Here, again as before, the observation of product distribution of 2-ethylnaphthalene oxidation led to one conclusion, that reaction performed in propionitrile is selective to aliphatic carbons, because naphthalene-2yl-ethanol (14A) was detected in the product mixture, however the selectivity towards this product was relatively low as can be seen in figure 5-8.

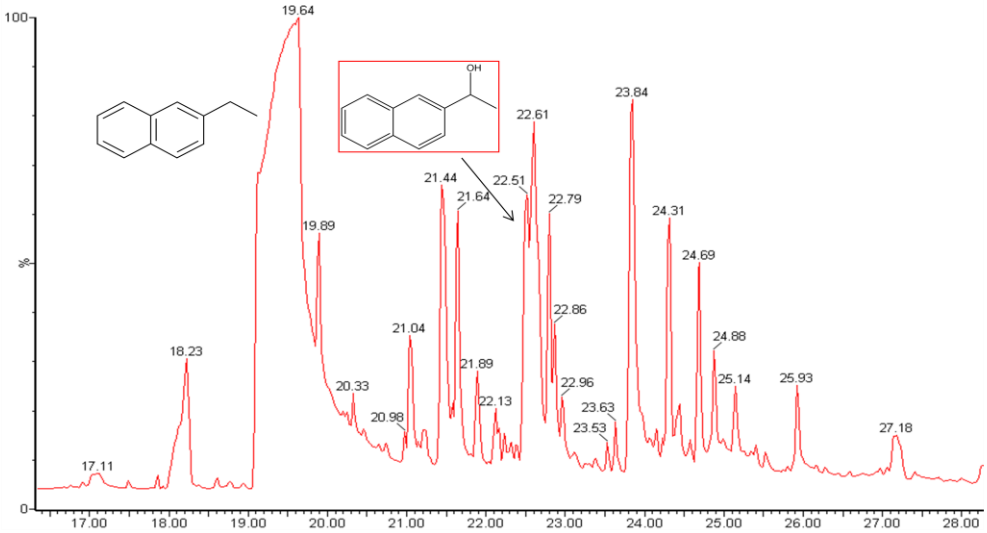
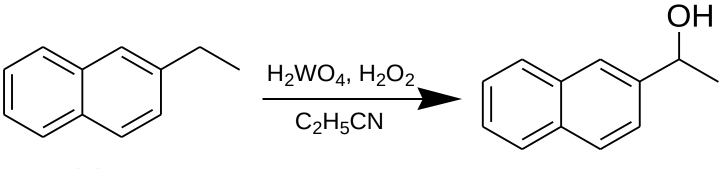


Figure 5–8: 2-Ethylnaphthalene oxidation in propionitrile: GC-MS analysis



14 **13A**

Scheme 5-7: Product of 2-ethylnaphthalene oxidation with oxidized aliphatic chain
Substrate 18.8mmol, H_2WO_4 0.153g (0.614mmol), H_2O_2 35% 12ml, Aliquat 336 0.24ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, T=75°C, t=6h

5.2.6. Acetonitrile

The exceptional properties of acetonitrile has been recognised in the RICO reaction and though used catalytic system is different from ruthenium chemistry, it was proposed to use acetonitrile as a solvent in the reaction. First, 2-ethylnaphthalene, then naphthalene, phenanthrene and pyrene were used as model compounds for oxidation reactions.

5.2.6.1. 2-Ethylnaphthalene

When the reaction was performed in acetonitrile no products with oxidized aliphatic carbon were detected. This conclusion was drawn by comparison of the ^{13}C NMR spectra of pure acetonaphthone and reaction mixture after 20h, where no characteristic peak from C=O group was detected as presented in the figure 5-9.

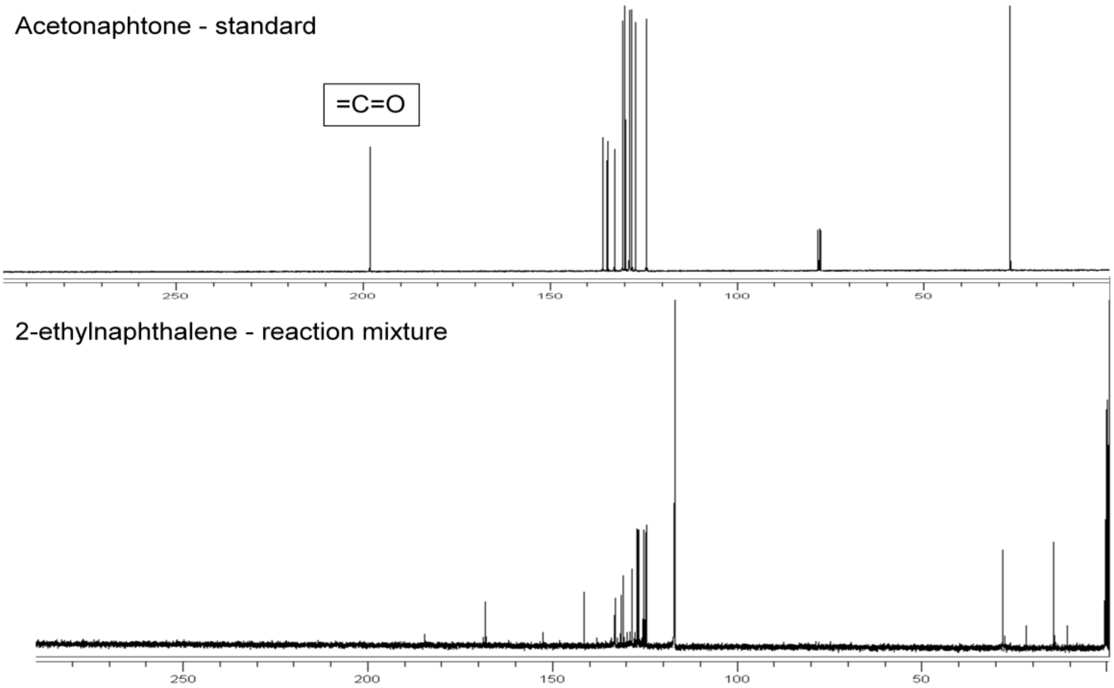
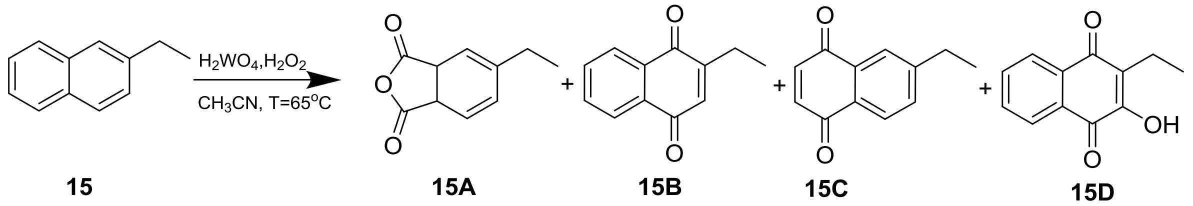


Figure 5–9: Comparison of ^{13}C NMR spectra of 2-acetonaphtone standard in $CDCl_3$(top) and reaction mixture from 2-ethylnaphthalene oxidation in DMSO-d_6 (bottom)
Reaction Conditions: Substrate 18.8 mmol, H_2WO_4 0.153g (0.614mmol), H_2O_2 35% 12ml, Aliquat 336 0.24ml, H_3PO_4 10% 0.14ml, CH_3CN 8ml, T=65°C, t=20h

Using the same methodology for peak integration in the ^1H NMR spectra, as previously described in section 4.7.3., it was possible to compare the ratio between aromatic and aliphatic Hs before and after the reaction. The aromatic to aliphatic Hs ratio changed from 1.36 to 1.06 after 20h of reaction, which suggests that no alkyl chain oxidation occurred. Products detected after the reaction contained an intact aliphatic chain and oxidized aromatic carbon as outlined in the scheme below.



Scheme 5-8: Products of 2-ethylnaphthalene oxidation
Reaction conditions: Substrate 18.8mmol, H_2WO_4 0.153g (0.614mmol), H_2O_2 35% 12ml, Aliquat 336 0.24ml, H_3PO_4 10% 0.14ml, CH_3CN 8ml, T=65°C t=20h

These experiments have shown that by changing the reaction solvent, selectivity can be switched towards aromatic carbons. However, the use of acetonitrile as a solvent raises a problem of substrate solubility and reaction temperature because of the relatively low solvent boiling point. Conversely, the selectivity toward acids still remains a question, so naphthalene, phenanthrene and pyrene were tested in the presence of acetonitrile used as a reaction solvent and the product distribution was investigated.

5.2.6.2. Naphthalene

Naphthalene, even after 20 hours did not undergo reaction and no oxidation products were detected. GC-MS and ^{1}H NMR analysis show only signals corresponding to naphthalene (starting material).

5.2.6.3. Phenanthrene

In the case of phenanthrene oxidation similar products to that seen when the reaction was performed in chlorobenzene were observed: phenanthrene-9,10-dione, biphenyl-2,2'-dialdehyde and biphenyl anhydride. However, the conversion for reaction performed in acetonitrile was lower than when chlorobenzene was used as a reaction solvent and was only 9% even after 20h reaction.

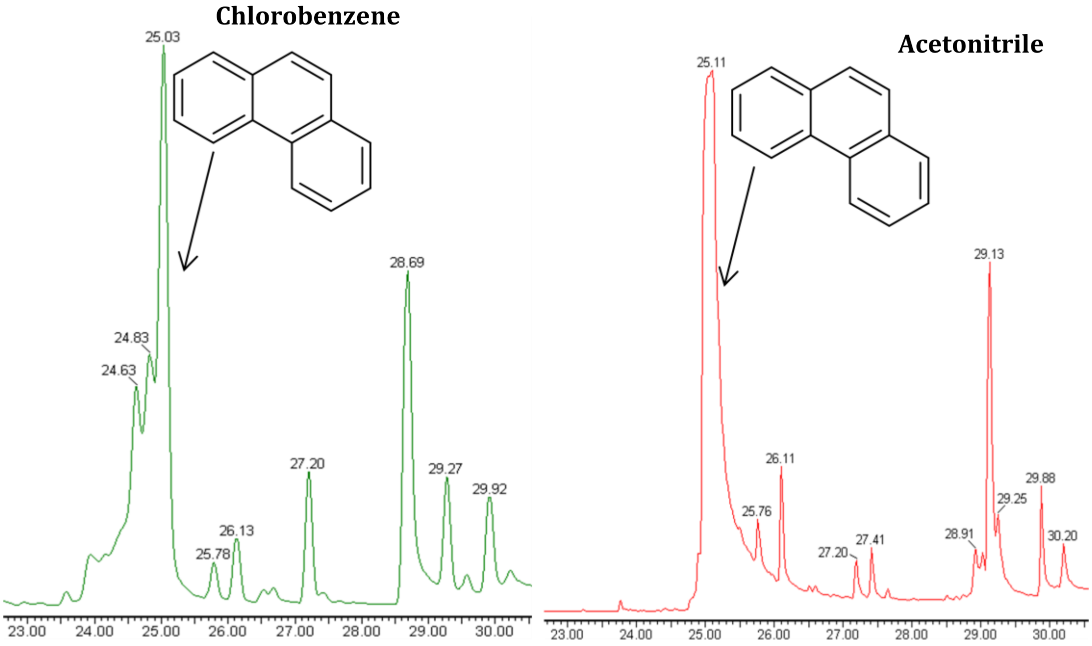


Figure 5–10: Phenanthrene oxidation performed in chlorobenzene and in acetonitrile; Comparison of GC chromatograms

5.2.6.4. Pyrene

Here, as when the reaction was performed in chlorobenzene, phenanthrene-4,5-dicarboxylic acid was detected as proven by HPLC-MS analysis. The ^{1}H NMR spectrum shows a peak at 9.78ppm, which suggests the presence of an aldehyde or acid group.

Conversion in this reaction was 18%. What is more, pyrene-4,5-dione was detected and the ratio between dione and acid, based on ^{1}H NMR analysis was found to be 1:1 based on comparison of signals intensity at 8.405ppm and 8.415ppm.

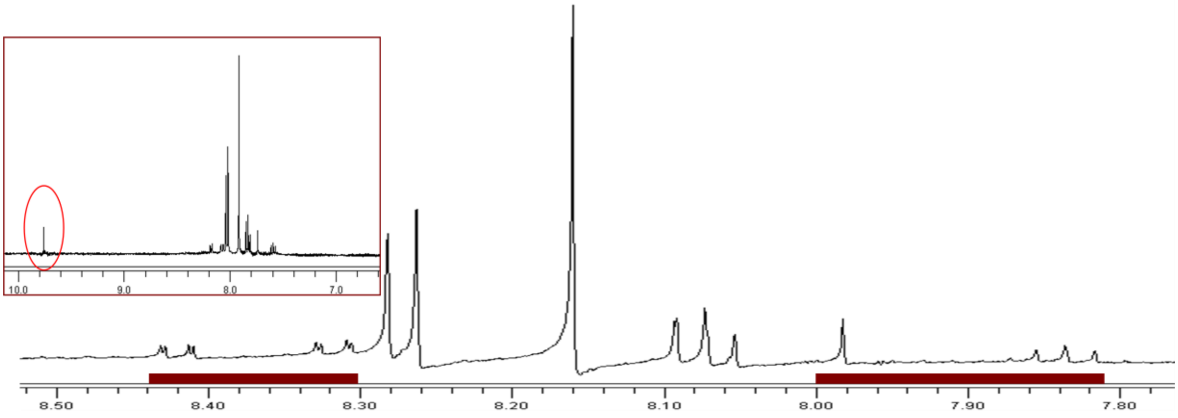


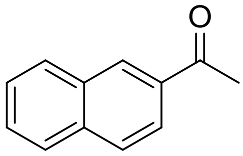
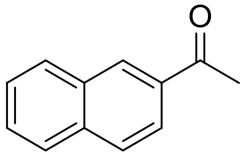
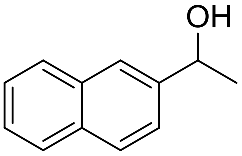
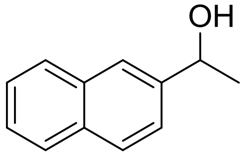
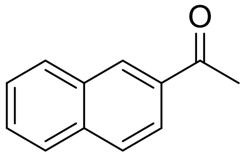
Figure 5–11: ^{1}H NMR analysis: Pyrene oxidation in acetonitrile with underlined signals from products /Above: full spectra with marked signal from an acid group

This finding suggests that pyrene-4,5-dione is probably an intermediate of aldehyde, which undergoes further oxidation to the diacid.

5.2.7. Comments on oxidation performed in different solvents

2-Ethylnaphthalene oxidation performed in chlorobenzene, 2-chlorobutane, toluene, propionitrile and toluene solvents mixture leads to the formation of products containing oxidized alkyl chain. Selectivity towards them was never recorded as 100%, however, it depends on the solvent used. Only reaction carried out in acetonitrile resulted in preservation of aliphatic chain, thus it can be said that selectivity in this reaction was directed towards aromatic carbons. Looking at the data presented below (Table 5-1), it is clear that the nature of solvent and temperature may also play a role in oxidation selectivity. 2-Acetonaphtone was obtained in the reactions where non polar solvents were used, while naphthalene-2yl-ethanol was a product of oxidation when propionitrile was present during reaction. This observation lead to the conclusion that polarity of the solvent used during the oxidation is closely related to the oxidation selectivity.

Table 5-1: 2-ethylnaphthalene oxidation in different solvents: Comparison of products with oxidized alkyl chain

Solvent	Temperature	Products with oxidized alkyl chain
Chlorobenzene	80°C	
2-Chlorobutane	65°C	
Toluene	80°C	
Toluene **Propionitrile**	90°C	 
Propionitrile	75°C	
Toluene **Acetonitrile**	75°C	
Acetonitrile	65°C	No products with oxidized alkyl chain

While analyzing the data from naphthalene, phenanthrene and pyrene oxidation, it can be seen that the reaction rate increases with the number of fused aromatic rings in the reactant molecules. When comparing the different solvent systems employed, it is clear that the rate of reaction in acetonitrile is slower than in chlorobenzene as shown in table 5-2.

Table 5-2: Oxidation of naphthalene, phenanthrene and pyrene: Comparison of obtained products and conversion

Substrate	**Chlorobenzene T=80°C**		**Acetonitrile T=65°C**	
	Products	**Conversion**	**Products**	**Conversion**
Naphthalene	• naphthalene-1,4-dione (7A) • phthalic anhydride	10%	-	0%
Phenanthrene	• phenanthrene 9,10-dione • biphenyl-2,2' dicarbaldehyde • biphenyl epoxide	32%	• phenanthrene 9,10-dione • biphenyl-2,2' dicarbaldehyde • biphenyl epoxide	9%
Pyrene	• phenanthrene 4,5-diacid	79%	• phenanthrene 4,5-diacid • pyrene-4,5-dione	18%

This can be attributed to the boiling point of acetonitrile, where the reaction temperature needs to be changed from 80°C to 65°C when using acetonitrile as a solvent. On the other hand, solubility also plays a role and therefore reactant concentration was decreased to keep the solvent volume constant (8ml), yet the ratio *substrate: oxidant: catalyst* was maintained at the same level as when the reaction was carried out in C_6H_5Cl.

Acetonitrile is an excellent solvent for the oxidation of PAHs using H_2WO_4 and H_2O_2. It directs the selectivity of oxidation to the aromatic carbons and leads to products with open rings. Unfortunately, it cannot be used commercially because of its inability to dissolve high molecular weight PAHs.

5.3. Mass Balance

As discussed in earlier chapters, mass balance determination was important due to the issue of CO_2 and waste generation. First step to minimize or even exclude waste production was to use toluene as a solvent. Although when the reaction is performed in toluene, it is not selective towards aromatic carbons. Toluene can be easily obtained during gasoline production, therefore the petroleum industry has easy access to this solvent [5]. Pyrene was chosen as a model compound for the mass balance investigation. The experiment was scaled up and the change in mass was determined gravimetrically by taking the weight of the solid reactants before and after the oxidation. After reaction, the aqueous layer was separated from the organic layer and the solvents evaporated. The mass of products generated were compared with the initial mass of the solid reactants, the total yield was found to be 113%. This value suggests that the solvent was also oxidized. This was confirmed by GC-MS analysis, where benzaldehyde and benzoic acid were found, known toluene oxidation products. Above all, it is clear that waste generation in this reaction is relatively low.

5.4. Kinetic studies

As with previous catalytic systems, kinetic studies were performed to investigate the rate of reaction for molecules with a different number of aromatic rings.

5.4.1. Competitive reactions between non alkylated PAHs

When naphthalene, phenanthrene and pyrene were used in the same reaction, it was observed that reaction rate increased with molecule size as illustrated in figure 5-12. Naphthalene did undergo oxidation, yet the conversion was only 6%, which clearly shows that this catalytic system is more selective in the oxidation of higher molecular weight PAHs. Reaction rate calculated for the first 5 h of the reaction was found 0.449 for pyrene, 0.113 and 0.016 for phenanthrene and naphthalene, respectively.

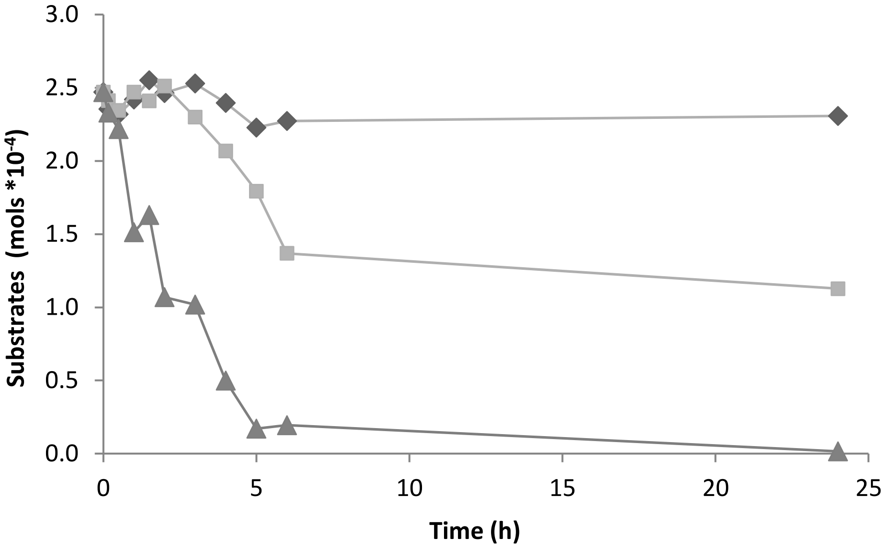


Figure 5–12: Competitive reaction between naphthalene ◆, phenanthrene ■ and pyrene ▲ Reaction conditions: substrate 0.247mmol, H_2WO_4 0.025mmol, H_2O_2 35% 2.5ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, Aliquat 336 0.24ml, T=80°C

5.2.1. Competitive reaction alkylated Vs non-alkylated PAHs

Competitive reaction studies between aromatics and their alkylated derivatives were carried out to determine if the aliphatic side chain plays a role in the kinetics of the reaction. Firstly, naphthalene and 1-decylnaphthalene were studied. As is graphically illustrated below (Figure 5-13), there was no difference in reaction rate between either of the compounds studied, conversion was low in both cases, 9% for naphthalene and 20% for 1-decylnaphthalene.

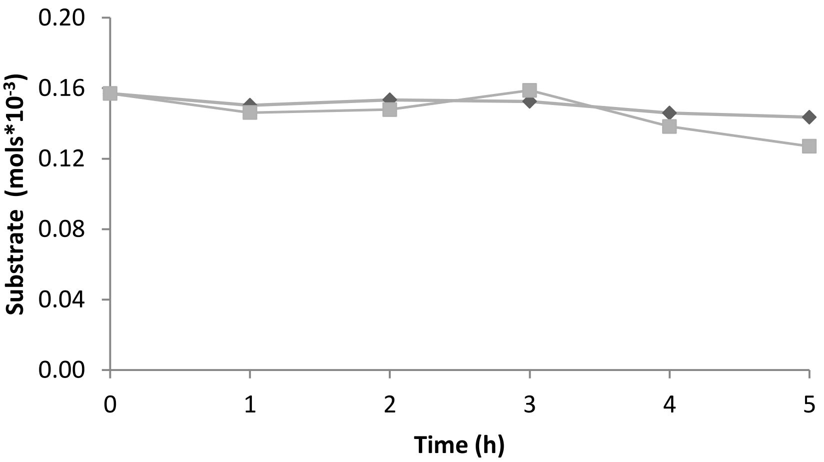


Figure 5–13: Competitive reaction between naphthalene ◆ and 1-decylnaphthalene ■ Reaction conditions: substrate 0.157mmol, H_2WO_4 0.01mmols, H_2O_2 35% 2ml, H_3PO_4 10% 0.03ml, C_6H_5Cl 8ml, Aliquat 336 0.06ml, T=80°C

A similar observation was made when phenanthrene and 2-nonylphenanthrene were used as substrates in the reaction (Figure 5-14). Although the conversion was higher for alkylated molecule (25% against 10%), the difference in reactivity between them was not significant. When comparing reaction rates, 0.001mmols/h for phenanthrene and 0.002mmols/h for 2-nonylphenanthrene, it is seen that the rate for the alkylated aromatic is slightly higher.

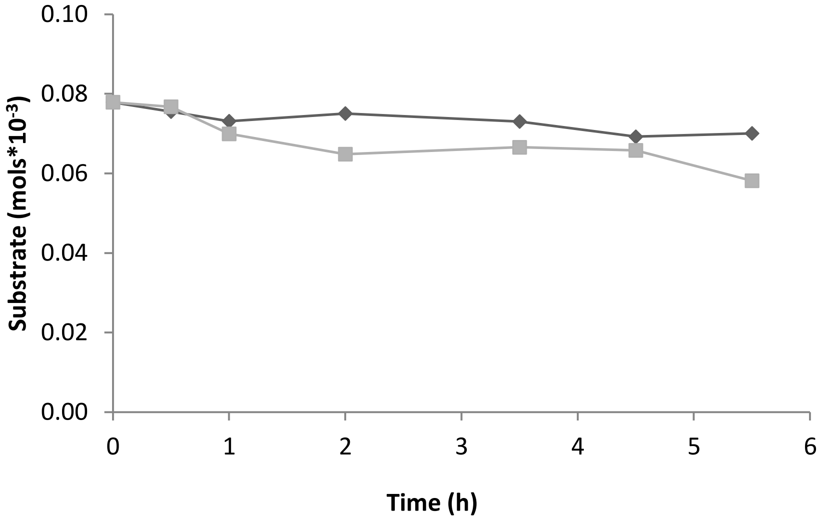


Figure 5–14: Competitive reaction between phenanthrene ◆ and 2-nonylphenanthrene ■ Reaction conditions: substrate 0.0779 mmol, H_2WO_4 0.01mmols, H_2O_2 50% 1.4 ml, H_3PO_4 10% 0.014ml, C_6H_5Cl 8ml, Aliquat 336 0.06ml, T=80°C

The last competitive oxidation reaction was performed on pyrene and 1-octadecylpyrene. Here, as shown in figure 5-15, 1-octadecylpyrene reacts slightly faster than pyrene, yet the difference in reaction rate is minor: 0.003mmols/h for pyrene and 0.004mmols/h for 1-octadecylpyrene.

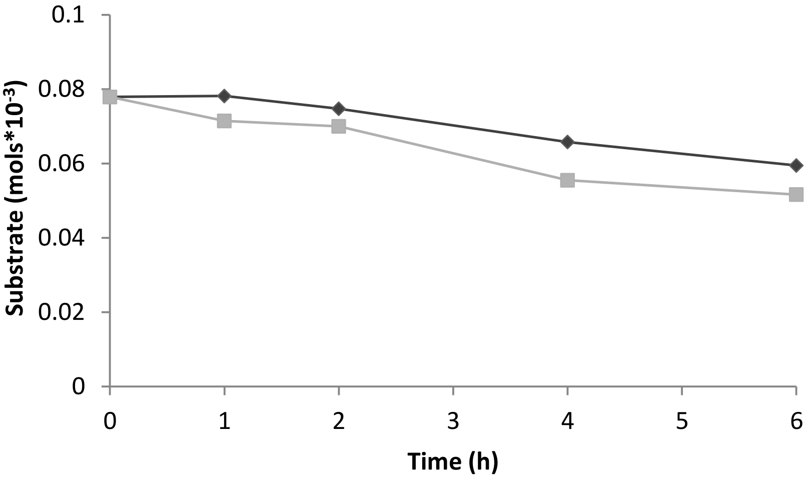


Figure 5–15: Competitive reaction between pyrene ◆ and 1-octadecylpyrene ■
Reaction conditions: substrate 0.0779 mmol, H_2WO_4 0.01mmols, H_2O_2 50% 1.4 ml, H_3PO_4 10% 0.014ml, C_6H_5Cl 8ml, Aliquat 336 0.06ml, T=80°C

These experiments show that the presence of aliphatic carbons influence the oxidation process, but the effect is relatively minor. The major factor determining the oxidation rate is the size of aromatic molecule. Therefore it can be stated, that the reaction mechanism is not based on electrophilic attack as was the case in the RICO reaction. Here, the mechanism is totally different from that presented in chapter 3 and 4 due to the presence of H_2O_2 and formation of peroxo species.

5.4.2. Kinetic studies of alkylated PAHs

Previously in chapter 4 it was stated that bigger molecules with longer alkyl chain react faster than smaller molecules, therefore two factors, number of fused aromatic rings and length of alkyl chain determine the reaction rate. Considering earlier results obtained using the H_2WO_4/ H_2O_2 system it is clear that aliphatic chain does contribute in a lower range, than the molecule size (number of fused aromatic rings) to the kinetics of the reaction. To prove this, an competitive oxidation experiment involving 3 alkylated aromatics, 1-decylnaphthalene, 2-nonylphenanthrene and 1-octadecylpyrene was performed. As seen in figure 5-16, the difference in reaction rate between 1-decylnaphthalene and 2-nonylphenanthrene is minor. The difference in alkyl chain length is only one methylene group, so this fact should not be taken into account. On the whole, it is clear that phenanthrene derivative reacts faster than naphthalene ones. Moreover, 1-octadecylpyrene was oxidized with a higher conversion than the rest of substrates, which confirms the above statement that molecule size determines the rate of oxidation.

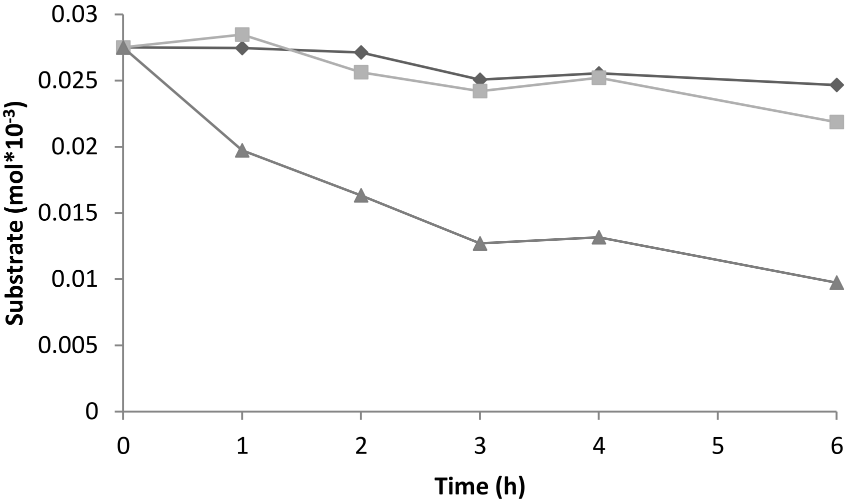


Figure 5–16: Competitive reaction between 1-decylnaphthalene ◆, 2-nonylphenanthrene ■ and 1-octadecylpyrene ▲
Reaction conditions: substrate 0.0275 mmol, H_2WO_4 0.01mmols, H_2O_2 50% 1.4 ml, H_3PO_4 10% 0.03ml, C_6H_5Cl 8ml, Aliquat 336 0.06ml, T=80°C

It is worth mentioning that an experiment with 1-decylpyrene would be an ideal proof for conclusions made earlier, but it was impossible to perform it due to the shortage of this substrate.

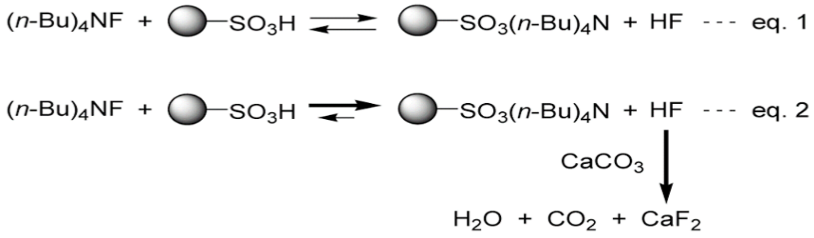
5.5. Oxidation of PAHs with long alkyl chain

Earlier investigations showed that the tungsten chemistry employed in this chapter is selective for aromatic carbons, yet only when the reaction is carried out in acetonitrile. Unfortunately acetonitrile cannot be used as a solvent for further investigation due to the limited solubility of higher molecular weight PAHs. On the other hand, chlorobenzene or toluene did not deliver the expected selectivity. Yet this observation was only made for 2-ethylnaphthalene, a molecule with a relatively short aliphatic chain. The question was raised, if this observation will be the same for molecules with longer alkyl side chains. Therefore the oxidation of 1-octadecylpyrene, 2-nonylphenanthrene and 9-octadecylphenanthrene was investigated and the % of preserved alkyl chain determined.

5.5.1. Aliquat 336 removal

A methodology used to calculate the % of preserved alkyl chain was presented in section 4.7.3. However, this methodology had to be modified before being applied to the tungsten acid system, because of the inability to source the deuterated reactant (D_2O_2). What is more, aliquat 336, a phase transfer reagent, the role of which is to transfer the active component between phases, gives a number of sharp peaks in aliphatic region of the ^{1}H NMR spectrum which masks the product signals. Several attemps were made to remove the aliquat 336 from the reaction mixture and thus simplify the ^{1}H NMR spectrum. Firstly, it was found that the reaction does not occur without aliquat 336 and its presence is crucial, so the phase transfer reagent could only be removed post reaction.

It was decided to attempt to remove the aliquat after the reaction using a sulfonic acid ion exchange resin based on similar literature report [6]. The mechanism of phase transfer catalyst removal using the ion exchange resin is shown below (Scheme 5-9).



Scheme 5-9: Equations presenting reaction between TBAF and sulfonic acid resin in the absence (eq. 1) or presence (eq. 2) of $CaCO_3$ [6]

A test experiment was performed using an aliquat solution in toluene (C=0.062M), which was treated with 0.5g of Dowex 50 WX8 for 20mins under constant stirring. Subsequently the required amount of $CaCO_3$ (37mg) was added and stirred for 2h. The whole mixture was filtered and the filtrate analyzed by GC. Analysis found that the aliquat was not removed from the solution.

The next experiment was performed using TBAB (tetra-n-butylammonium bromide) as a phase transfer reagent, a direct replacement for aliquat 336. TBAB is a water soluble compound and therefore would not mask peaks from products in the organic layer.

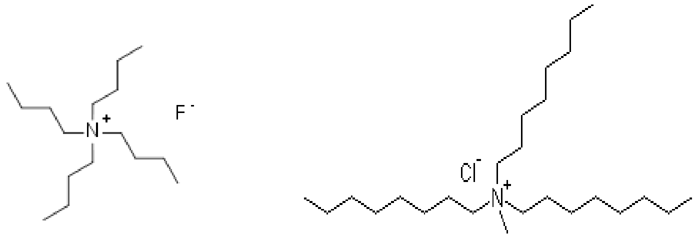


Figure 5–17: Structure of TBAF (tetra-n-butylammonium fluoride)(left) and Aliquat 336 (right)

After reaction with TBAB and pyrene, conversion was only 3%, after 20h of reaction. This result suggests that contact between oxidant and catalyst was limited and TBAB did not have the same beneficial effect as aliquat when it was used during the oxidation reaction. It was decided to use aliquat 336 at a lower concentration than previously reported and to increase the concentration of PAHs. These reaction conditions and reaction work up described in 2.6.2.2. resulted in aliquat removal which was proved by GC analysis. Only then, ^{1}H NMR analysis and proton quantification was possible.

5.5.2. ^{1}H NMR study of the oxidation of aromatic protons Vs aliphatic protons

To determine the selectivity of the oxidation reaction, the same methodology previously described in 4.7.3. and 4.7.4. was applied. It is worth repeating that the protons of interest which are used to calculate the % of preserved alkyl chain are protons A in the side chain that are α to the aromatic ring and protons D which are terminal protons. First, experiment with 1-octadecylpyrene was performed. Products obtained from the reaction and purified as described in 2.6.2.2. from organic phase, were dissolved in $CDCl_3$ and transferred to the NMR tube fitted with a glass insert containing 1%TMS in $CDCl_3$. Residues from aqueous layer were dissolved in D_2O and analyzed using ^{1}H NMR. However, no products were detected in the aqueous layer. ^{1}H NMR spectrum showing signals from products from organic layer is presented below (Figure 5-18).

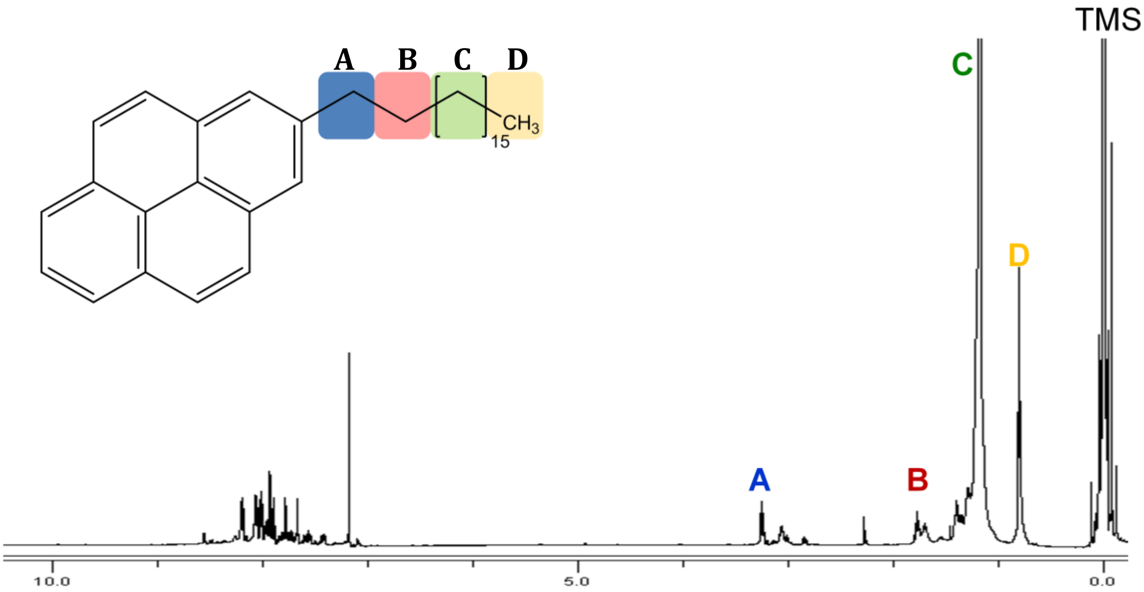


Figure 5–18: ^1H NMR of 1-octadecylpyrene oxidation products in $CDCl_3$

The objective of this experiment was to understand the effect of aromatic ring size, aliphatic chain length and the position of the alkyl chain on selectivity. Therefore, 3 different compounds were chosen for this study: 1-octadecylpyrene, 2-nonylphenanthrene and 9-octadecylphenanthrene. For the experiment with 9-octadecylphenanthrene, the reaction conditions applied for the other 2 compounds, were not efficient to obtain satisfactory conversion. Using these reaction conditions reported in 2.6.2.2. only 4.6% conversion was obtained, therefore it was necessary to use more oxidant in addition to more catalyst. The results obtained for 9-octadecylphenanthrene also showed that the position of the aliphatic chain attachment is a crucial factor in determining substrate reactivity**.** The reaction conditions were adjusted to obtain at least 40% conversion as described in 2.6.2.2. Conversion data and the %preserved alkyl chain for all substrates tested is outlined in table 5-3.

It is clear that the length of alkyl chain determines the % of preserved alkyl chain, thus the longer the aliphatic chain, the more aliphatic Hs are preserved. It is also apparent that location of the alkyl chain plays a crucial role in reaction selectivity. When comparing the data of 9-octadecylphenanthrene and 2-nonylphenanthrene, it is clear that the carbon at position 9 is more susceptible to oxidation than the carbon at position 2. This was also observed in theoretical energy calculations, which shown that position 9 or 10 in phenanthrene are the most energetically favourable positions for oxidation. It is clear, from the data presented in table 5-3, that conversion is dependent upon the number of fused aromatic rings present in the substrate and that alkyl chain length influence only partially the conversion of the reaction.

Table 5-3: Effect of chain length and ring number on the molecule reactivity and oxidation selectivity

No.	Substrate	Conversion (%)	Preserved aliphatic Hs (%)
1.	2-Nonylphenanthrene	48	78
2.	9-Octadecylphenanthrene	46	40
3.	1-Octadecylpyrene	95	93

5.5.3. Products identification: 1-octadecylpyrene oxidation

It was calculated that 93% of 1-octadecylpyrene oxidation products have preserved alkyl chain, it was deemed important to identify these products using qualitative analysis such as: MS, IR and NMR techniques. Mass analysis (ES-) of the organic layer shows a strong signal at *m/z* 581.3142 which corresponds to the mass of 4-octadecylbiphenyl-2,2',6,6'-tetracarboxylic acid (MW=582.32 $gmol^{-1}$). The right resolution theoretical mass value of this product is 581.3112, which would indicate an error in analysis lower than 0.001%. IR analysis of this product mixture showed broad peak at 1698.5 cm^{-1} and 1735.6 cm^{-1}, which is characteristic for a C=O stretching bond associated with saturated non aromatic aldehyde and aromatic carboxylic acids aromatic, respectively. What is more, a broad peak in –OH region was also observed, which suggests the presence of an alcohol and based on previous observations, most probably the –OH group of an acid. This data proves the presence of products with preserved alkyl chain and the presence of oxidized pyrene carbons at positions 4,5,9,10 associated with acids as it can be seen in figure 5-19.

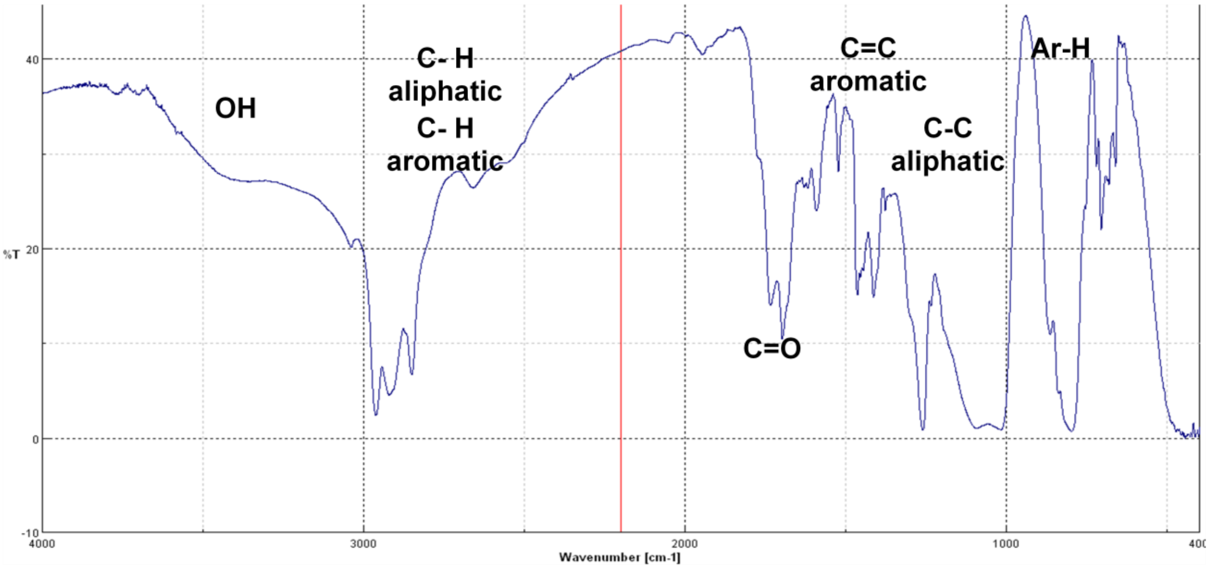


Figure 5–19: IR analysis of 1-octadecylpyrene oxidation products (organic layer)

The most reliable technique, to help identify products of oxidation is NMR. Firstly, considering the obtained ^{1}H NMR spectra (figure 5-18), several conclusions can be made. Regarding protons A, oxidation and conversion of these protons to ketone is a known reaction and would reduce the intensity of the 3.20 ppm absorption (A protons). A new absorption may appear at 3.00 or 2.90 ppm which are now α to a ketone and ß to the aromatic ring. This is a typical chemical shit for these types of protons. What is more, the chemical shift of protons A can also be caused by oxidation of aromatic carbons, which are located in the neighbourhood of carbon from the side of alkyl chain attachment. This option is more likely to happen, because no products with oxidized aliphatic carbons were detected during MS analysis. ^{13}C NMR technique can help to identify aromatic as well as aliphatic C=O species. The only problem can be a sample concentration, therefore the experiment needed to be scaled up. Although the necessary steps were taken, ^{13}C NMR spectrum was obtained with too low sensitivity to identify signals. Therefore it was decided to use an NMR technique which helps to correlate chemical shifts of two types of nuclei separated from each other with two or more chemical bonds, which is called Heteronuclear Multiple Bond Correlation (HMBC). Using this technique is was possible to observe aromatic protons which were correlated to C from C=O region, even when those carbons do not give visible signals during standard ^{13}C NMR analysis. The HMBC spectra obtained is presented below (figure 5-20), with marked region where mentioned correlation took place. Also correlating elements are marked by *star* (*).

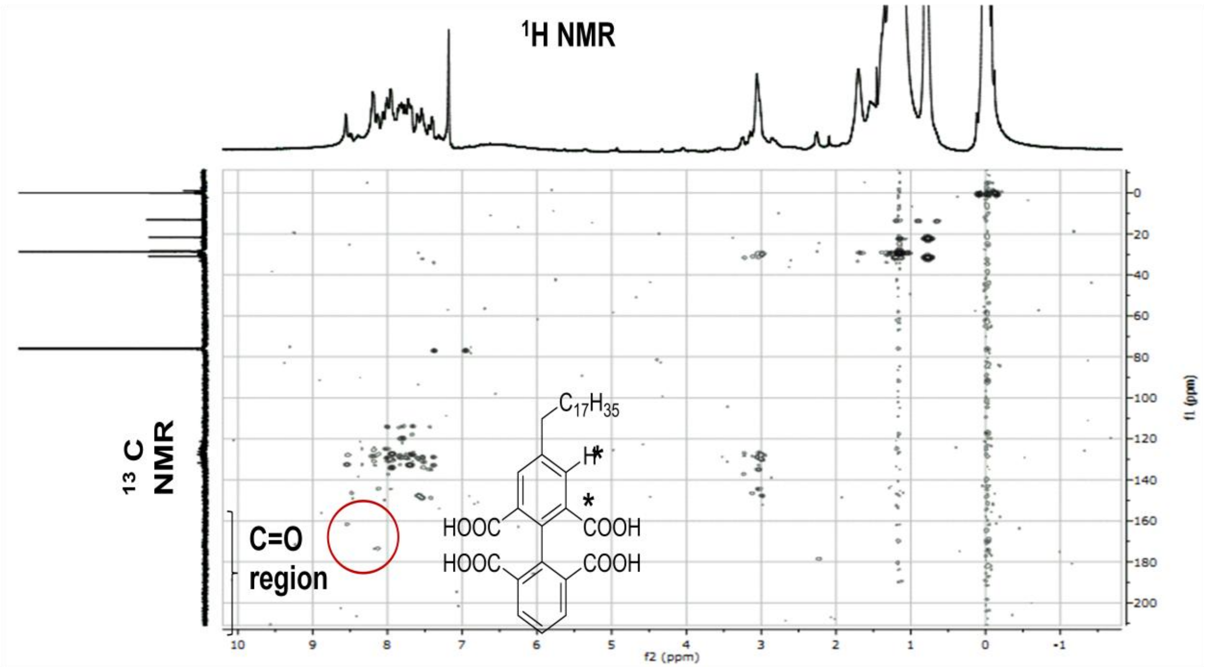
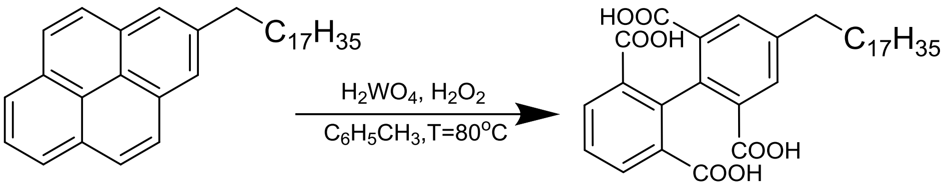


Figure 5–20: HMBC spectrum of 1-octadecylpyrene oxidation products (organic layer)
Reaction conditions: Substrate 0.2mmol, H_2O_2 30% 4ml, H_2WO_4 0.038 g (0.154mmol), H_3PO_4 10% 0.02ml, Aliquat 336(0.0036g)(solution in toluene), Toluene 2ml, T=80°C, t=16h

As previously stated and proven by HMBC NMR analysis, the major product of 1-octadecylpyrene oxidation is a product with a preserved aliphatic chain containing four carboxylic acid groups: 4-biphenyl-2,2',4,4'-tetracarboxylic acid (16A) (Scheme 5-10). This observation confirms that the H_2WO_4/H_2O_2 system delivers the desired reaction selectivity. The length of alkyl chain also influences the selectivity towards aromatic carbons.

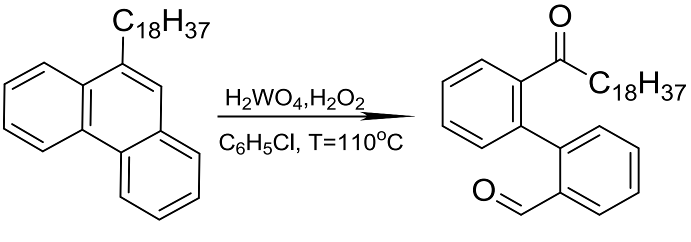


16 **16A**

Scheme 5-10: 1-octadecylpyrene and its major oxidation product
Reaction Conditions: Substrate 0.1mmol, H_2O_2 30% 2ml, H_2WO_4 0.019g (0.077mmol), H_3PO_4 10% 0.01ml, Aliquat 336(0.0012g)(solution in toluene),$C_6H_5CH_3$ 1ml, T=80°C, t=16h

5.5.4. Product identification of 9-octadecylphenanthrene oxidation

The major product identified in 1-octadecylpyrene oxidation has a preserved alkyl chain. This is not a big surprise, because the most susceptible for oxidation position in the molecule was not blocked by any substitute. A completely different situation occurs when the substrate is changed to a compound with an alkyl chain attached at the carbon position, which most likely undergoes oxidation. Here, the model compound, 9-octadecylphenanthrene was used. The conversion data obtained suggests that 40% of products have a preserved alkyl chain, yet when taking into account the conversion factor, this value 46%, it is clear that this value comes from unreacted substrate. That is why the product identification is so crucial. Using MS analysis (EI) possible products from the organic layer were determined. MS spectra showed an intense peak m/z 462.34 (Figure 5-21), which may correspond to 2-nonadecanoylbiphenyl-2-carbaldehyde, which structure (17A) is shown below (Scheme 5-11).



17 **17A**

Scheme 5-11: 9-Octadecylphenanthrene and its possible product of oxidation detected by MS analysis
Reaction conditions: Substrate 0.043g (0.1mmol), H_2O_2 50% 4ml, H_2WO_4 0.038g (0.154mmol), H_3PO_4 10% 0.02ml, Aliquat 336 (0.0024g) (solution in toluene), C_6H_5Cl 3ml, T=110°C, t=16h

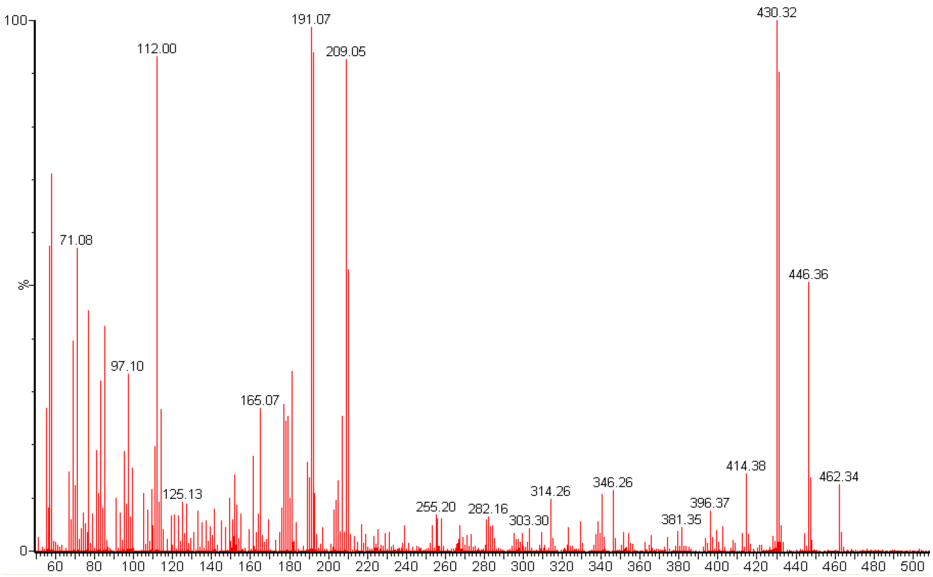


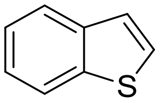
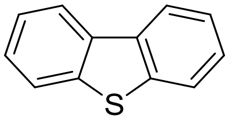
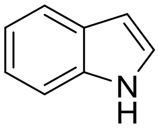
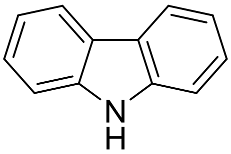
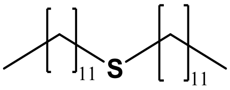
Figure 5–21: MS analysis of 9-octadecylphenanthrene oxidation

Presence of this product is really interesting as it suggests that the aromatic C=C bond was cleaved, yet the oxidation was mild enough not to break the aromatic –aliphatic C-C bond. What is more, the presence of the aldehyde group is confirmed by ^{1}H NMR spectroscopy, where a peak at 10.3ppm is observed. This data sheds new light on the tungsten chemistry and proves that selectivity in this reaction is high enough to potentially commercialise this process.

5.6. Oxidation of Heteroaromatics

Heteroaromatics are often present in crude oil. They are considered as unwanted compounds due to the presence of sulphur or nitrogen in their structure. These elements behave as a catalytic poison during the processes of petrol enrichment and they are a source of SO_x and NO_x. Therefore it is important to remove S and N from the reaction [7]. There are well known methods of desulfurization and denitrogenation which remove these elements, however the processes require multistep reactions, input of extra energy and are limited due to the presence of the alkyl substituent [8-9]. Here, the H_2WO_4/H_2O_2 system was tested for sulphur and nitrogen removal and several molecules were chosen as model compounds. The use of this system is known for desulfurization [10], however, here we performed reaction with several substrates and used chlorobenzene as a solvent. The heteroaromatics: benzothiophene, dibenzothiophene, carbazole, indole in addition to the heteroaliphatic compound, dodecyl sulfide, were used in the reaction. The structures of these compounds are shown below (Table 5-4).

Table 5-4: Structure of heteroaromatics and heteroaliphatic molecule tested in the oxidation using H_2WO_4/H_2O_2 system.

Heteroaromatic compounds	**Structure**
Benzothiophene	
Dibenzothiophene	
1*H*-Indole	
9*H*-Carbazole	
Heteroaliphatic compound	
Dodecyl sulfide	

5.6.1. Kinetic studies

Kinetic studies were carried out to determine if the presence of heterocompounds will have an influence on PAHs reactivity. A simple, competitive reaction was performed between naphthalene, phenanthrene, indole and benzothiophene. The results show that heteroaromatics react faster than naphthalene and phenanthrene (Figure 5-22). This is a good result because in the petroleum chemistry it is important to firstly eliminate compounds which are not important and then focus on the substrates which are valuable.

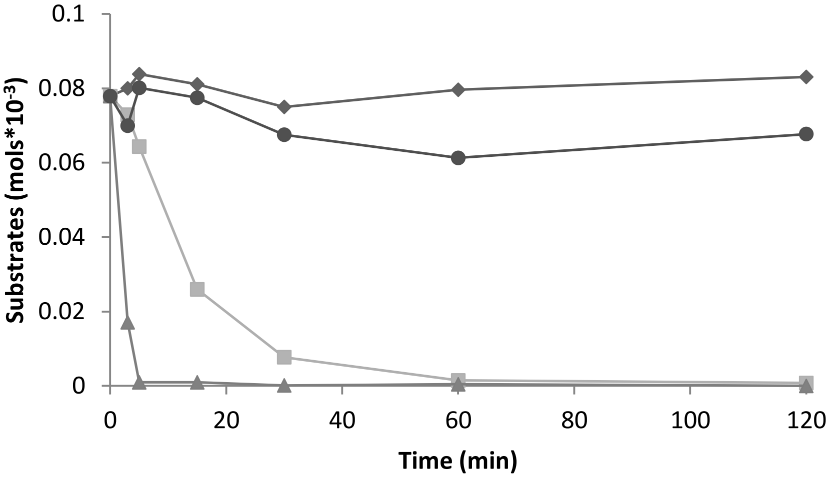


Figure 5–22: Competitive reaction between naphthalene ◆, phenanthrene ●, benzothiophene ■ and indole ▲
Reaction conditions: Substrate 0.0779 mmol, H_2WO_4 0.01mmols, H_2O_2 35% 2ml, H_3PO_4 10% 0.03ml, C_6H_5Cl 8ml, Aliquat 336 0.06ml, T=80°C

A similar experiment was performed using compounds containing 2 and 3 aromatic rings, dibenzothiophene and carbazole (Figure 5-23). Here, an analogous observation was made, that compounds containing S and N were consumed much quicker than the PAHs. Carbazole was oxidized slower than dibenzothiophene, but as in the previous experiment it was the heteroaromatic containing N that was consumed quicker than benzothiophene. This suggests that the size of molecule, in this case 1 or 2 aromatic rings determines the reaction rate for heteroaromatics containing nitrogen or sulphur.

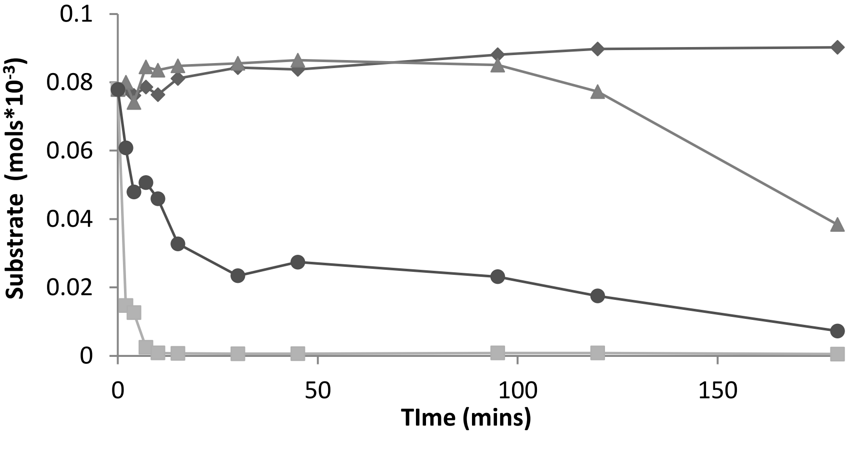


Figure 5–23: Competitive reaction between naphthalene ◆, phenanthrene ▲, dibenzothiophene ■ and carbazole ●
Reaction conditions: substrate 0.0779 mmol, H_2WO_4 0.01mmols, H_2O_2 35% 2ml, H_3PO_4 10% 0.03ml, C_6H_5Cl 8ml, Aliquat 336 0.06ml, T=80°C

The addition of pyrene which is known to react faster than phenanthrene did not change reaction kinetics and the same trend was observed, that dibenzothiophene was oxidized faster than the 4 ring aromatic molecule, pyrene. (Figure 5-24).

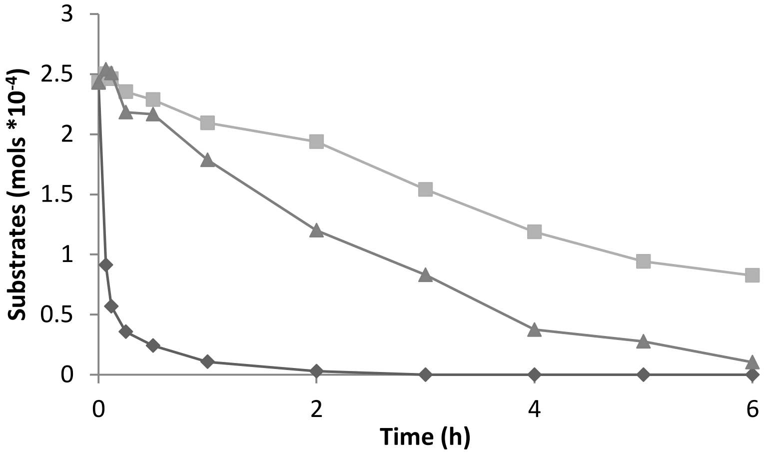


Figure 5–24: Competitive reaction between dibenzothiophene ◆, phenanthrene ■ and pyrene ▲
Reaction conditions: Substrate 0.247mmol, H_2WO_4 (0.025mmol), H_2O_2 35% 2.5ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, Aliquat 336 0.24ml, T=80°C

It was observed that dibenzothiophene reacts slower than benzothiophene, which is not in agreement with literature reports made by Fierro, who used similar reaction conditions. Fierro reported that this unexpected observation could be explained by S–C bond stabilization [10]. Here, benzothiophene gives rise to a higher rate of oxidation than in the more sterically hindered dibenzothiophene.

The competitive reaction between carbazole, phenanthrene and pyrene illustrated that the reaction rate of carbazole and pyrene is similar and that heteroaromatic compounds containing nitrogen react slower than those containing sulphur (Figure 5-25).

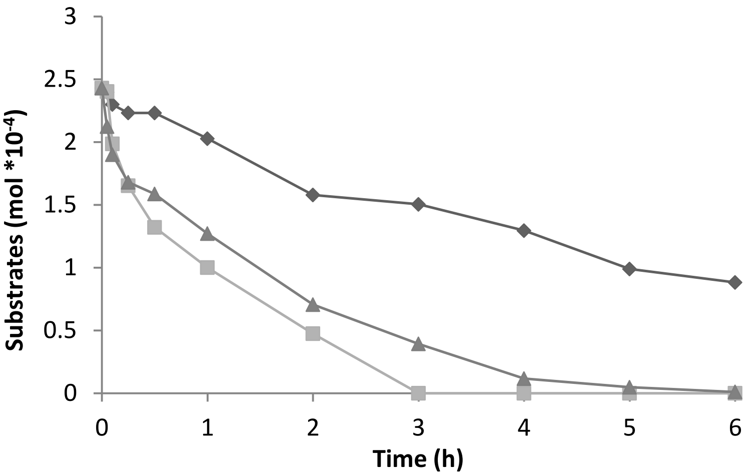


Figure 5–25: Competitive reaction between carbazole ■, phenanthrene ◆ and pyrene ▲ Reaction conditions: Substrate 0.247mmol, H_2WO_4 (0.025mmol), H_2O_2 35% 2.5ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, Aliquat 336 0.24ml, T=80°C

To answer the question about the influence of heteroaromatic compounds on the kinetics of PAHs, it is necessary to compare the reaction rates of these substrates. Table 5-5, shows the oxidation reaction rates for phenanthrene and pyrene calculated in the presence and absence of the heteroaromatic compounds.

Table 5-5: Reaction rates (mols x 10^{-4}/h) of phenanthrene and pyrene with and without the presence of heteroaromatics
Reaction conditions: Substrate 0.247mmol, H_2WO_4 (0.025mmol), H_2O_2 35% 2.5ml, H_3PO_4 10% 0.14ml, C_6H_5Cl 8ml, Aliquat 336 0.24ml, T=80°C

Substrate	**Reaction rate**	
	Without Heteroaromatic	In the presence of Dibenzothiophene
Phenanthrene	0.157	0.291
Pyrene	0.394	0.429
	Without Heteroaromatic	In the presence of Carbazole
Phenanthrene	0.157	0.260
Pyrene	0.394	0.384

It is important to mention, that reaction rate values for phenanthrene and pyrene were taken from the competitive reaction, where naphthalene was used as a third substrate, which was subsequently replaced by a equimolar ratio of heteroaromatic to keep the reactant ratio constant. As can be seen from the data presented in Table 5-5, the rate of

PAHs oxidation increased in the presence of the heteroaromatics, which implies that the catalyst is not poisoned by the sulphur or nitrogen containing compounds. Considering the fact that rate values for pyrene did not change drastically, it can be stated that they are within the range of experimental errors, so the presence of heteroaromatics does not have an influence on pyrene reactivity. However, the rate value for phenanthrene increased almost by a factor of 2. This is a very encouraging result which again emphasizes the benefits of using the H_2WO_4/H_2O_2 system for oxidation of PAHs.

5.6.2. Product identification and heteroatom removal

As shown above, the substrates containing sulphur or nitrogen are successfully oxidized relatively quickly, which is an important observation, yet the question still remains as to the identity of these products and if they still contain the heteroatom. GC-MS and ICP analysis were used to answer this question.

5.6.2.1. Indole

Products from indole oxidation were analyzed using GC-MS. The analysis did not lead to any clear conclusion as to the identity of the product. The GC-MS chromatogram showed a number of peaks, which suggests that the oxidation is unselective. However, the important observation was that all products suggested by GC-MS library contained nitrogen, thus most probably no denitration occurred.

5.6.2.2. Benzothiophenone

Benzothiophene oxidation saw benzothiophene-2,2'-dioxide, as the major product (Figure 5-26, Scheme 5-12) with selectivity around 97%.

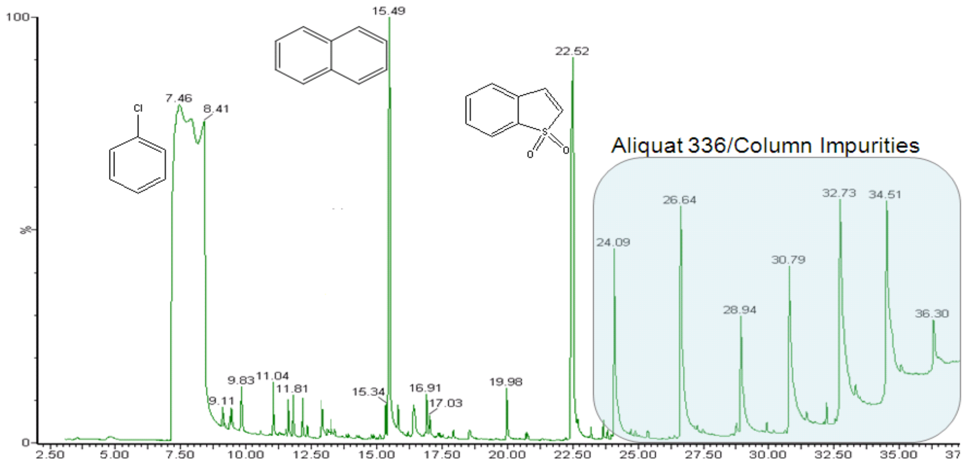
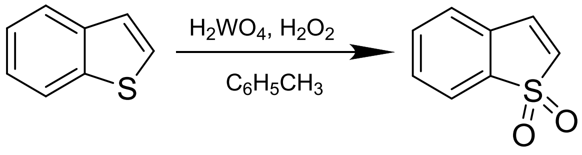


Figure 5–26: Benzothiophene oxidation: GC-MS analysis

This reaction proved that sulphur was not removed from the substrate molecule and that sulphur and not carbon, underwent oxidation. It was decided to continue the oxidation process by using benzothiophene-2,2'-dioxide (18A) as a substrate. However, even after 15h of reaction and using additional oxidant, oxidation did not occur, which suggest that benzothiophene-2,2'-dioxide is resistant to oxidation.



18 **18A**

Scheme 5-12: Oxidation of benzothiophene

5.6.2.3. Carbazole

As it was the case for the other nitrogen containing heteroaromatic - indole, oxidation of carbazole was not selective and the products obtained were not able to be reliably identified by GC-MS library. However, the analysis did suggest the presence of nitrogen in every component, which is confirmed by ICP analysis. The nitrogen level in the organic layer was found to be 4.06%wt/wt and in the aqueous 0.00%wt/wt .

5.6.2.4. Dibenzothiophene

The major product of the oxidation of dibenzothiophene was dibenzothiophene-5,5'-dioxide with a selectivity of 99% as seen in Figure 5-27.

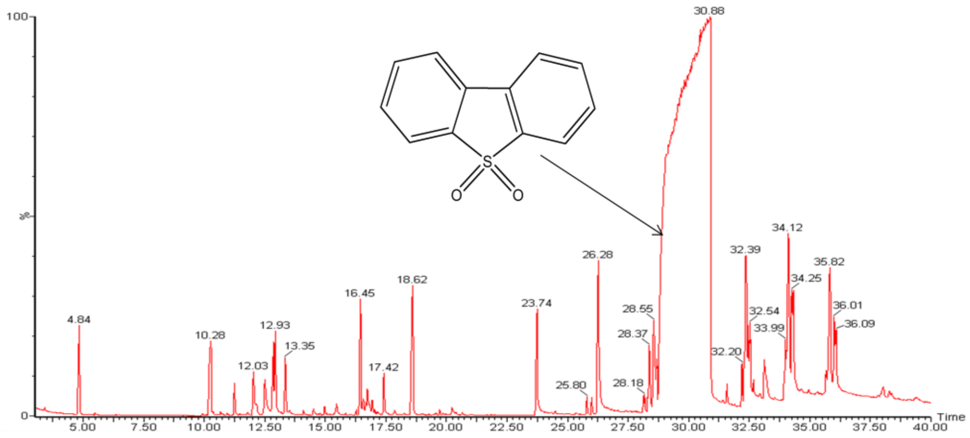


Figure 5–27: Dibenzothiophene oxidation: GC-MS analysis

This result is similar to the one when the oxidation was performed with benzothiophene, with only one sulphur containing product observed. This illustrated that reaction conditions are sufficient to oxidize sulphur, but not to break the C-S bond and remove sulphur from the molecule. As was the case for benzothiophene-2,2'-dioxide, further oxidation of dibenzothiophene-5,5'-dioxide was performed and resulted in a similar observation, that no secondary oxidation was observed. After the analysis of the aqueous and organic layer by ICP MS, sulphur was determined at a level of 11.83%wt/wt in the organic layer and <0.04%wt/wt in the aqueous layer.

5.6.2.5. Dodecyl sulfide

GC-MS analysis of the dodecyl sulfide oxidation reaction suggested the presence of one major product, dodecyl sulfoxide. After ICP MS analysis it was found that sulphur was detected in the organic layer at a level of 6.67%wt/wt, while in the aqueous layer 0.11%wt/wt, which indicates that 87.4% of the sulphur remains in the organic layer after the reaction. This result suggests that it is easier to remove a heteroatom from an heteroaliphatic than from a heteroaromatic compound.

5.7. Oxidation of Porphyrins

In the previous sections it has been shown that H_2WO_4/H_2O_2 chemistry can be successfully used for PAHs oxidation resulting in expected selectivity. What is more, this system has been shown to be active in the oxidation of heteroaromatic compounds, which are present in crude oil. One more, unwanted group of compounds found in crude oil are porphyrins. Here, similar as in section 4.7. porphyrins were oxidized in order to remove metal from its structure using H_2WO_4 chemistry. The combination of polar and apolar phase (H_2O_2 and organic solvent) in reaction, can lead to the transfer of removed metal from organic to aqueous layer. As previously, nickel (II) tetraphenylporphyrin and vanadyl tetraphenylporphyrin were used as model substrates in the reactions and the metal removal was investigated using UV-Vis spectroscopy [11].

5.7.1. Nickel (II) tetraphenylporphyrin

The first experiment was carried out with nickel (II) tetraphenylporphyrin. To confirm the removal of the metal from the compound after the oxidation process, the reaction mixture (organic layer) was analyzed using a UV-Vis spectrometer and a sample from both the organic and aqueous layer were analyzed using ICP-MS. In the UV-Vis spectrum, attention was paid to the peak at 526 nm, which is characteristic for presence of nickel in a porphyrin structure [12]. The disappearance of the peak indicates metal removal from the compound. Three reactions with different *substrate : oxidant & catalyst* ratio were performed. When the reaction was carried out with a *substrate : catalyst* ratio of *1:4*, no colour change was observed. The use of catalyst to substrate ratio of 40:1 and 80:1 resulted in a change of the reaction mixture colour from pink to colourless, which also indicates the end of the reaction. Organic layers from all reactions were analyzed using a UV-Vis Spectrometer. Figure 5-28 illustrates the changes in the UV-Vis spectrum for the oxidation of nickel porphyrin when different amounts of oxidant and catalyst were used. Only the use of a *substrate: catalyst* ratio 1:80 assures 100% conversion and the full nickel removal from substrate and its transfer to the aqueous layer. From the spectra presented in figure 5-28, it can be seen that they are identical to what was observed when RICO chemistry was employed in the oxidation of the same substrate (4.7.1.).

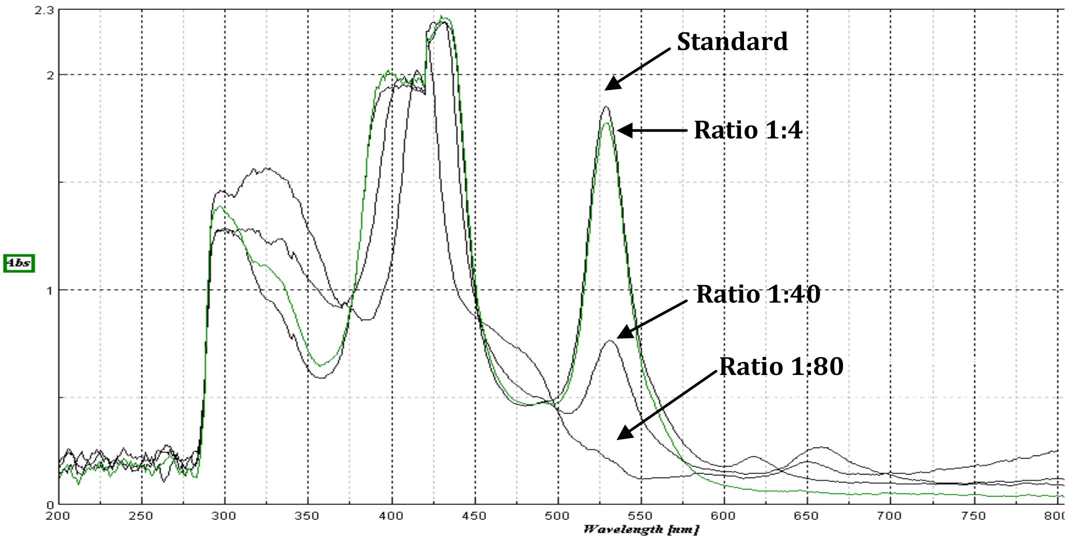


Figure 5–28: UV-Vis analysis: Oxidation of NiTPP using different substrate : catalyst ratios Reaction conditions: Substrate: C= 1.19×10^{-4} M, 1)Ratio 1:4 (H_2O_2 35% 0.1ml, H_2WO_4 0.001g),2) Ratio 1:40 (H_2O_2 35% 1ml, H_2WO_4 0.01g), Ratio 1:80 (H_2O_2 35% 2ml, H_2WO_4 0.02g), C_6H_5Cl 8 ml, H_2O_2 35%, H_3PO_4 10%, Aliquat 336, T=80°C, t=16h

ICP-MS analysis of the aqueous layer from reaction ratio 1:80 proved that 98% of the Ni was present in the aqueous layer.

In order to get information about differences in product distribution from the oxidation of metalloporhyrin and 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine, MS analysis of two reaction mixtures were performed. As it is shown below (Figure 5-29) the MS spectra of reaction mixture obtained after oxidation of nickel tetraphenylporphyrin contained more signals than the one from the oxidation of non metal containing porphyrin, what can be a result of high fragmentation of the molecule. What is more, no signals having the same m/z ratio in those spectra were found, indicating that porphyrins were oxidized in different ways, thus the metal present plays a role during oxidation processes.

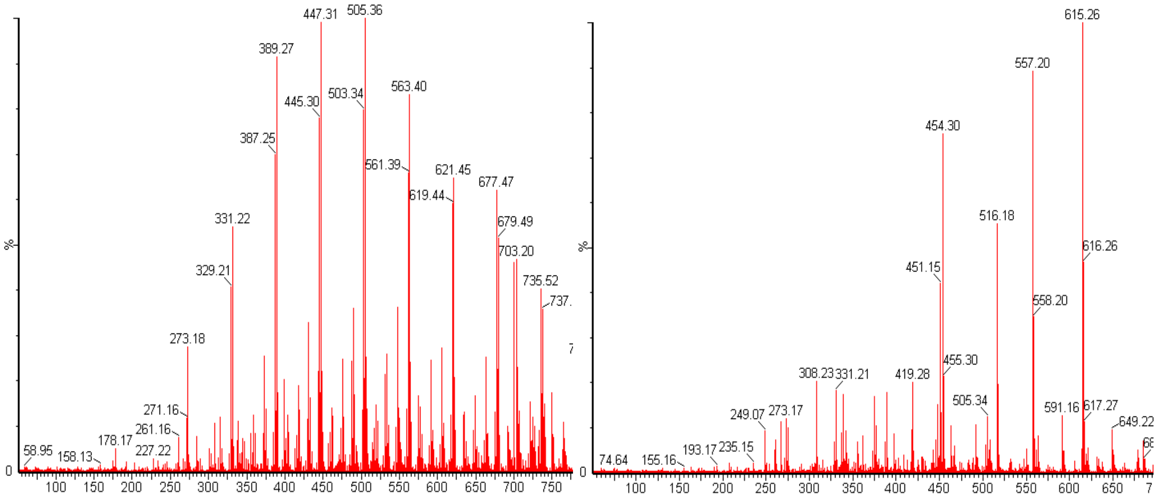


Figure 5–29: Comparison between Mass Spectrometry (ES+) spectra of reaction mixture after oxidation of NiTPP(A, left) and 5,10,15,20-tetraphenyl-21H, 23H-porphine (B, right) t=20h, Substrate: C= $1.19*10^{-4}$ M, Ratio substrate : catalyst 1:80

The oxidation processes in the presence of porphyrins and H_2O_2 are well known in chemistry [13]. Thus, it was decided to use only H_2O_2, without H_2WO_4, for the oxidative process of metal removal from NiTPP. 2ml of H_2O_2 was used without catalyst and all other analysis steps kept constant. After 20h of reaction, the peak at 526nm became smaller which suggested that the reaction had reached a conversion of 84%, in addition to the nickel being removed from the porphyrin, even in the absence of the catalyst (Figure 5-30). Results from ICP MS analysis showed that 86% of the Ni was detected in the aqueous phase.

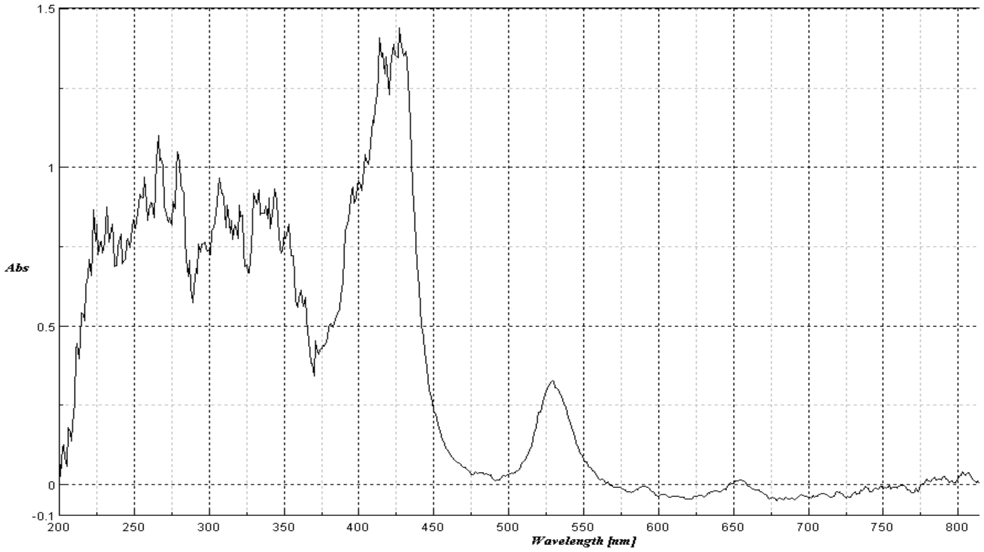


Figure 5–30: UV-Vis analysis: Oxidation of NiTPP
*Reaction conditions: Substrate: C= 1.19 *10^{-4}, C_6H_5Cl 8ml, H_2O_2 35% 2ml, H_3PO_4 10% 0.02g, T=80°C, t=20h*

What is more, spectrum from the mass spectrometry analysis of the resultant mixture obtained after the reaction with H_2O_2 (Figure 5-31), show different m/z signals to the one where H_2O_2 was used in the presence of H_2WO_4 (Figure 5-29A). This observation suggests that oxidation must proceed via different pathway, thus there are two mechanisms active in the metal removal of metalloporphyrins.

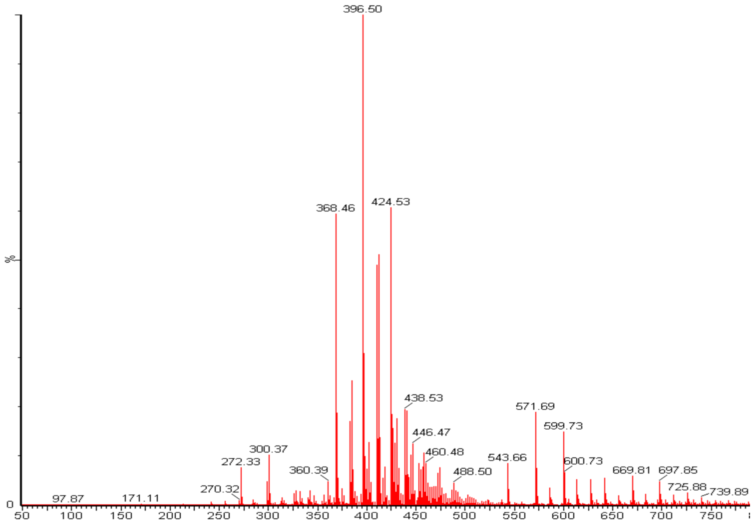


Figure 5–31: MS spectrum of reaction mixture after oxidation of NiTPP,
*Reaction conditions: Substrate: C= 1.19*10^{-4} M, C_6H_5Cl 8ml, H_2O_2 35% 2ml, H_3PO_4 10% 0.02g, T=80°C, t=20h*

5.7.2. Vanadyl tetraphenylporphyrin

Once it was discovered that the presence of a catalyst is not necessary to remove Ni from NiTPP, it was decided to test another compound in this way. Vanadyl tetraphenylporhyrin was used as a substrate and after a 20h reaction, the organic layer was analyzed using a UV-Vis spectroscopy. In figure 5-32, it can be seen, that the peak at λ 548 nm is no longer present after 20h of reaction, suggesting removal of the vanadium from the substrate. This interesting finding was confirmed by ICP MS analysis, which indicated that 92% of the metal was deposited in the aqueous layer.

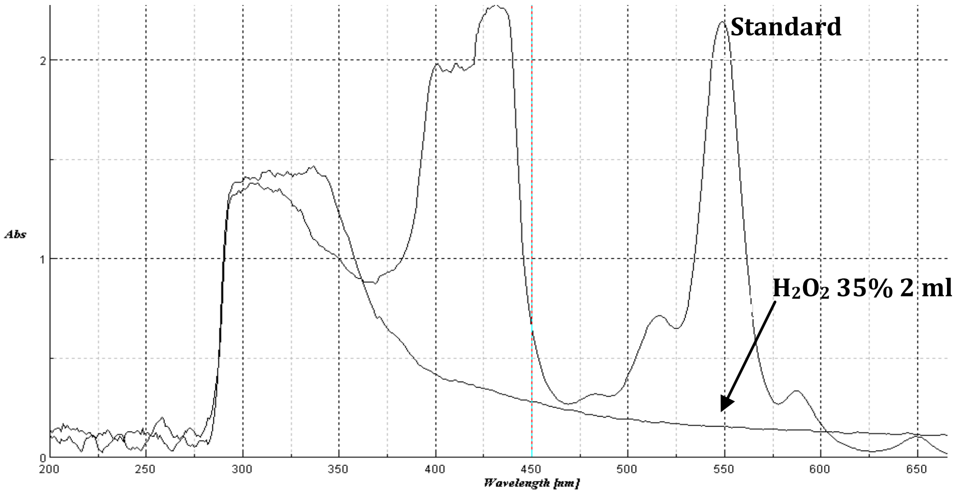
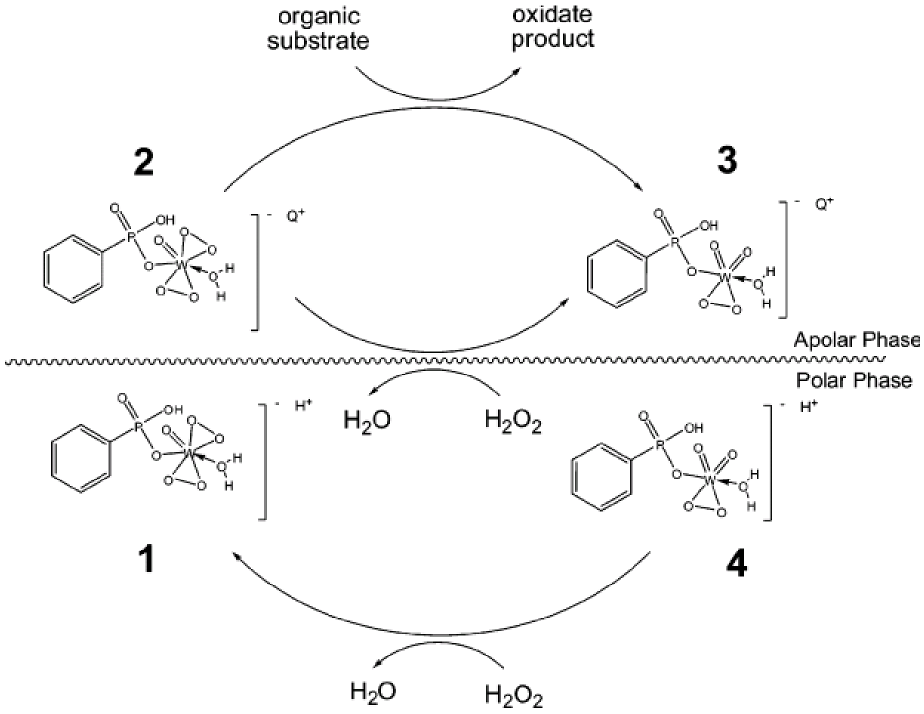


Figure 5–32: UV-Vis analysis: Oxidation of VOTPP
Reaction conditions: Substrate: C= 1.19 $*10^{-4}$ *M,* C_6H_5Cl *8 ml,* H_2O_2 *35% 2ml,* H_3PO_4 *10% 0.02g, T=80°C, t=20h*

5.8. Discussion and Conclusions

The results presented in this chapter clearly indicate that H_2WO_4/H_2O_2 is a system that can be used for the selective oxidation of polynuclear aromatic hydrocarbons, in addition to those aromatic compounds, which contain an aliphatic chain. It has been shown, that the selectivity of oxidation can be directed by changing the solvent employed in the reaction. Acetonitrile was the best solvent tested and directed the selectivity of oxidation towards aromatic carbons, leaving the aliphatic carbons intact. Using this solvent it is possible to keep monophasic solvent system which facilitates the transfer of products and reagents [10].

It is clear that the mechanism of oxidation is completely different to that seen in the RICO chemistry and this is the main reason responsible for acid production. In RICO chemistry, the ruthenium catalyst drives the chemistry through changes in oxidation state at the metal. This does not appear to be the case with tungsten. The tungsten catalyst does not change oxidation state, its role as catalyst is to activate the H_2O_2 and bring it into contact with the substrate within the coordination sphere of the metal as is shown in the scheme proposed by Noyori and Fierro [1, 10, 14].



Scheme 5-13: Proposed mechanism of Phase Transfer Oxidation of Organic Compounds with H_2O_2/H_2WO_4 [1]

It is believed that the mechanism proceeds through a range of different intermediates, there is an alternative first step in the mechanism which yields epoxide. Considering these intermediates in pyrene oxidation, it is possible that the pyrene could go directly to the pyrene-4,5-dione. The second possibility may lead to the production of the epoxide and there are reports in the literature to support this in the case of olefin oxidation [14-15]. Several findings described in this chapter contribute to a better understanding of the reaction mechanism and the role tungsten chemistry plays in this. It has been shown that the choice of solvent and change in reaction temperature plays an important role in the oxidation process. It is believed that this factor has an influence on C=C bond stability and hence the production of acids. On the other hand it has been shown that the aliphatic side chain does not significantly affect the rate of the reaction, thus it can be concluded that the aliphatic side chain does not play a role in the reaction mechanism. The effect of pH on the oxidation process must also be considered. Addition of 10% H_3PO_4 to the reaction slows down hydrogen peroxide decomposition and improves the phase transfer catalyst process [4].

As observed in the RICO chemistry, the rate of oxidation increases with an increasing number of fused aromatic rings. The tungsten chemistry applied here has expected selectivity and attacks mainly aromatic carbons, leaving the aliphatic side carbon chain untouched. This observation is only valid for molecules with long aromatic chains, as 2-ethylnaphthalene underwent oxidation resulting in production of acetonaphthone, when other than acetonitrile solvents were used. It was also shown that oxidative desulfurization (ODS) transformed the sulphur-containing species into the corresponding sulfoxide or sulfone species which subsequently can be removed in a second extraction step. It is worth mentioning, that oxidation of compounds containing heteroatoms (sulphur, nitrogen), thus oxidation of heteroatom combined with its removal, occurs better in aliphatic than in aromatic heteromolecules. In addition the tungsten chemistry described in this chapter, can be applied to the demetallation of metalloporphyrins. However, similar results can be achieved using solely H_2O_2 under relatively mild reaction conditions [16-17].

5.9. References

1. Barrio, L., Campos-Martin, J.M., and Fierro, J.L.G., *Journal of Physical Chemistry A*, **2007**, 111(11), 2166
2. Lane, B.S. and Burgess, K., *Chemical Reviews*, **2003**, 103(7), 2457
3. Young, E.R.R. and Funk, R.L., *Journal of Organic Chemistry*, **1998**, 63(26), 9995
4. Saito, Y., Shinichi, A., Yoshio, S., and Naoji, K., *Process for Producing Aromatic Dicarboxylic Acids*. 1989: United States.
5. Speight, J.G., *The Chemistry and Technology of Petroleum*. 4th ed **2006**, Taylor & Francis Group.
6. Kaburagi, Y. and Kishi, Y., *Organic Letters*, **2007**, 9(4), 723
7. Speight, J.G., *The Desulfurization of Heavy Olis and Residua*. **1981**, New York, Marcel Dekker.
8. Song, C. and Ma, X.L., *Applied Catalysis B-Environmental*, **2003**, 41(1-2), 207
9. Jeno, H., Szoboszlai, Z., Tamas, K., Hollo, A., Thernesz, A., and Kallo, D., *Catalysis Today*, **2011**, 176(1), 177
10. Campos-Martin, J.M., Capel-Sanchez, M.C., and Fierro, J.L.G., *Green Chemistry*, **2004**, 6(11), 557
11. Galimov, R.A. and Krivonozhkina, L.V., *Chemistry and Technology of Fuels and Oils*, **1993**, 29(5-6), 300

12. Shcherbakova, N.P., *Chemistry and Technology of Fuels and Oils*, **1994**, 30(1-2), 42
13. Giri, N.G. and Chauhan, S.M.S., *Catalysis Communications*, **2009**, 10(4), 383
14. Noyori, R., Aoki, M., and Sato, K., *Chemical Communications*, **2003**(16), 1977
15. Dickman, M.H. and Pope, M.T., *Chemical Reviews*, **1994**, 94(3), 569
16. Mandal, P.C., Wahyudiono, Sasaki, M., and Goto, M., *Journal of Hazardous Materials*, **2011**, 187(1-3), 600
17. Shiraishi, Y., Hirai, T., and Komasawa, I., *Industrial & Engineering Chemistry Research*, **2000**, 39(5), 1345

6. Oxidation of PAHs using other catalytic systems

6.1. Introduction

This chapter is devoted to the investigation of catalytic systems other than RICO and H_2WO_4/H_2O_2 for PAHs oxidation. Selective catalytic oxidation of these compounds using low cost, environmentally benign oxidant and catalysts, is important from an economical and practical standpoint. As a result, H_2O_2 has become one of the most attractive oxidants and has stimulated the search for efficient catalysts to achieve H_2O_2 activation [1-2]. Based on the previous experiences, the H_2WO_4/H_2O_2 system was modified and similar chemicals used so as to better understand the chemistry and proceed in the direction of heterogenisation, using H_2O_2 as an oxidant. Firstly, several tests based on tungsten chemistry were carried out and the corresponding heterogeneous catalysts prepared. In addition, this chapter considers the use of tungsten and molybdenum based heteropolyacids for PAHs oxidation. Needless to say that tungsten and molybdenum compounds are efficient catalysts for H_2O_2 activation [1], so consequently $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ were tested for PAHs oxidation in the presence of H_2O_2 as well as *tert*-butyl hydroperoxide (TBHP). It is important to emphasize that heteropolyacids (HPAs) are considered to be one of the most important catalysts due to their strong Brönsted acidity and their ability to initiate multielectron redox transformations under relatively mild conditions [3]. In addition, several developments to heteropolyacids have been achieved to increase their surface area and thermal stability. Special interest was paid to the incorporation of cesium cations into the heteropolyacids (HPAs) and its heterogenisation. In the very last part of this chapter, different heterogeneous catalysts were tested for PAHs oxidation. Among a wide range of possible catalysts, ruthenium and gold based catalysts were chosen. The reason to test a ruthenium catalyst was based on the fact, that for many years this element has been widely used in oxidation reactions and when deposited on a catalyst support is highly efficient in the activation of O_2 and air. What is more a ruthenium supported catalyst posses obvious advantages in product isolation and catalyst recycling [4-5]. Conversely, gold supported catalysts have attracted much attention over the last 3 decades, because of the high activity they exhibit in oxidation reactions and their practical application in industry for the synthesis of a number of compounds e.g. propylene oxide, vinyl acetate monomer, cyclohexanol/cyclohexanone, gluconic acid and glyceric acid.[6] Here, gold based bimetallic catalysts which has previously exhibit high activity for the oxidation of alcohols in the presence of molecular oxygen were tested for pyrene and 2-ethylnaphthalene oxidation [7].

6.2. Tungsten based catalyst for the oxidation of PAHs

As presented in chapter 5, H_2O_2 in combination with H_2WO_4 provides the required selectivity for PAHs oxidation and theoretically it could be used for larger scale reaction in the petroleum industry. However, the chances of it actually being used as a solution to the industrial processes are negligible due to economical requirements. Consequently, tungsten based catalysts with combinations of different oxidants were tested.

Instead of using H_2O_2 it was proposed to use TBHP in the presence of H_2WO_4 for the oxidation of pyrene. TBHP is a known oxidant, often used in oxidation chemistry. In contrast to H_2O_2, it is miscible with most organic solvents, e.g. toluene, thus its application in this reaction means that the reaction can be carried out in a monophasic solvent system. TBHP was tested in the presence of solvents: acetonitrile, toluene and chlorobenzene using different reaction time and temperature as is shown in table 6-1. No phase transfer catalyst was used. Comparing the conversion data from reaction 1,2 and 3 it can be seen that 10% conversion was reached after 20h of reaction with reaction temperature maintained at 110°C. This result shows that temperature is an important factor; however, the results were not encouraging enough to continue the investigation. Most probably the mechanism here is different to that of the H_2O_2/H_2WO_4 system, where the presence of aliquat 336 helped to overcome the difficulties related to the biphasic system. Here, the main thrust of the work was to simplify the reaction system by excluding aliquat 336 and create a monophasic reaction system.

TBHP was also tested in the presence of O_2 and H_2WO_4. The aim of this experiment was to investigate the influence of TBHP on catalyst and oxygen activation. However, even after 7h no reaction was observed indicating that tungstic acid and TBHP does not activate molecular oxygen in the reaction and there is no active species which could lead to pyrene oxidation.

Table 6-1: Oxidation of pyrene
Reaction Conditions: Solvent volume: 8 ml, substrate 0.09g, H_2WO_4 0.045g, TBHP 1ml (R1, R2, R3), TBHP 10µl (R4) T=80°C (R1), T=110°C (R2, R3, R4)

No.	Oxidant	Solvent	O_2 Pressure	Reaction time (h)	Conversion %
1	TBHP 70%	MeCN	-	16	3
2	TBHP 70%	C_6H_5Cl	-	16	8
3	TBHP 70%	$C_6H_5CH_3$	-	20	10
4	TBHP 70%+O_2	$C_6H_5CH_3$	20 bar	7	-

6.2.1. WO_3 and H_2O_2

In a further extension of the work it was decided to substitute H_2WO_4 with WO_3. WO_3 is a metal oxide which can be easily immobilized and produces metal oxide catalysts of the type: WO_x-TiO_2, WO_x-ZrO_2, WO_x-Al_2O_3 [8].

When WO_3 was used as a catalyst in the reaction, the same products were observed as seen in the H_2WO_4 system. However, the selectivity and level of conversion was different to that observed in the H_2WO_4 system. The HPLC chromatogram displayed below (Figure 6-1) obtained after the oxidation of pyrene, indicated the presence of 2 products: pyrene-4,5-dione and phenanthrene 9,10-dicarboxylic acid.

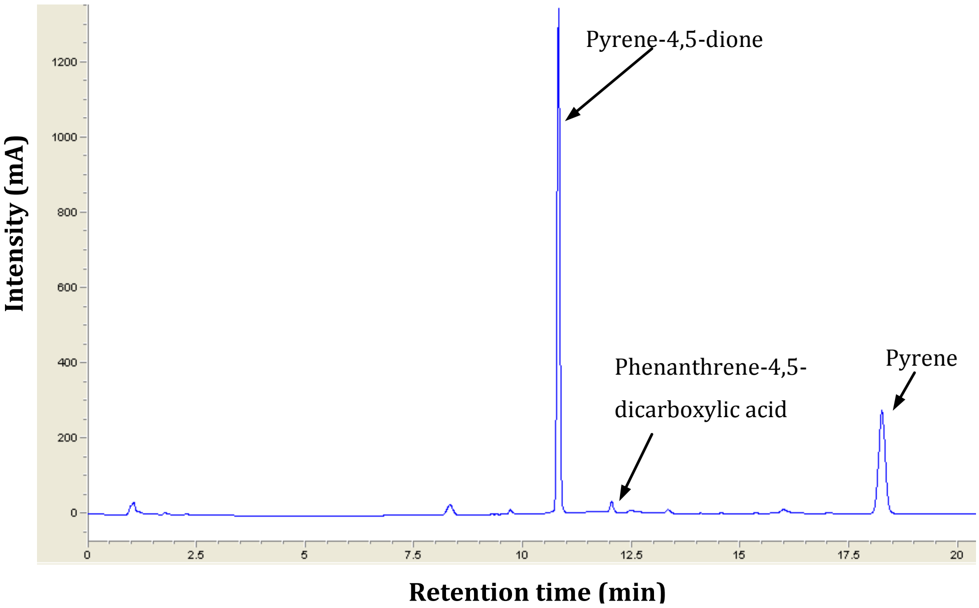


Figure 6–1: HPLC analysis of the products of pyrene oxidation
Reaction conditions: Pyrene 1.2 g, H_2O_2 35% 1.2ml, WO_3 0.0141g, H_3PO_4 10% 0.01ml, Aliquat 336 (0.012g),Toluene 8ml, T=80°C, t=16h

^{1}H NMR analysis showed signals which could be assigned to pyrene-4,5-dione and phenenthrene-9,10-dicarboxylic acid. ^{13}C NMR analysis showed a strong signal in the carbonyl region at δ 180ppm, which also proves the presence of the dione (Figure 6-2).

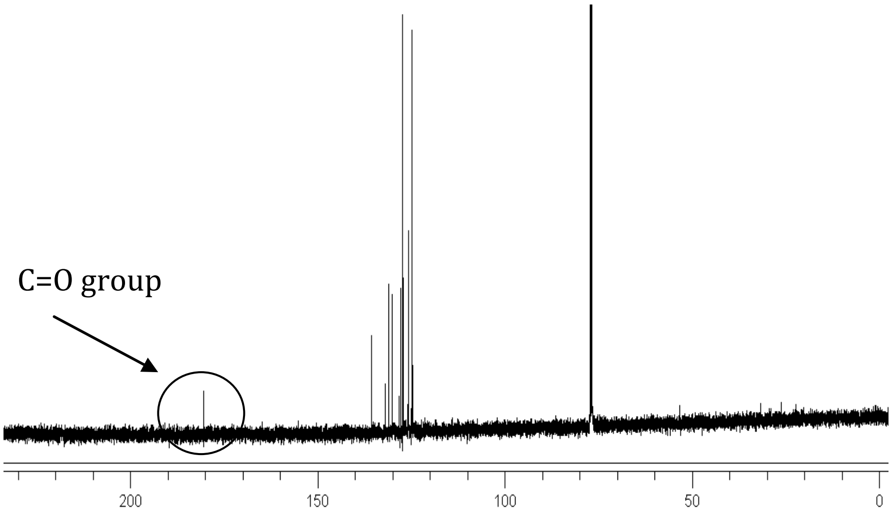


Figure 6–2: Pyrene oxidation: ^{13}C NMR analysis,
Reaction Conditions: Substrate 1.2 g, H_2O_2 35% 1.2ml, WO_3 0.0141g, H_3PO_4 10% 0.01ml, Aliquat 336 (0.012g), $C_6H_5CH_3$ 8ml, T=80°C, t=16h

The conversion level obtained, indicates that during the reaction a peroxospecies was formed which were produced in a similar way as to when the reaction was conducted with tungstic acid.

The positive outcome of this experiment is that H_2WO_4 can be replaced by WO_3 as a catalyst and as a result, it was decided to use a heterogeneous tungsten catalyst for the oxidation of PAHs.

6.2.2. Tungsten oxides WO_3/TiO_2

The heterogeneous catalysts used for further testing in the oxidation of PAHs were chosen from a range of supported tungsten oxide catalysts. These catalysts have received a great deal of attention during the last three decades, because of their wide range of catalytic applications e.g. WO_3/Al_2O_3 catalysts are known for catalyzing the skeletal isomerization of n-butene to isobutene [9], WO_3/SiO_2 catalysts are effective for the metathesis of 1-octene and 1-heptene [10-11]. However, the most important tungsten oxide catalyst is WO_x-ZrO_2 which can be used for n-alkane isomerisation [12-13]. It is believed that this catalyst ubiquitous properties are the result of their strong acidity [8]. Here, it was decided to test a WO_3/TiO_2 catalyst in the oxidation of PAHs.

TiO_2 is a widely used catalyst support and is known to enhance activity in many reactions because of the strong interaction between the active phase and the support [14].

Two catalysts with different tungsten loadings were prepared, a 1% WO_3/TiO_2 catalyst and a 20% WO_3/TiO_2 catalyst. Details of the catalyst preparation method are described in section 2.4.1 based on the method reported in the literature [15]. Both catalysts were tested for pyrene oxidation in both monophasic and biphasic solvent systems. In the monophasic system, acetonitrile was used as a solvent, while in the biphasic system, toluene was introduced. When comparing the ^1H NMR spectra obtained after pyrene oxidation using 1%WO_3/TiO_2 in both systems, it was clear that the catalyst activity was very low. Only signals from the substrate and solvent ($CDCl_3$) were observed (Figure 6-3). HPLC analysis confirmed the presence of the substrate and the product, pyrene-4,5-dione. Conversion in the biphasic system was found to be lower than 5%.

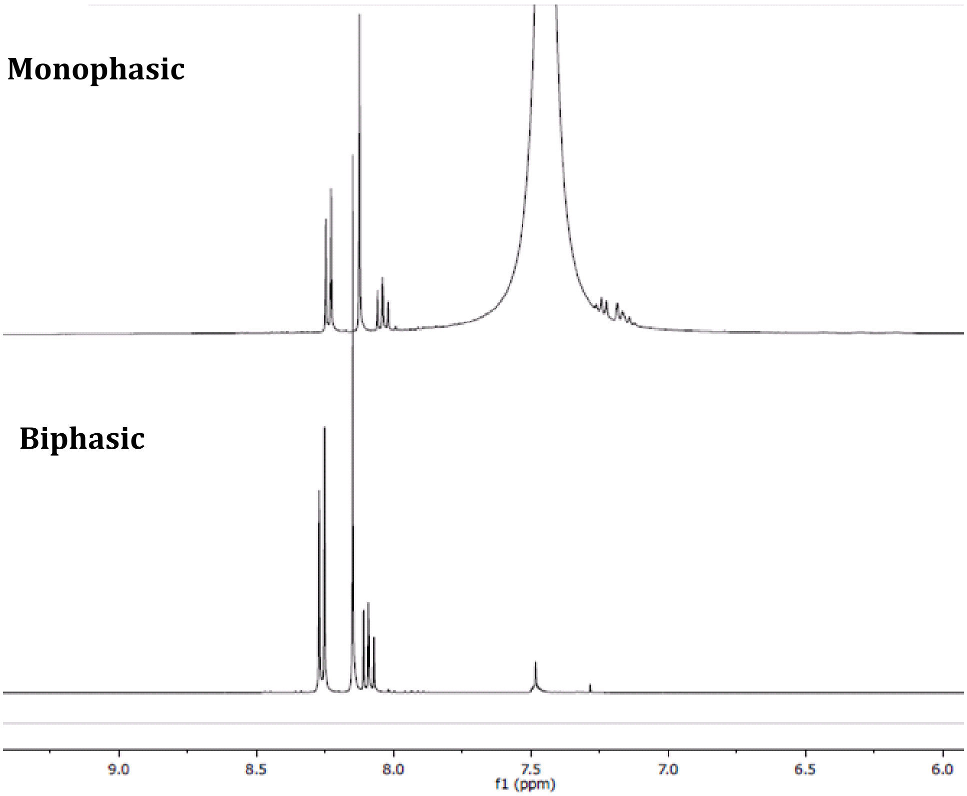


Figure 6–3: ^1H NMR analysis: Oxidation of pyrene using 1%WO_3/TiO_2 in monophasic (top) and biphasic system (bottom)
Reaction Conditions: Monophasic: Pyrene 0.164 mmol, 1%WO_3/TiO_2 0.12g, H_2O_2 35% 2 ml, CH_3CN 4ml, H_3PO_4 10% 0.014ml, T=65°C, t=20h, Biphasic: Pyrene 0.328mmol, 1%WO_3/TiO_2 0.24g, H_2O_2 35% 4 ml, $C_6H_5CH_3$ 8ml, H_3PO_4 10% 0.028ml, Aliquat 336 0.014g, T=80°C, t=20h

The catalyst with a metal loading of 20% showed greater activity in the biphasic solvent system compared to when the reaction was conducted in the monophasic solvent system. ^{1}H NMR and HPLC analysis detected no pyrene implying 100% conversion was achieved in this reaction (Figure 6-4).

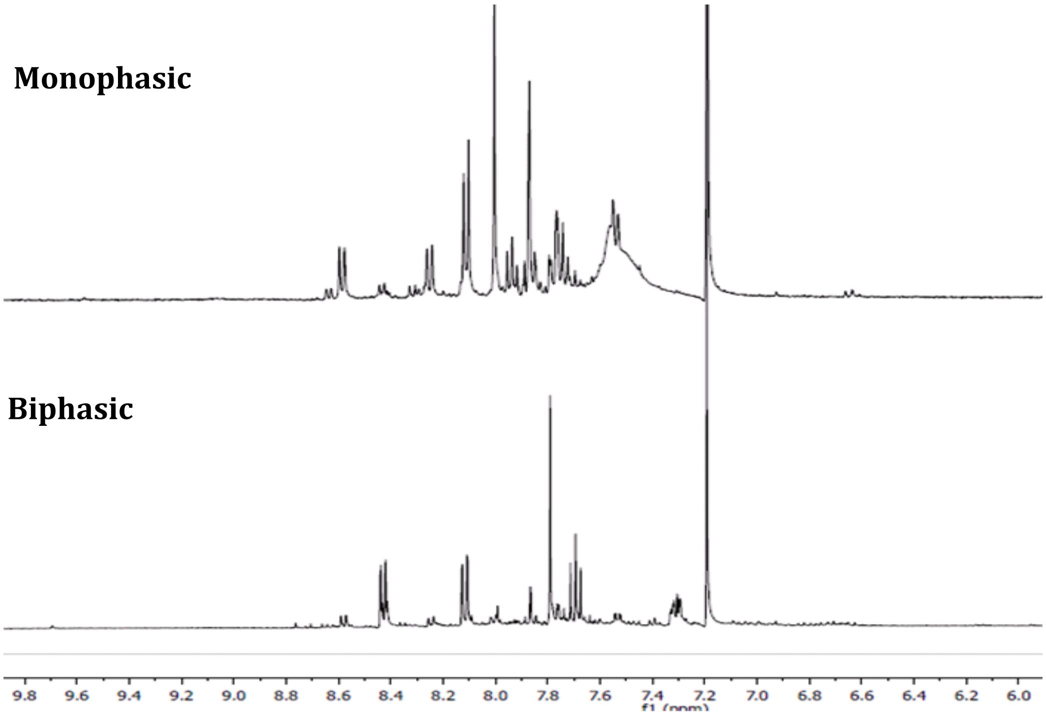


Figure 6–4: ^{1}H NMR analysis: Oxidation of pyrene using 20%WO_3/TiO_2 in monophasic (top) and biphasic system (bottom)
Reaction Conditions: Monophasic: Pyrene 0.164 mmol, 20%WO_3/TiO_2 0.12g, H_2O_2 35% 2 ml, CH_3CN 4ml, H_3PO_4 10% 0.014ml, T=65°C, t=20h, Biphasic: Pyrene 0.06g, 20%WO_3/TiO_2 0.24g, H_2O_2 35% 4ml, $C_6H_5CH_3$ 8ml, H_3PO_4 10% 0.028ml, Aliquat 336 0.014g, T=80°C, t=20h

HPLC analysis suggests the oxidation of pyrene mainly into pyrene-4,5-dione. Phenanthrene-4,5-dicarboxlic acid was also detected but at a much lower concentration as seen below (Figure 6-5).

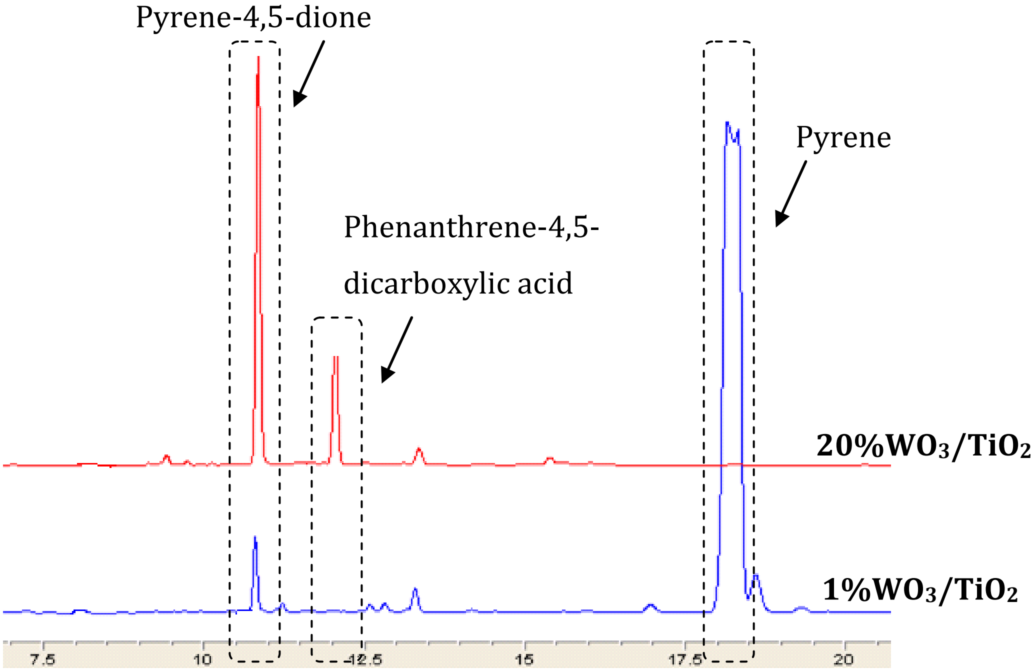


Figure 6–5: HPLC analysis: Oxidation of pyrene using 1% WO_3/TiO_2 *and 20%*WO_3/TiO_2 *in biphasic solvent system*

To prove that obtained conversion was the result of a heterogeneous catalyzed reaction, not the result of tungsten leaching from the catalyst, a hot filtration method was applied. The catalyst, H_2O_2, $C_6H_5CH_3$, aliquat 336 and H_3PO_4 were continuously stirred at 80°C for 2 hours. The mixture was filtered and the hot filtrate added to pyrene and stirred for 15h at 80°C. The reaction mixture was analyzed using HPLC and the resultant chromatograph showed signals which corresponded to the diketone, in addition to substrate. Pyrene conversion was calculated at 57%, which suggests partial catalyst leaching. A second experiment was carried out to determine if at least some conversion comes from the heterogeneous catalyst. To answer this question second experiment was run and all reactants, apart from substrate, along with recovered catalyst were stirred for 15h at 80°C. Then the catalyst was filtered, dried and reused again. Pyrene was mixed with all the new reactants, recovered catalyst and the process of stirring was repeated for 15h at the same temperature. Conversion for this reaction was calculated to be 31%. Then the same procedure was repeated for a third time and the conversion was found to decrease to 7%.

This experiment clearly illustrates that catalyst activity was the result of homogeneous tungsten species in solution as a consequence of catalyst leaching. Raman analysis of the used catalyst indicated, that there was no WO_3 species on the TiO_2 surface (Figure 6-6).

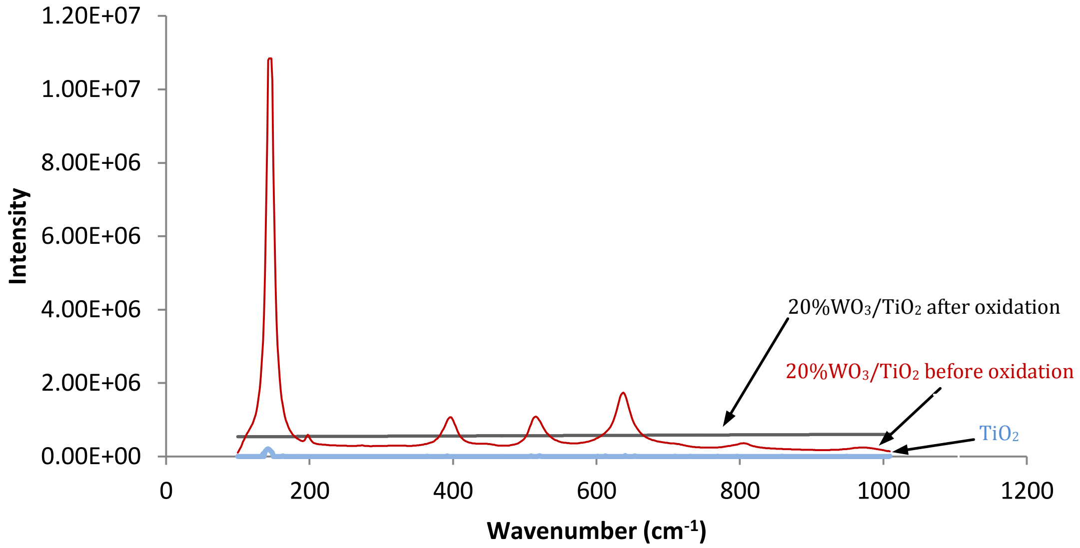


Figure 6–6: Raman Spectroscopy of TiO_2 (●), 20%WO_3/TiO_2 before(●) and after (●) oxidation of pyrene

6.3. Heteropolyacids (HPAs)

Heteropolyacids (HPAs) and heteropoly-catalysts have attracted much attention in recent years. The attractiveness lies in their variety, their potential as catalysts and economic importance from green chemistry point of view. Heteropolyacids possess, a very strong acidity and appropriate redox properties which can be modify by replacing the protons with metal cations and/or by changing the heteroatom [16]. Among many heteropolyacids, special attention has been paid to heteropolyacids possessing the Keggin structure, which have shown good catalytic properties [3].

6.3.1. HPAs with Keggin structure

The Keggin heteropolyanion structure is typically $XM_{12}O_{40}^{n-}$, where X is the central atom e.g.: P, Si ; M is the metal ion as molybdenum Mo^{6+} or tungsten W^{6+} [3]. Two HPAs were applied to the experiments described in this chapter. Firstly, $H_3PW_{12}O_{40}$, considered to be the strongest heteropolyacid in the Keggin series, was used. The acid strength of these crystalline heteropolyacid's decreases in the order PW > SiW ≥ PMo [3]. $H_3PW_{12}O_{40}$ based catalysts are known not to catalyse side reactions which frequently occur with mineral acids, they are noncorrosive and environmentally benign [17][18]. The prepared catalyst was used in the oxidation of phenanthrene oxidation to check catalyst activity and in the oxidation of 2-ethylnaphthalene to investigate reaction selectivity. H_2O_2 was used as an oxidant while acetonitrile was chosen as the solvent as it prevents the formation of a biphasic solvent system. However, this solvent system leads to poor substrate solubility. Firstly, phenanthrene was used as a substrate in this reaction, after 15h of reaction, the solvent was evaporated and the residues dissolved in $CDCl_3$ and analyzed by ^1H NMR. Comparing the ^1H NMR spectra of phenanthrene and the reaction mixture (Figure 6-7), it is clear that there are visible changes in the ^1H NMR spectra, which suggests the presence of oxidation products.

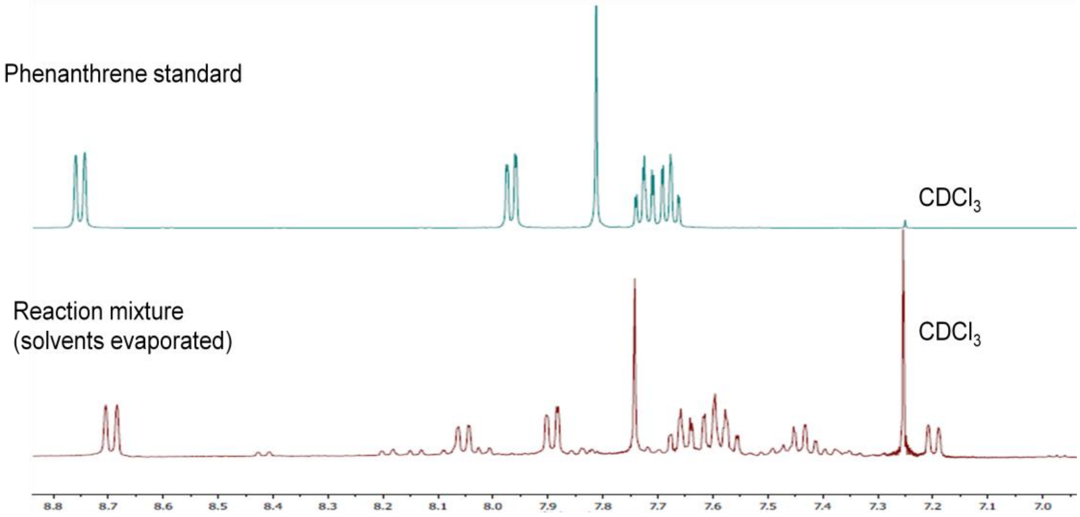


Figure 6–7: ^1H NMR analysis: Comparison of standard phenanthrene solution (top) and reaction mixture after oxidation of phenanthrene using $H_3PW_{12}O_{40}$ (bottom).
Reaction conditions: Substrate 0.164mmol, $H_3PW_{12}O_{40}$ 0.025mmol (0.072g), H_2O_2 35% 1.2ml, MeCN 20ml, T=65°C, t=20h

The use of heteropolyacid results in the phenanthrene oxidation indicating an active catalytic system, but it was also important to examine the selectivity of this catalyst. 2-Ethylnaphthalene was used for this test reaction. GC analysis showed very low reaction conversion, however, one of the products detected was 2-acetonaphthone. This experiment showed that although $H_3PW_{12}O_{40}$ acid system does not provide the required reaction selectivity, its activity is promising. Another catalyst tested, prepared and used in the same way as reported above was $H_3PMo_{12}O_{40}$. The catalyst was used for pyrene oxidation, this catalyst showed activity with the ^1H NMR spectrum showing visible changes post reaction as seen in figure below (Figure 6-8).

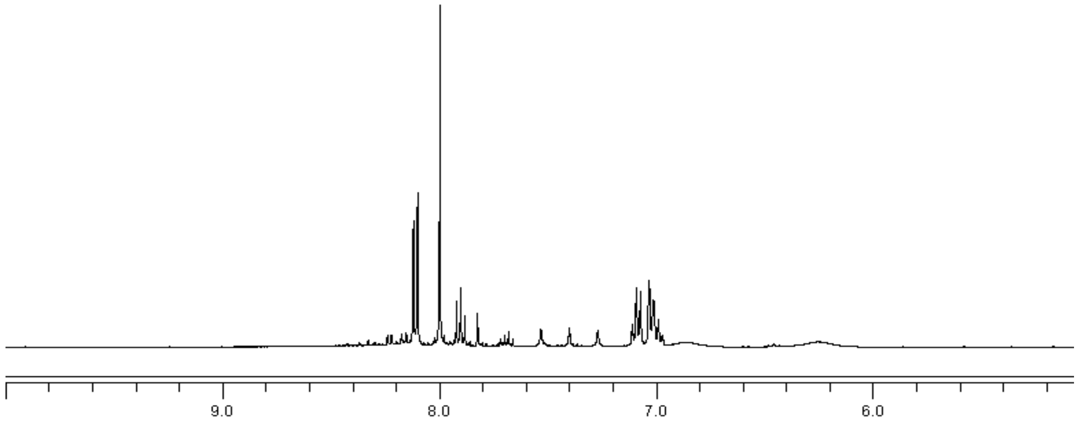


Figure 6–8: ^{1}H NMR analysis: Pyrene oxidation
Reaction Conditions: Substrate 0.164 mmol, $H_3PMo_{12}O_{40}$ 0.025mmol (0.072g), H_2O_2 35% 1.2ml, MeCN 20ml, T=65°C, t=20h

6.3.2. $Cs_{2.5}H_{0.5}PM_{12}O_{40}$

Although the data presented in the previous sections indicate that HPAs are active in the oxidation there are also a number of disadvantages in using HPAs as oxidation catalysts, like low thermal stability, low surface area and poor solubility in organic solvents. To overcome this problem, often Cs^+ cations are introduced into the HPA structure as a substitute for protons [19]. It has been demonstrated in the literature that acidic Cs salts have strong acid sites, high surface area and are efficient solid acid catalysts for a variety of organic reactions and are especially promising for liquid-phase reactions [20]. Detailed descriptions of the preparation of $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ can be found in section 2.4.2. and are based on previous literature preparations [21-22]. Firstly, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was used for pyrene oxidation using similar reaction conditions to those outlined in section 6.3.1. ^{1}H NMR analysis showed almost non-visible changes in the spectrum profile obtained post reaction. (Figure 6-9).

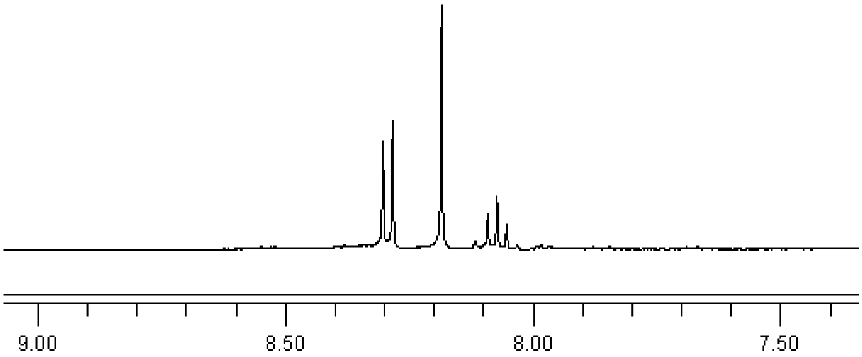


Figure 6–9: ^1H NMR analysis: pyrene oxidation using $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and H_2O_2
Reaction conditions: Pyrene 0.164 mmol, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ 0.025mmol, H_2O_2 35% 2.4ml, MeCN 20ml, T=65°C, t=20h, Visible signals from pyrene: d δ 8.30ppm, s δ8.18ppm, t δ 8.075ppm

HPLC analysis of the reaction mixture generated a chromatogram, which showed peak at retention time 12.01mins, corresponding to phenanthrene 9,10-dicarboxylic acid, however the conversion was relatively low (Figure 6-10). A second reaction was performed using the same acid, but in toluene in the presence of TBHP (70%). This experiment was carried out to avoid the formation of a biphasic solution and to allow the reaction temperature to be increased. Despite the changes made to the reaction so as to increase catalyst activity, no significant conversion based on ^1H NMR analysis was observed.

The cesium exchanged phosphotungstic acid did not exhibit any higher conversion compared to when the reaction was carried out with the pure acid form. Conversely, it is well known that improvement of catalytic performance, activity and selectivity is observed for the $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ when compared to $H_3PMo_{12}O_{40}$ [22-23]. For this reason $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ was also tested for the oxidation of pyrene. $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ when used in the presence of acetonitrile and H_2O_2 showed high activity, which was confirmed by ^1H NMR and HPLC analysis. Conversion was found to be 100% and the major product detected in the HPLC chromatogram had a retention time identical to the standard phenanthrene-9,10-dicarboxylic acid. This experiment showed that $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ is more active than $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for the oxidation of pyrene. Cesium exchanged molybdophosphoric acid was also active in combination with TBHP, which was used instead of H_2O_2. ^1H NMR analysis showed the presence of new signals in the spectrum and obtained conversion was higher than for the same reaction with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Figure 6-10).

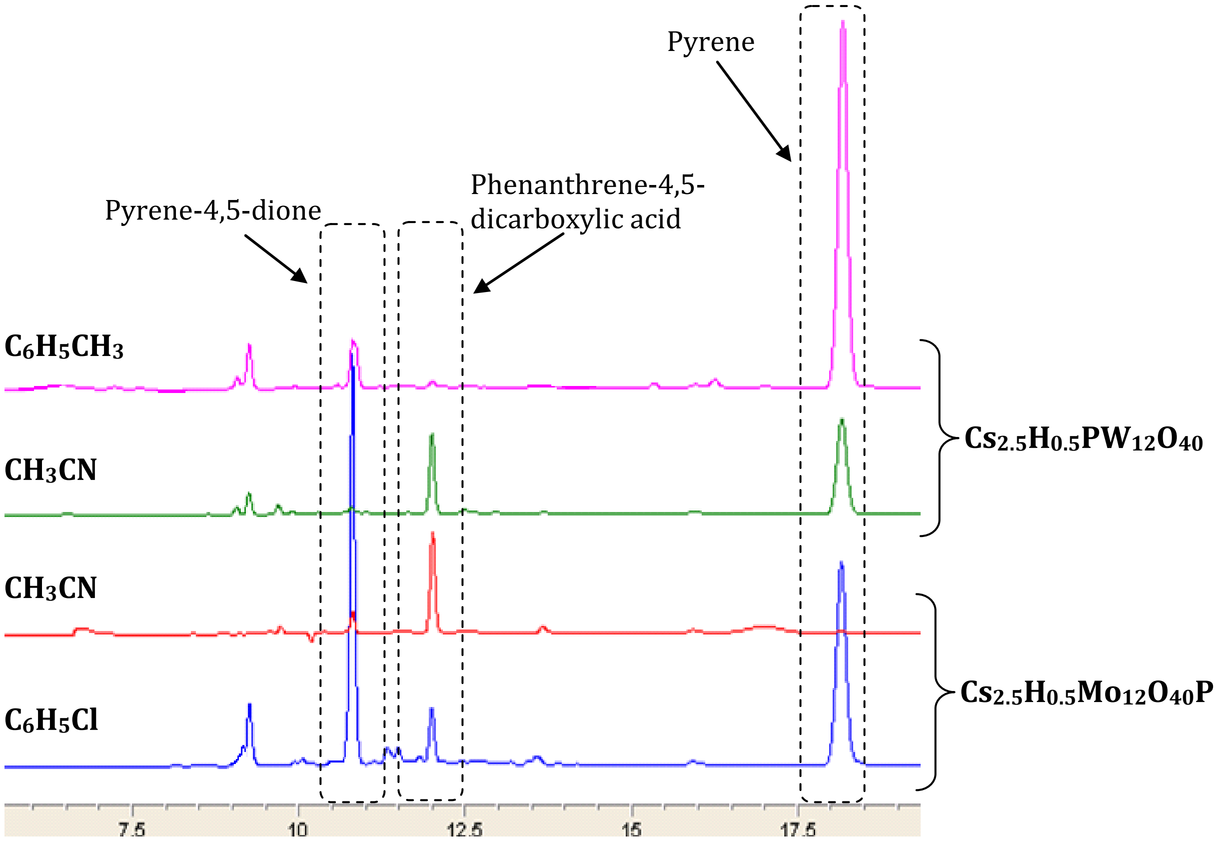


Figure 6–10: Pyrene oxidation using different CsHPAs: Comparison of HPLC chromatograms

6.3.3. Supported HPA

It is becoming more popular to impregnate HPAs on metal or non-metal oxide supports. The reason for impregnation is to increase the accessible external surface and to attain the protonic form of the heteropolyacid [24-25]. Supporting HPAs is a step towards heterogenisation of the catalyst, which will allow the catalyst to be reuse, thus increasing system efficiency and reducing costs. Here, $H_3PW_{12}O_{40}$ was supported on SiO_2 as previously described in the literature [26]. The catalyst was tested for pyrene oxidation and the results were analyzed using ^{1}H NMR and compared against the results generated using the non supported acid. The same amount of tungstophosphoric acid was used in the reaction (0.072g). As seen in figure 6-11, no signals corresponding to pyrene oxidation products were observed in the ^{1}H NMR spectrum when the supported acid was used. This observation indicates that the heterogeneous catalyst was not active for pyrene oxidation and that only the homogeneous phosphotungstic acid is active in this reaction.

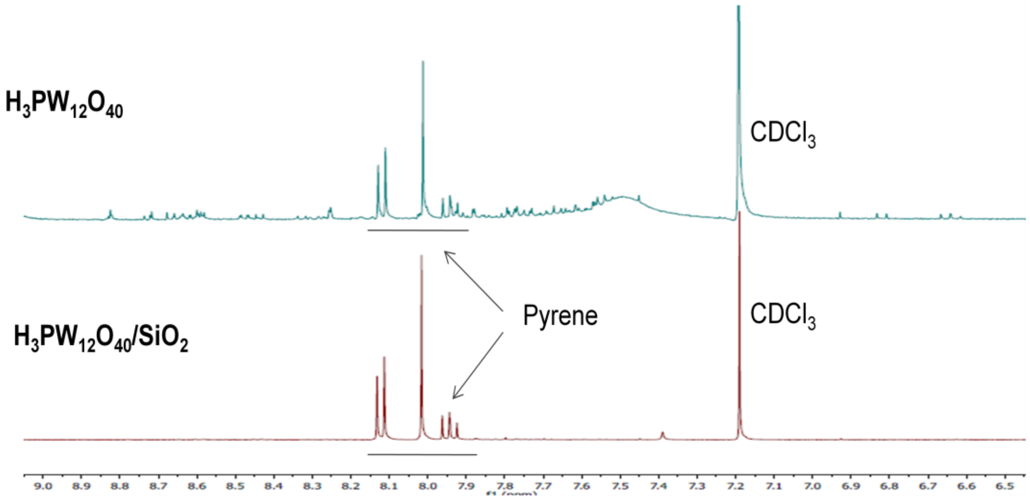


Figure 6–11:^{1}H NMR analysis: Comparison of pyrene oxidation using pure $H_3PW_{12}O_{40}$ (top)and supported $H_3PW_{12}O_{40}/SiO_2$ (bottom).
Reaction conditions: Substrate 0.164 mmol, $H_3PW_{12}O_{40}$ 0.025mmol(0.072g)(top), 36% $H_3PW_{12}O_{40}/SiO_2$ 0.025mmol (0.2g) (bottom), H_2O_2 35% 1.2ml, MeCN 20ml, T=65°C, t=20h

6.3.1. Cs-HPAs supported on ZrO_2

As previously stated, there are two ways of increasing the activity of HPAs. Firstly, by exchanging the protons with alkali metal ions like Cs^+, secondly, by supporting the HPAs on a suitable inert support. The data presented above indicates that supporting the HPAs on SiO_2, did not deliver expected activity. However, it was reported earlier that cesium exchange of the HPAs increased the catalytic activity. Thus the preparation of a cesium exchanged HPA in a supported form could be essential to fully realise the potential of these materials. Instead of using SiO_2, it was decided to use zirconia, a metal oxide having amphoteric character which attracted much attention as a catalyst support [27-28]. Two catalysts, $Cs_{2.5}H_{0.5}PW_{12}O_{40}/ZrO_2$ and $Cs_{2.5}H_{0.5}Mo_{12}O_{40}P/ZrO_2$ were prepared and tested for pyrene oxidation in the presence of TBHP. HPLC analysis of the reaction mixture, found that $Cs_{2.5}H_{0.5}PW_{12}O_{40}/ZrO_2$ yielded conversion of 69% in the reaction, while $Cs_{2.5}H_{0.5}Mo_2O_{40}P/ZrO_2$ gave only 9.7%. The $Cs_{2.5}H_{0.5}Mo_2O_{40}P/ZrO_2$ was more selective with one major product, pyrene-9,10-dione detected as displayed in figure 6-12.

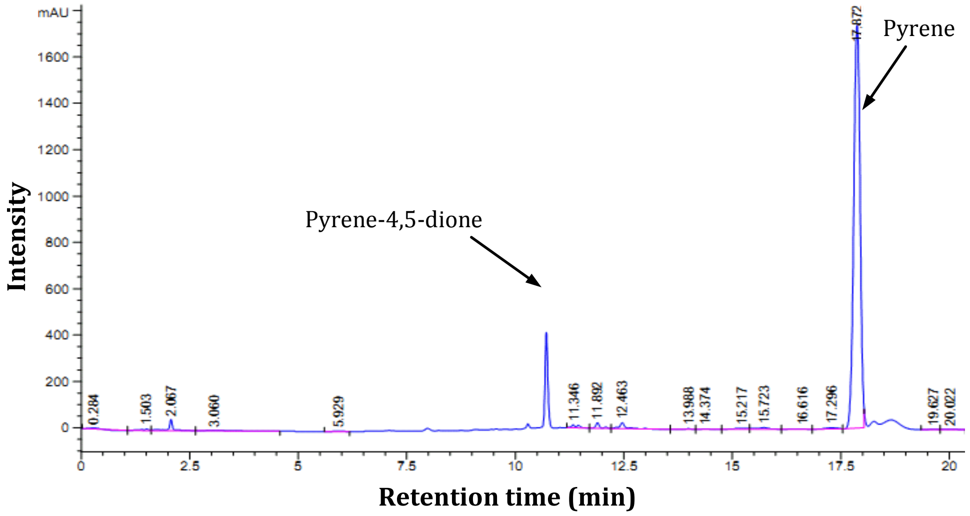


Figure 6–12: HPLC analysis: Pyrene oxidation using $Cs_{2.5}H_{0.5}Mo_{12}O_{40}P/ZrO_2$ and TBHP Reaction conditions: $Cs_{2.5}H_{0.5}Mo_{12}O_{40}P/ZrO_2$ 0.75g, Pyrene 0.1g, C_6H_5Cl 10ml, TBHP 70% 3.5ml, T=90°C, t=20h

Although the high activity displayed by $Cs_{2.5}H_{0.5}PW_{12}O_{40}/ZrO_2$ was a encouraging result, it was essential to test this catalyst for leaching in order to verify this result. Firstly, the reaction mixture in the absence of pyrene was stirred for 6h at 90°C and subsequently filtered. In the next step pyrene was added to the hot filtrate and stirred for 20h at 90°C. ^1H NMR analysis of the reaction mixture showed no significant differences to that observed for the standard reaction. However, conversion based on HPLC analysis was found to be 57%, which was 12% lower than that observed in the standard reaction, thus it was decided to carry out further leaching tests. First step from the previous leaching test was repeated, the catalyst was then filtered and reused. This dried catalyst was loaded into a round bottom flask which contained pyrene, chlorobenzene and TBHP, the solution was subsequently stirred for 20h at 90°C. ^1H NMR and HPLC analysis were carried out on the mixture post reaction with conversion determined at 9.3%. The whole process was repeated for a second run using the same catalyst. Analysis of the second reaction found conversion to be 9.1%. The graphical representation of the conversion obtained versus turn of catalyst runs is given below (Figure 6-13).

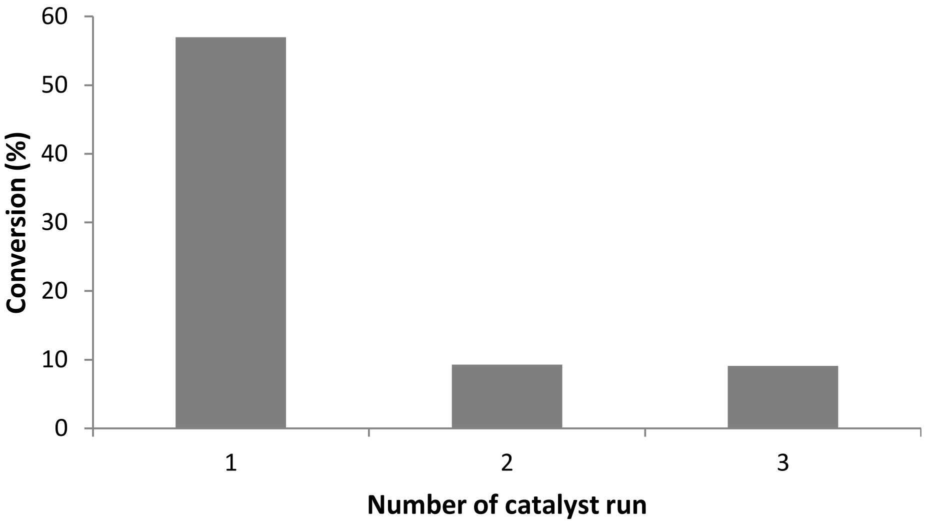


Figure 6–13: Leaching test carried out for $Cs_{2.5}H_{0.5}PW_{12}O_{40}/ZrO_2$ *catalyst*

These results indicate that approximately 9% of the observed conversion comes from the heterogeneous catalyst.

However, data presented above display different activity for Cs exchange heteropolyacids and supported Cs exchanged heteropolyacids. It section 6.3.2. was shown that $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ is more active for pyrene oxidation in comparison to $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. In contrast, when Cs HPAs were supported on ZrO_2, the use of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ /ZrO_2 lead to higher reaction conversion. What is more, it was proved that activity of this catalyst was a result of catalyst leaching. Those findings suggest that the treatment of $H_3PW_{12}O_{40}$ or $H_3PMo_{12}O_{40}$ with Cs salt and ZrO_2 have different influence on final material structure and properties than treatment of $H_3PW_{12}O_{40}$ with only Cs salt.

6.4. Metal supported catalysts

Heterogeneous catalysts are considered desirable from a green chemistry and an engineering point of view. It is impossible to screen every catalyst which has been used in oxidation chemistry. Thus, only a few catalysts containing ruthenium and gold were tested.

6.4.1. Ru-supported catalysts

Ruthenium is a well known metal used in oxidation chemistry and can be used in the form of nanosized metal particles immobilized on different supports. This type of catalyst was used in the oxidation of PAHs, the results of which are presented in the following sections. Catalysts were prepared based on previous literature reports.

6.4.1.1. 5% Ru/TiO_2

TiO_2 was chosen as a support because of its high surface area and thermal stability. Two catalysts with a Ru loading of 5% were prepared by a impregnation method. A detailed description of the preparation method is given in section 2.4.3.1. Uncalcined and calcined catalysts (0.1g) were used in the oxidation of naphthalene. GC-MS analysis showed that when uncalcined catalyst was used, naphthalene, isobenzofuranone and benzoic acid 2-hydroxymethyl were detected. However, when a calcined catalyst was used in the reaction, no oxidation products were detected. It was possible, that the activity displayed by dried catalyst could be the result of metal leaching. Comparison of the UV spectra generated by a standard $RuCl_3$ solution with that of the reaction mixture were found to be identical which suggests the activity displayed by the dried Ru/TiO_2 catalyst was the result of ruthenium leaching into the solvent phase promoting a homogeneous oxidation process (Figure 6-14).

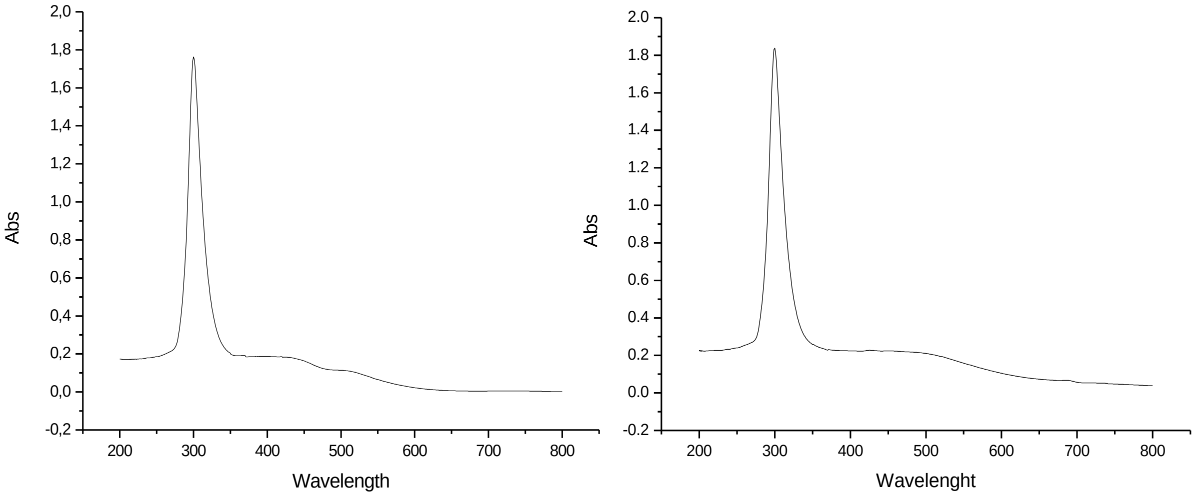


Figure 6–14: UV-Vis analysis: left 5 mg $RuCl_3$ dissolved in 20ml ACN; right: 0.1g 5%Ru/TiO_2 (dried), added to 20ml ACN, Naphthalene 0.05g, $NaIO_4$ 0.6g,H_2O 10ml, t=20h

6.4.1.2. 2.5%Ru/Co_3O_4

Another transition metal oxide support, which was tested in the oxidation of PAHs was Co_3O_4. Here, the catalyst was prepared using adsorption – precipitation method. Catalyst preparation was carried out following a reported literature method outlined in section 2.4.3.2.[5]. A 2.5%Ru/Co_3O_4 catalyst (0.05g) was used in the oxidation of naphthalene as the substrate. $NaIO_4$ (0.3g) was used as a oxidant in the presence of catalyst (50mg), the solvent system was made of 20 ml MeCN and 10ml H_2O. ^1H NMR and GC-MS analysis confirmed the presence of naphthalene and associated oxidation products. A major concern in this reaction was the stability of the catalyst, thus leaching tests using UV-Vis spectroscopy were performed on the postreaction mixture, which showed that observed catalyst activity was due to leaching from the catalyst.

6.4.1.3. Ru/nano-hydroxyapatite

The next ruthenium containing catalyst, screened for PAHs oxidation was a Ru supported nano-hydroxyapatite material, prepared by using a procedure previously reported in the literature [29]. Hydroxyapatite is a highly porous and thermally stable material, suitable as a catalyst support. The Ru catalyst was used in the oxidation of phenanthrene. After 2h of reaction, GC-MS was used to determine the presence of any oxidation product. Phenanthrene 9,10-dione and biphenyl 2,2'-dialdehyde were detected as illustrated below (Figure 6-15).

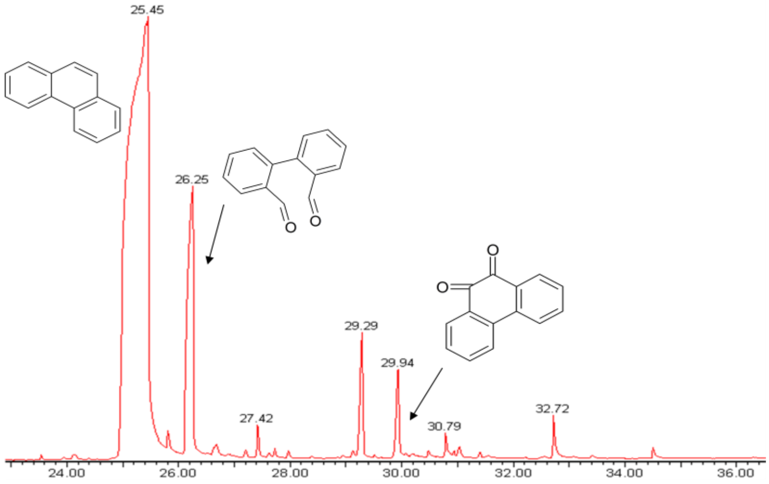


Figure 6–15: GC-MS analysis of phenanthrene oxidation using Ru-nano-HAP Reaction Conditions: Phenanthrene 2 mmols, $NaIO_4$ 3 mmols, Nano Ru-HAP 40 mg, H_2SO_4 0.4N 2ml, EtOAc : MeCN 1:1 (v/v) 12ml, t=2h, T=296K, Conversion 21%

It was necessary to confirm, that the observed activity comes from the heterogeneous catalyst, therefore the system was tested for Ru leaching into the liquid phase. All the reactants, apart from substrate, were stirrer together for 2h and the resultant mixture sent for ICP analysis. Using this technique it was possible to detect Ru in concentration of 1 mg/ml, in the solution which equivalents to 90% of the Ru catalyst loading being leached into solution.

6.4.2. Au-Pd supported catalysts

Supported gold catalysts have lately gain lots of attention due to its high activity and selectivity in oxidation reactions. Although monometallic gold catalysts are active for the oxidation reactions, it was shown that the addition of a second metal, palladium, thus forming an alloy with the gold, significantly enhanced the activity of the catalyst [7]. This synergistic effect led to the wider use of bimetallic catalysts in many oxidation reactions [30-32]. Another important factor, which has an influence on catalyst activity is the preparation method [33]. The differences between the impregnation and sol-immobilization method were highlighted by Hutchings *et al.* [34]. In this chapter we compare the modified impregnation and sol-immobilization methods of catalyst preparation. The modified impregnation method is an upgraded version of standard impregnation method, catalysts prepared via this method contain a large excess of anionic ligands, namely Cl^-, which help disperse the Au and Pd species [35]. The sol-immobilization method permits a greater control of the particle size distribution. During preparation, the method requires the addition of a ligand to prevent particles agglomerating. However, the ligand is known to coat the metal particle and damage catalyst activity [34, 36]. Taking this information into account, it is worth repeating that support choice can be a useful parameter for changing not only catalyst activity but also selectivity in the reaction [37].

Based on the previous literature reports it was decided to test several catalysts with identical metal loading. Results generated during these oxidation reactions are presented in table 6-2. Catalysts prepared by sol immobilization did not exhibit any activity. Amongst all the catalysts prepared by the modified impregnation method, only the 1% (Au-Pd)/C catalyst in the presence of TBHP, used here as co-oxidant, displayed any activity. It has been previously reported that the ubiquitous properties of a carbon support coupled with the addition of a radical initiator, TBHP in the presence of Au nanoparticles often results in high reaction activity [38]. The addition of TBHP helps to activate radicals on the carbon surface whilst the presence of gold activates molecular oxygen. Taken these considerations into account, it can be stated that the different catalyst preparation method led to the differences in conversion observed for the 1%Au-Pd/C catalysts. No activity was observed in the absence of TBHP indicating that the supported gold nanocrystals alone could not activate dioxygen at this reaction temperature. Conversely, conversion of 2.2% was observed when TBHP was added to the reaction mixture in the absence of the catalyst. These experimental observations show that TBHP activated radicals in conjunction with Au nanoparticles are not active for the oxidation of PAHs under the conditions employed.

Table 6-2: Pyrene Oxidation
Reaction Conditions, No. 1,2,3,4: Pyrene 0.1g, catalyst 0.01g, pO_2=20bar T=120°C, $C_6H_5CH_3$ 10ml, t=16h; No.6: pO_2=30bar, C_6H_5Cl 10 ml, T=130°C, t=20h

No.	Catalyst	Method of preparation	Oxidant	Conversion %
1	1%(Au-Pd)/TiO_2	Sol. Immob.	O_2	-
2	1% (Au-Pd)/C	Sol. Immob.	TBHP(15μl)+O_2	-
3	1% (Au-Pd)/MgO	Mod. Impregn.	O_2	-
4	1%(Au-Pd)/TiO_2	Mod. Impregn.	O_2	-
5	1% (Au-Pd)/C	Mod. Impregn.	TBHP(15μl)+O_2	4%
6	-	-	TBHP(15μl)	2.2%

Comparing entries 5 and 6 (Table 6-2), it is clear that the Au-Pd catalyst plays a partial role in this reaction. Calculation of the TON and TOF numbers for reactions 5 and 6 shows a much higher TON/TOF value when the catalyst is used in the reaction (Table 6-3).

Table 6-3: Oxidation of pyrene using different reaction conditions
Reaction Conditions: Pyrene 0.000495mols (0.1g), TBHP n=0.000117mols, p=30bar O_2, T=130°C, t=20h

Catalyst	TON	TOF (h^{-1})
No catalyst	0.094	0.0047
1%Au-Pd/C ($N_{Metals}=6.59*10^{-7}$mols)	30.03	1.502

The main focus of this project was to determine the oxidation selectivity between aliphatic and aromatic carbons in PAHs. The same goals were set for both homogeneous as well as heterogeneous catalysts, so it was important to investigate the oxidation selectivity using a supported gold catalyst. As previously studied, 2-ethylnaphthalene was used as a substrate. All catalysts showed activity with conversion in the range 7%

to 12% as illustrated in table 6-4. However, as was the case in all previous reactions, the major product was 2-acetonaphthone, thus the required selectivity was not achieved. The presence of TBHP increased the reaction activity due to the same reasons as described above. Among all these catalysts prepared by the modified impregnation method, the highest conversion was achieved when MgO was used as a catalyst support.

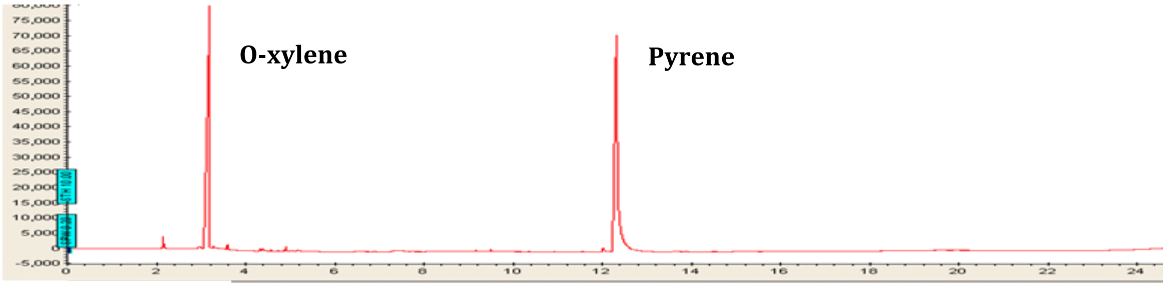
Table 6-4: 2-ethylnaphthalene oxidation
Reaction conditions: Catalyst 0.01g, T=120°C, Reaction 1,2: substrate 10ml, pO_2=20 bar, Reaction 3,4,5: substrate 1 ml, pO_2=25bar

No.	Catalyst	Method of preparation	Oxidant	Conversion %
1	1%(Au-Pd)/C	Sol. Immob.	O_2	7
2	1% (Au-Pd)/C	Sol. Immob.	TBHP(10µl)+O_2	12
3	1% (Au-Pd)/C	Mod. Impregn.	O_2	8
4	1%(Au-Pd)/TiO_2	Mod. Impregn	O_2	10
5	1% (Au-Pd)/MgO	Mod. Impregn	O_2	12

The MgO support is basic in character and most probably interacted with the Cl^- anions resulting in the Au-Pd nanoparticles being strongly bond to the support. However, it was previously observed that oxidation of alcohols to aldehydes occurs solely in the presence of MgO and O_2. This is also likely to be the case in this present study, and we strongly believe that more detailed studies are required to conclusively determine the nature of the active species.

In the last part of experimental work, oxidation of pyrene by the combined oxidants and catalysts was performed. Taking into account the activity displayed by H_2WO_4, it was decided to test this catalyst in the presence of Au-Pd/C catalyst. Reaction was performed in the autoclave under 30bar O_2 pressure, with addition of TBHP. Based on GC analysis it can be stated that the reaction resulted in complete pyrene consumption as shown below (Figure 6-16).

Before reaction



After reaction

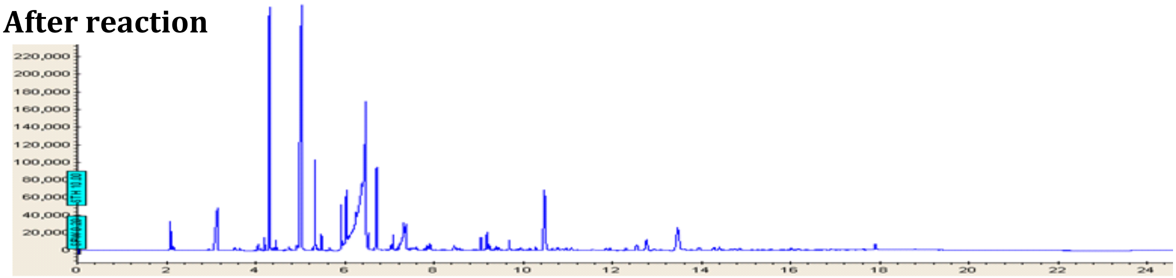


Figure 6–16: GC analysis: Comparison of reaction mixture before and after pyrene oxidation
Reaction Conditions: Pyrene 0.2g, O-xylene 10ml, 1%Au-Pd/C(mod. impr.) 0.1g, H_2WO_4 0.01g, TBHP 15µl, T=140°C, t=20h, p=30bar

However, no identification of the products obtained during the reaction was performed. What is more, o-xylene, used here as a solvent, also underwent oxidation, what can be deduced from GC chromatogram. Here, Au-Pd catalyst in combination of H_2WO_4, molecular oxygen and TBHP turned out to be a system, which displayed high activity for the oxidation of pyrene. It is believed, that this finding can open a whole new are of study on the selective oxidation of PAHs.

6.5. Conclusions

The results presented and discussed in this chapter clearly show that many different catalysts can be applied to the oxidation of polynuclear aromatic hydrocarbons.

Firstly, tungsten based catalysts were investigated. It was found that WO_3 can be used as a replacement for H_2WO_4. Therefore, it is believed that mechanism of the oxidation is the same for WO_3 and H_2WO_4 with combination of H_2O_2. However, to the best of our knowledge this is the first report where those two catalysts are compared and used for PAHs oxidation.

It has been shown that WO_3 can be supported on TiO_2 and in theory used as a heterogeneous catalyst. Leaching testing of the catalyst showed that WO_3/TiO_2 did not behave like a heterogeneous catalyst which is not in agreement with the literature. Yang *et al.* used a catalyst prepared by incipient-wetness for the oxidation of cyclopentene and no obvious loss of tungsten from the WO_3/TiO_2 catalyst was observed [14]. This is probably due to the core shell structure of the catalyst where a titania shell is surrounding the WO_3 layer. Jin *et al*. used similar catalyst, WO_3/SiO_2 prepared by incipient wetness impregnation for the same reaction and observed oxidative cleavage of carbon-carbon double bond and formation of glutaraldehyde [39]. Based on the results presented here, it is difficult to comment on the catalyst structure as no characterization of the catalyst was carried out. However, the authors of the preparation method applied in this thesis, reported that obtained catalyst consist of TiO_2 surface, partially coated by WO_3 layer [15]. Most probably, introduction of H_2O_2 to the reaction system caused rinsing off the WO_3 coating.

It was presented that Keggin structure heteropolyacids are active for phenanthrene, pyrene and 2-ethylnaphthalene oxidation. However, the oxidation of 2-ethylnaphthalene did not provide the required selectivity. These results are similar to that observed when the oxidation was carried out using transition metal substituted polyoxometalates including mono, di-and tri-substituted Keggin-type anions. In the literature, oxidation of 2-ethylnaphthalene occurs predominantly at the alkyl side chains [40]. These active catalysts were then supported on SiO_2, which was seen as a step towards heterogenisation. However, impregnation of the SiO_2 with the acids, did not lead to the expected results and the catalyst was inactive for PAHs oxidation. Lukasiewicz *et al*. supported a similar HPA, tungstoboric acid, on a SiO_2 and reported its activity during microwave assisted oxidation of some aromatics. However, the authors of this work did not test for catalyst leaching, so it is difficult to judge the heterogeneity of this catalyst [18]. Moreover, it was shown that Cs exchanged heteropolyacids supported on ZrO_2 also exhibit high activity for PAHs oxidation. Unfortunately, only 9% of the total conversion comes from the heterogeneous catalysts, leaching of the Cs from the catalyst contributes to the overall reaction conversion. No characterization of the catalyst was performed, which may of helped identify the source of the leaching. Most probably the catalyst preparation method employed will have an influence on catalyst leaching. Immobilization of HPA onto mesoporous silica has gain much attention recently. It was reported that by grafting molybdovanadophosphoric acid onto modified SBA-15 it was possible to oxidize anthracene with a conversion of more than 50% [41].This is an approach which may benefit PAHs oxidation and should be considered in future plans.

Considering the results obtained after the oxidation using Ru supported catalysts, it is clear that homogeneity of this reaction remains an issue. Catalysts prepared following the literature methods did not show the reported stability. Unfortunately, no characterization of the catalyst was carried out which raises the question about the heterogeneity of the catalytic system. The catalysts tested were chosen from many Ru based catalyst with the main attention paid to its heterogeneity and simplicity. In the literature there are a number of papers describing the use of $RuCl_3$ with H_2O_2 for phenanthrene and naphthalene oxidation. Although the system is very simple, there are safety concerns surrounding the use of these materials [42-43].

In reference to the Au-Pd catalysts it is clear that the method of preparation has an influence on catalyst activity. It is believed that particle size could play a major role. It has been previously reported by Hutchings *et al*. that the median particle size for the sol-immobilised Au–Pd alloy are 5.1 nm and 3.8 nm, respectively, on the C and TiO_2 supports [30]. Catalyst particles prepared by modified impregnation exhibit a homogeneous dispersion of metal nanoparticles and were observed to be in the 2-5 nm size range [35]. This clearly shows that the metal nanoparticles generated are smaller when a modified impregnation method was used in catalyst preparation. When the experiment was carried out in the absence of catalyst but in the presence of TBHP it was observed that only 50% of the total conversion is attributed to heterogeneous oxidation. It is difficult to discuss the active site of the catalyst, as limited data on the catalyst was collected. Another interesting observation came with the oxidation of 2-ethylnaphthalene. This molecule, undergoes an oxidation more easily than pyrene. The reason may be the size of the molecule or the presence of the aliphatic chain and therefore aliphatic C. The aliphatic C was oxidized to the corresponding C=O and thus 2-acetonaphthone was observed. Because no detailed product distribution was studied, it is difficult to propose a mechanism for this oxidation. It was also shown that bimetallic catalyst, Au-Pd/C in the presence of H_2WO_4, TBHP and molecular oxygen is active for the oxidation of pyrene. However, further investigation in this field is needed.

To conclude, it is clear that the field of heterogeneous catalysis is potentially applicable to PAHs oxidation and the use of molecular oxygen as oxidants is possible thread of research in this area.

6.6. References

1. Strukul, G., *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*. ed. G. Strukul **1992**, Kluwer Academic Publishers.
2. Noyori, R., Aoki, M., and Sato, K., *Chemical Communications*, **2003**(16), 1977
3. Kozhevnikov, I.V., *Chemical Reviews*, **1998**, 98(1), 171
4. Mori, K., Yamaguchi, K., Mizugaki, T., Ebitani, K., and Kaneda, K., *Chemical Communications*, **2001**(5), 461
5. Li, F., Chen, J., Zhang, Q., and Wang, Y., *Green Chemistry*, **2008**, 10(5), 553
6. Della Pina, C., Falletta, E., Prati, L., and Rossi, M., *Chemical Society Reviews*, **2008**, 37(9), 2077
7. Enache, D.I., Edwards, J.K., Landon, P., Solsona-Espriu, B., Carley, A.F., Herzing, A.A., Watanabe, M., Kiely, C.J., Knight, D.W., and Hutchings, G.J., *Science*, **2006**, 311(5759), 362
8. Barton, D.G., Soled, S.L., and Iglesia, E., *Topics in Catalysis*, **1998**, 6(1-4), 87
9. Benitez, V.M., Querini, C.A., Figoli, N.S., and Comelli, R.A., *Applied Catalysis a-General*, **1999**, 178(2), 205
10. Spamer, A., Dube, T.I., Moodley, D.J., van Schalkwyk, C., and Botha, J.M., *Applied Catalysis a-General*, **2003**, 255(2), 133
11. van Schalkwyk, C., Spamer, A., Moodley, D.J., Dube, T., Reynhardt, J., and Botha, J.M., *Applied Catalysis a-General*, **2003**, 255(2), 121
12. Hino, M. and Arata, K., *Journal of the Chemical Society-Chemical Communications*, **1988**(18), 1259
13. Soled, S., Dispenziere, N., and Saleh, R., *Anion-Treated Solid Acids for Butene Dimerization*. Progress in Catalysis, ed. K.S.E. Smith. **Vol. 73 1992**. 77.
14. Yang, X.L., Dai, W.L., Guo, C.W., Chen, H., Cao, Y., Li, H.X., He, H.Y., and Fan, K.N., *Journal of Catalysis*, **2005**, 234(2), 438
15. Tsukamoto, D., Ikeda, M., Shiraishi, Y., Hara, T., Ichikuni, N., Tanaka, S., and Hirai, T., *Chemistry-a European Journal*, **2011**, 17(35), 9816
16. Mizuno, N. and Misono, M., *Chemical Reviews*, **1998**, 98(1), 199
17. Heydari, A., Khaksar, S., Akbari, J., Esfandyari, M., Pourayoubi, M., and Tajbakhsh, M., *Tetrahedron Letters*, **2007**, 48(7), 1135
18. Lukasiewicz, M., Bogdal, D., and Pielichowski, J., *Molecular Diversity*, **2006**, 10(3), 491
19. Rao, K.T.V., Rao, P.S.N., Prasad, P.S.S., and Lingaiah, N., *Catalysis Communications*, **2009**, 10(10), 1394
20. Okuhara, T. and Misono, M., *Journal of Synthetic Organic Chemistry Japan*, **1993**, 51(2), 128
21. Shiju, N.R., Williams, H.M., and Brown, D.R., *Applied Catalysis B-Environmental*, **2009**, 90(3-4), 451
22. Dimitratos, N. and Vedrine, J.C., *Applied Catalysis a-General*, **2003**, 256(1-2), 251
23. Marosi, L. and Arean, C.O., *Journal of Catalysis*, **2003**, 213(2), 235
24. Nowinska, K., Fiedorow, R., and Adamiec, J., *Journal of the Chemical Society-Faraday Transactions*, **1991**, 87(5), 749
25. Misono, M., *Catalysis Reviews-Science and Engineering*, **1987**, 29(2-3), 269
26. Staiti, P., Freni, S., and Hocevar, S., *Journal of Power Sources*, **1999**, 79(2), 250
27. Devassy, B.M. and Halligudi, S.B., *Journal of Catalysis*, **2005**, 236(2), 313
28. Jagadeeswaraiah, K., Balaraju, M., Prasad, P.S.S., and Lingaiah, N., *Applied Catalysis a-General*, **2010**, 386(1-2), 166

29. Viau, G., Brayner, R., Poul, L., Chakroune, N., Lacaze, E., Fievet-Vincent, F., and Fievet, F., *Chemistry of Materials*, **2003**, 15(2), 486
30. Dimitratos, N., Lopez-Sanchez, J.A., Anthonykutty, J.M., Brett, G., Carley, A.F., Tiruvalam, R.C., Herzing, A.A., Kiely, C.J., Knight, D.W., and Hutchings, G.J., *Physical Chemistry Chemical Physics*, **2009**, 11(25), 4952
31. Dimitratos, N., Lopez-Sanchez, J.A., Meenakshisundaram, S., Anthonykutty, J.M., Brett, G., Carley, A.F., Taylor, S.H., Knight, D.W., and Hutchings, G.J., *Green Chemistry*, **2009**, 11(8), 1209
32. Edwards, J.K., Solsona, B., N, E.N., Carley, A.F., Herzing, A.A., Kiely, C.J., and Hutchings, G.J., *Science*, **2009**, 323(5917), 1037
33. Porta, F., Prati, L., Rossi, M., and Scari, G., *Journal of Catalysis*, **2002**, 211(2), 464
34. Lopez-Sanchez, J.A., Dimitratos, N., Miedziak, P., Ntainjua, E., Edwards, J.K., Morgan, D., Carley, A.F., Tiruvalam, R., Kiely, C.J., and Hutchings, G.J., *Physical Chemistry Chemical Physics*, **2008**, 10(14), 1921
35. Sankar, M., Morad, M., Pritchard, J., He, Q., Freakley, S.J., Edwards, J.K., Taylor, S.H., Carley, A.F., Knight, D.W., Kiely, C.J., and Hutchings, G.J., *ACS Nano*, **2012**, submitted,
36. Lopez-Sanchez, J.A., Dimitratos, N., Hammond, C., Brett, G.L., Kesavan, L., White, S., Miedziak, P., Tiruvalam, R., Jenkins, R.L., Carley, A.F., Knight, D., Kiely, C.J., and Hutchings, G.J., *Nature Chemistry*, **2011**, 3(7), 551
37. Sankar, M., Nowicka, E., Tiruvalam, R., He, Q., Taylor, S.H., Kiely, C.J., Bethell, D., Knight, D.W., and Hutchings, G.J., *Chemistry-a European Journal*, **2011**, 17(23), 6524
38. Edwards, J., Landon, P., Carley, A.F., and Hutchings, G.J., *Journal of Materials Research*, **2007**, 22(4), 831
39. Jin, R.H., Li, H.X., and Deng, J.F., *Journal of Catalysis*, **2001**, 203(1), 75
40. Estrada, A.C., Simoes, M.M.Q., Santos, I.C.M.S., Neves, M.G.P.M.S., Cavaleiro, J.A.S., and Cavaleiro, A.M.V., *Chemcatchem*, **2011**, 3(4), 771
41. Bordoloi, A., Lefebvre, E., and Halligudi, S.B., *Journal of Catalysis*, **2007**, 247(2), 166
42. Tandon, P.K., Baboo, R., Singh, A.K., Purwar, G., and Purwar, M., *Applied Organometallic Chemistry*, **2005**, 19(10), 1079
43. Tandon, P.K., Baboo, R., Singh, A.K., and Gayatri, *Applied Organometallic Chemistry*, **2006**, 20(1), 20

7. Final conclusions and future work

7.1. Final conclusions

The main aim of the work presented in this thesis was to investigate the possibility of upgrading heavy oils, resids and bitumens through the selective oxidation of Polynuclear Aromatic Hydrocarbons. As previously discussed in chapter 1, the controlled oxidation of heavy aromatics is more appealing to that of hydrocracking or coking, which are currently the most popular methods of heavy oils upgrading. Using a controlled oxidation protocol, molecules containing 4 aromatic rings would be oxidized to compounds containing 3 aromatic rings, lowering the amount of coke formation and moreover leading to product containing oxygen and olefins. The major requirements for controlled oxidation were:

1) To selectively oxidise aromatic carbon and not aliphatic carbon.
2) The rate of oxidation has to be faster for aromatics with more fused aromatic rings.
3) One aromatic ring at a time should be oxidized and subsequently ring opened.
4) Over oxidation must be minimized so that 4R is oxidized to 3R and not to 2R.

In this present study, the oxidation of PAHs was extensively studied on model compounds via the application of different approaches involving the use of homogeneous and heterogeneous catalysis. In addition, the oxidation of heteroaromatics and the removal of metals from metalloporphyrins has also been reported. The data obtained during this study confirmed that the introduction of controlled and selective oxidation of PAHs is possible and can become a major method of heavy oils, bitumens and resids upgrading.

Initial research described in chapter 3 focused on Ruthenium Ion Catalyzed Oxidation Chemistry (RICO). It was shown that changes to the solvent system, from a previously reported biphasic to a monophasic system resulted in the desired selectivity in the oxidation of polynuclear aromatic hydrocarbons (oxidation of one aromatic ring), thus fulfilling one of the major requirements of the project. One of the products of phenanthene oxidation was biphenyl 2,2'-dialdehyde while the oxidation of pyrene led to the production of phenanthrene-4,5-dialdehyde via the control of reaction time and the use of quenching reagents. To understand the phenomena of selective oxidation in a monophasic solvent system, a mechanistic investigation was performed. Primary Kinetic Isotope effect (H_2O/D_2O) and incorporation of O^{18} (H_2O^{18}) into the oxidation products clearly showed the involvement of water in the reaction mechanism. These experiments helped to gain a better understanding of RICO chemistry [1].

It was also demonstrated that ruthenium chemistry is selective for the oxidation of aromatic carbon while leaving the aliphatic carbon mainly untouched. Based on the experiments performed, it was found that more than 85% of 2-ethylnaphthalene oxidation products have a preserved alkyl chain. In chapter 3 and 4 much effort was given to the development of a NMR methodology, which would allow the quantification of preserved aliphatic protons versus aromatic protons, without using complicated analytical procedures [2]. Based on this methodology and the results obtained, a conclusion was formed that the reaction conversion is higher for molecules with longer alkyl chain and the reactivity of the alkyl chain in alkylated aromatics is chain length dependent and the longer the length of the alkyl chain, the greater amount of aliphatic carbons is preserved after oxidation. Investigating those results, it is clear that selectivity in RICO reaction is directed towards aromatic carbons, mainly due to the electron donating character of the aliphatic chain. Taking into account that the majority of naturally occurring resids and bitumens contain alkylated PAHs, this clearly confirms that RICO chemistry is a suitable system for PAHs upgrading .

The work presented in chapter 3 and 4 also contributes to a better understanding of PAHs oxidation rates. It was shown that bigger compounds react faster than smaller compounds, which is the results of electron stabilization inside the aromatic ring. This successfully confirmed that in RICO chemistry, the rate of oxidation increases with an increasing number of fused aromatic rings (4R > 3R).

An additional aim of this thesis, was to shown that RICO chemistry can be successfully used to remove metal from metalloporphyrins, which are well known as unwanted materials in the petroleum industry. The biggest advantage of using a biphasic solvent system for this application, is that during the reaction, the metal is transported from the organic phase to the aqueous phase. This simple migration allows the metal to be easily removed from the system post reaction.

Chapter 5 is related to the oxidation of PAHs using H_2WO_4/H_2O_2 and several key findings described there, need to be emphasized. It has to be highlighted that this chemistry fulfilled all the requirements set for selective oxidation of PAHs. Firstly, it was shown that the H_2WO_4/H_2O_2 system is highly selective with one aromatic ring being oxidized at a time, even without the addition of quenching reagents or control of the time of reaction. It is worth remind that when H_2WO_4/H_2O_2 system was applied for PAHs oxidation, pyrene was selectively converted to phenanthrene-4,5-dicarboxylic acid, while phenanthrene to biphenyl-2,2'-dicarboxylic acid. With reference to the requirement to selectively oxidise aromatic carbons, it was shown that selectivity can be controlled by changing the solvent system. The use of acetonitrile as a solvent led solely to the oxidation of aromatic carbons, no aliphatic carbons. The outstanding properties of acetonitrile and the formation of a monophasic solvent system with H_2O_2 as observed with RICO chemistry, had an influence on product distribution. The reason probably lies in the formation of different oxo or peroxospecies. Unfortunately, not enough experimental information was obtained to confirm it. It is also important to remember that in a monophasic solvent system the contact between oxidant, substrate and catalyst is facilitated by presence of one phase. It is worth pointing out, that from results obtained for the oxidation of bigger molecules, based on previously developed NMR methodology, was found that the aromatic carbon is oxidized, leaving aliphatic carbon untouched, even in non polar solvents like chlorobenzene. The reaction mechanism responsible for this transformation in a biphasic solvent system is much better known, however, it is believed that the exceptional nature of tungsten plays a major role in determining selectivity [3]. Although the character of this chemistry is completely different to that of RICO, it was shown that the rate of oxidation increases with an increasing number of fused aromatic rings. This chemistry undoubtedly has the potential to be used in the petroleum industry for heavy oil upgrading. What is more, the use of H_2WO_4 and H_2O_2 is more convenient from an economical and green chemistry point of view. It was also shown that this tungsten chemistry can be applied, to the oxidative desulfurization of heteroaromatics confirming previous literature reports [4]. What is more, the use of H_2O_2 in combination with H_2WO_4 is a convenient method for the removal of metals from metalloporphyrins.

Experiments presented in chapter 6 show the possibility of upgrading heavy oils, resids and bitumens using a wide range of different catalysts. Not only the presence of ruthenium or tungsten catalyst results in the successful and selective oxidation of PAHs, but also the application of Keggin structure polyoxometalates can transform presented aromatic compounds to useful oxygenated products. This preliminary study using a number of tungsten based catalysts, such as Cs–exchange and ZrO_2 supported heteropolyacids showed a large potential in the field of PAHs selective oxidation. It was also shown, that Au-Pd catalysts can be active for the oxidation of pyrene. The use of bimetallic catalysts, TBHP, molecular oxygen (as a replacement of H_2O_2) in the presence of H_2WO_4 is a new lead in this area of research. It is believed that TBHP, a known radical initiator, interacts with the carbon catalyst support and H_2WO_4 to form the active species. The role of gold is to activate molecular oxygen and the presence of palladium increase the overall rate of reaction due to the synergistic effect. However, the biggest advantage of Au-Pd supported catalysts is their heterogeneous character, stability and reusability.

To conclude, in this thesis it was shown that many different approaches can be undertaken for the selective oxidation of model PAHs substrates. What is more, the solutions presented here have the potential to be used for heavy oils, bitumens and residues upgrading. This can be achieved by controlling quenching agents, reaction time, amount of oxidant, type of catalyst, reaction temperature and solvent used.

7.2. Future plans

Future plans for this project are mainly focused on the application and development of the oxidation systems studied in this thesis and their application in the oxidation of petroleum derived heavy oils, resids and bitumens. First of all, this would include the application of RICO chemistry, where experimental principles and the reaction mechanism are well understood.

Further work would concentrate on the tungsten catalytic system containing H_2WO_4 and H_2O_2 and its use for the upgrading of petroleum materials. Simultaneously, it is proposed to investigate in detail the reaction mechanism when oxidation is carried out in a monophasic solvent system. Since different selectivity was observed for 2-ethylnaphthalene oxidation in acetonitrile and chlorobenzene, it is believed that diverse species can be responsible for substrate transformation. The study would include careful *in situ* investigation with the use of IR and UV-Vis as previously reported [5]. What is more, oxidation of PAHs with longer alkyl chains would be needed. The quantification of compounds with preserved alkyl chain was only carried out for 3 substrates, thus any future work should concentrate on the quantification of all compounds as was previously done for RICO chemistry.

One of the most important future research goals would be the heterogenisation of the tungsten system, which has shown great potential. It has been previously reported that W and W, P exchanged amberlite have been used for the oxidation of olefins [6]. It is possible that by applying small modifications, such as increasing the loading of W or thermal treatment during the catalyst preparation, the successful oxidation of PAHs can be achieved. It has also been reported that the incorporation of tungsten oxide into mesoporous silica performed as a highly efficient epoxidation catalyst in the presence of H_2O_2 and $NaHCO_3$, a cheap and easy accessible co-catalyst [7]. It seems logical that by increasing the reaction temperature (reported 30°C), this system can also be applied to PAHs oxidation.

As previously reported, preliminary studies with polyoxometalates showed great potential for PAHs oxidation and the upgrading of petroleum derivatives. The field of oxidation using HPAs is very broad and provides unlimited possibilities in its application. Firstly, the development in this field would include full product identification for model PAHs oxidation in conjunction with detailed, mechanistic and structure investigation. Conversely, heterogenisation of heteropolyacids is also very promising, thus future work in this field should also focus on the impregnation of HPAs onto different supports such as SiO_2[8], C[9] and γ-Al_2O_3 or their incorporation into mesoporous materials [9-10]. The exchange of metals into the heteropolyacids structure was reported by many researches to be a factor in increasing activity, thus it is proposed to perform several experiments where cobalt or vanadium is incorporated into the HPA material [11-12]. In addition, oxidation experiments using molecular oxygen in place of H_2O_2, will also be studied. To obtain a better understating of the oxidation mechanism the catalyst will have to be fully characterised. This would include a surface area study, X-ray diffraction, UV-Vis and IR analysis.

Results obtained from the Au-Pd supported catalyst studies clearly show the potential for improvement in this area. The application of heterogeneous catalysis for the oxidation of PAHs is rather unexplored with only preliminary experiments being undertaken. A modified impregnation catalyst in the presence of H_2WO_4 as co-catalyst was shown to be active for the oxidation of pyrene resulting in 100% conversion. Full characterization of Au-Pd catalyst including BET, XRD, SEM, TEM is needed. In addition, it is planed to investigate in detail the active species formed during the reaction with H_2WO_4, Au-Pd/C in the presence of TBHP. *In situ* IR studies could contribute to a better understanding of this reaction. What is more, optimization of the reaction conditions employed, such as changing oxygen pressure, temperature, catalyst loading, solvent, would hopefully contribute to better reaction conversion and selectivity towards products with one opened ring. Taking into account the outstanding properties of tungsten, gold and palladium, it is desirable to prepare a range of heterogeneous catalyst with different metal loadings (e.g.: 1%Au-Pd/WO_3), which may improve the activity exhibited for PAHs oxidation [13-14].

Following the requirements of green chemistry, the most important challenge for future work is the invention of a system applicable to heavy oil upgrading, where air would be used as an oxidant in the presence of a low cost catalyst at a temperature below 110°C. For preliminary studies, we propose the use of cheap nitrate salts, e.g.: $Fe(NO_3)_3$ or $Ni(NO_3)_2$, which are well known in oxidation reactions.

7.2. References

1. Tabatabaeian, K., Mamaghani, M., Mahmoodi, N.O., and Khorshidi, A., *Catalysis Communications*, **2008**, 9(3), 416
2. Artok, L., Murata, S., Nomura, M., and Satoh, T., *Energy & Fuels*, **1998**, 12(2), 391
3. Noyori, R., Aoki, M., and Sato, K., *Chemical Communications*, **2003**(16), 1977
4. Sato, K., Hyodo, M., Aoki, M., Zheng, X.Q., and Noyori, R., *Tetrahedron*, **2001**, 57(13), 2469
5. Barrio, L., Campos-Martin, J.M., and Fierro, J.L.G., *Journal of Physical Chemistry A*, **2007**, 111(11), 2166
6. Hoegaerts, D., Sels, B.F., de Vos, D.E., Verpoort, F., and Jacobs, P.A., *Catalysis Today*, **2000**, 60(3-4), 209
7. Bera, R. and Koner, S., *Inorganica Chimica Acta*, **2012**, 384, 233
8. Mao, J.X., Nakajo, T., and Okuhara, T., *Chemistry Letters*, **2002**(11), 1104
9. Bordoloi, A., Lefebvre, E., and Halligudi, S.B., *Journal of Catalysis*, **2007**, 247(2), 166
10. Wu, Y., Ye, X.K., Yang, X.G., Wang, X.P., Chu, W.L., and Hu, Y.C., *Industrial & Engineering Chemistry Research*, **1996**, 35(8), 2546
11. Shringarpure, P. and Patel, A., *Journal of Molecular Catalysis a-Chemical*, **2010**, 321(1-2), 22
12. Romanelli, G.P., Villabrille, P.I., Vazquez, P.G., Caceres, C.V., and Tundo, P., *Letters in Organic Chemistry*, **2008**, 5(5), 332
13. Kalidindi, S.B. and Jagirdar, B.R., *Chemsuschem*, **2012**, 5(1), 65
14. Hashmi, A.S.K. and Hutchings, G.J., *Angewandte Chemie-International Edition*, **2006**, 45(47), 7896

8. Appendix

8.1. Pyrene-4,5-dione

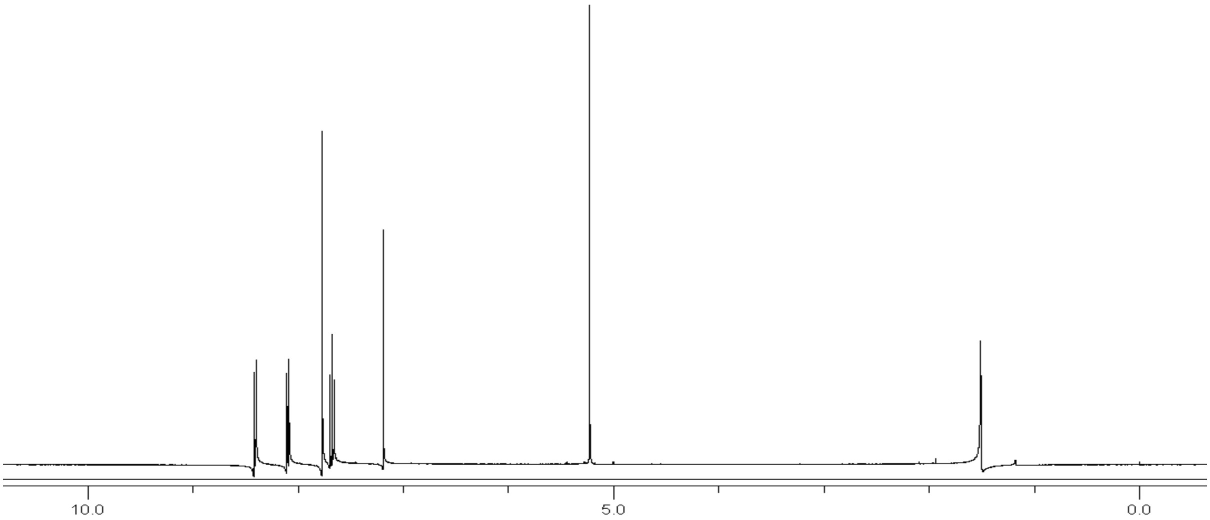


Figure 8–1: ^{1}H NMR analysis: Pyrene-4,5,-dione

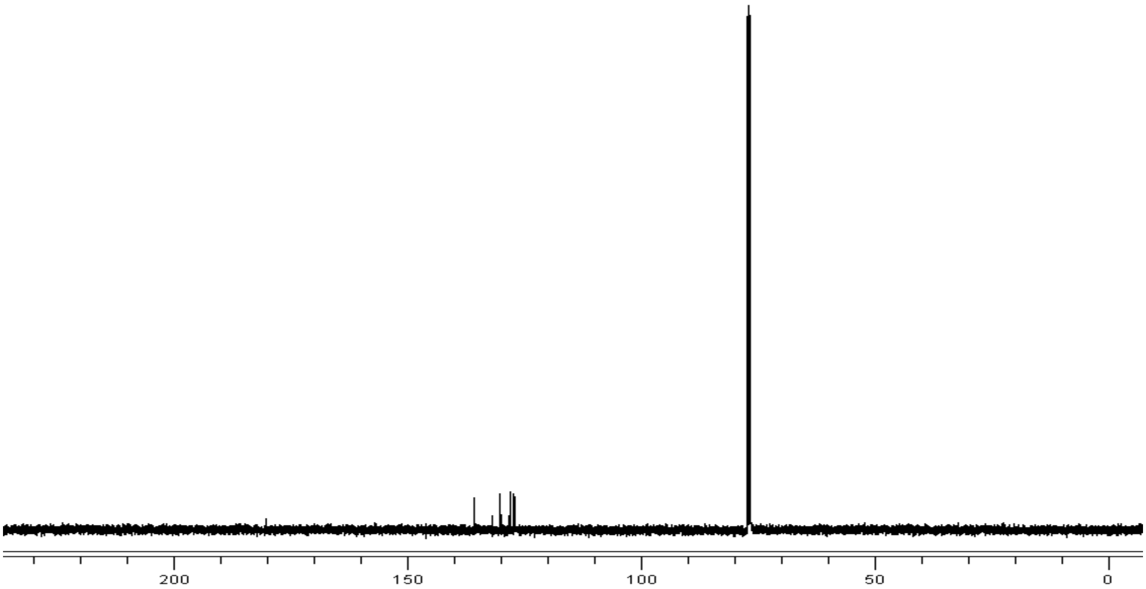


Figure 8–2: ^{13} C NMR analysis: Pyrene-4,5-dione

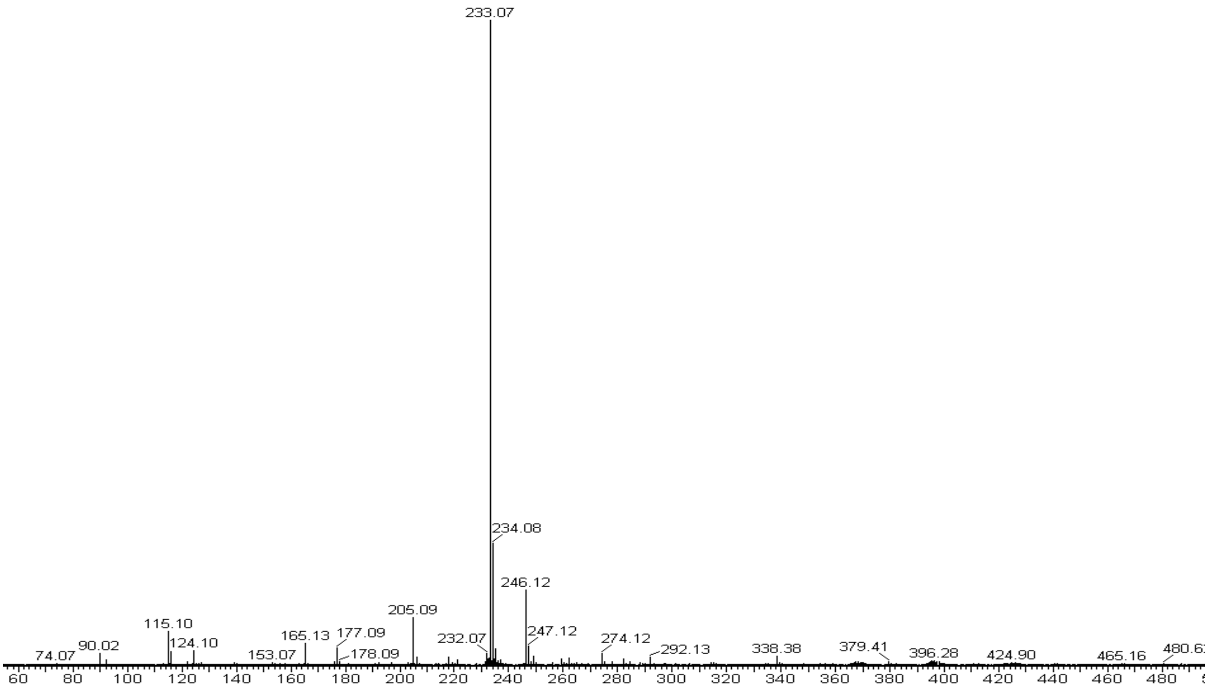


Figure 8–3: MS(ES+) analysis: Pyrene-4,5-dione

8.2. Pyrene-4,5,9,10-tetraone

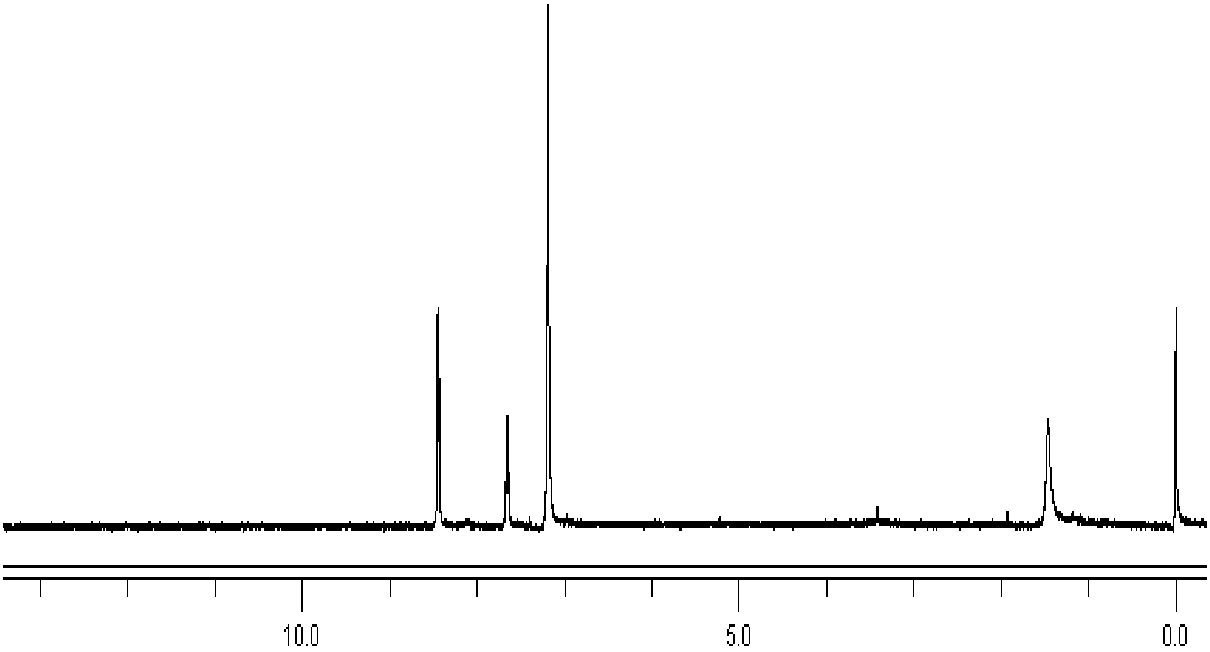


Figure 8–4: ^{1}H NMR analysis: Pyrene-4,5,9,10-tetraone

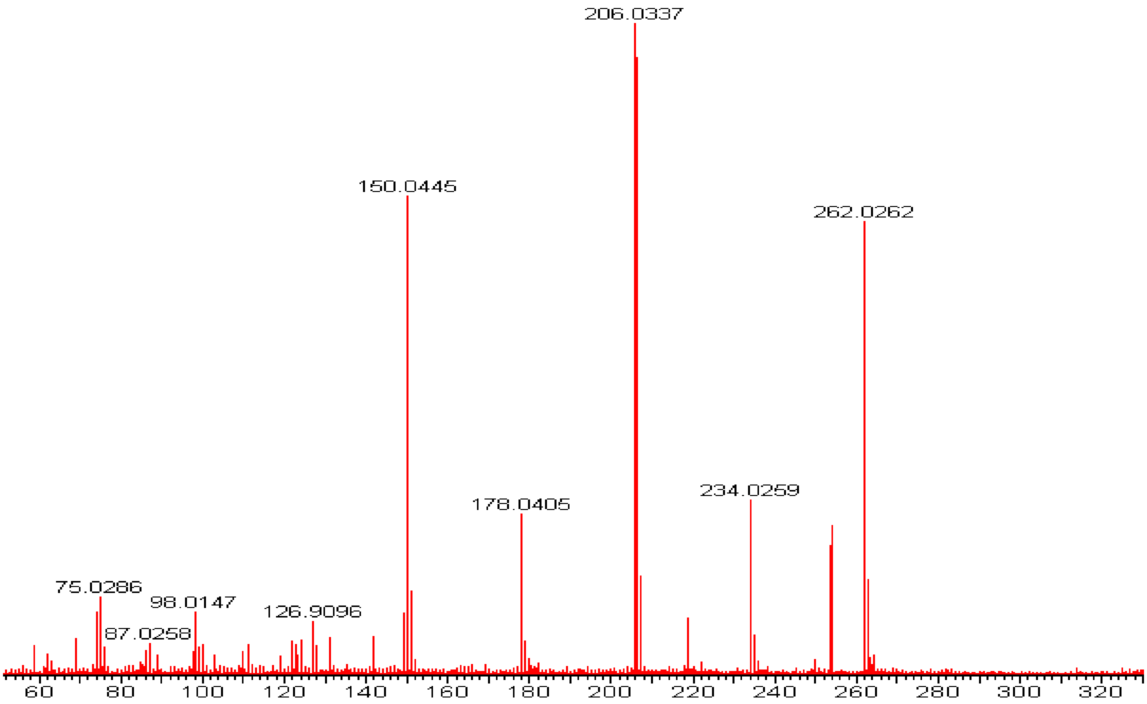


Figure 8–5: MS analysis: Pyrene-4,5,9,10-tetraone

8.3. Naphthalene

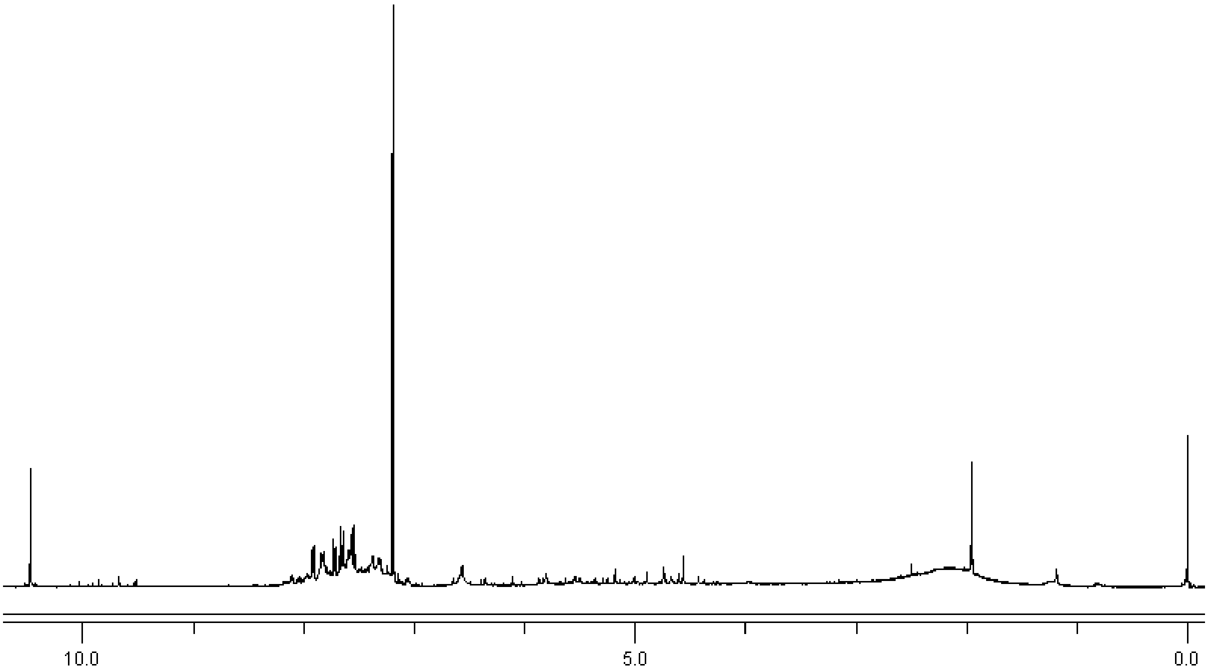


Figure 8–6: ^{1}H NMR analysis: Naphthalene oxidation in monophasic solvent system