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Oxidation of Polynuclear Aromatic Hydrocarbons using Ruthenium Ion Catalyzed Oxidation: The role of aromatic ring number in reaction kinetics and product distribution

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Abstract

Oxidation of aromatic hydrocarbons with differing numbers of fused aromatic rings (2-5), have been studied in two solvents environments (monophasic and biphasic) using ruthenium ion catalyzed oxidation (RICO). **RICO reduces the aromaticity of the polyaromatic core of the molecule in a controlled manner by selective oxidative ring opening. Moreover, the nature of the solvent system determines the product type and distribution, for molecules with more than 2 aromatic rings.** Competitive oxidation between substrates with different numbers of aromatic rings has been studied in detail. It was found that the rate of polyaromatic hydrocarbon oxidation increases with the number of fused aromatic rings. A similar trend was also identified for alkylated aromatic hydrocarbons. **The *proof-of-concept* investigation provides new insight into selective oxidation chemistry for upgrading of polyaromatic molecules.**

Introduction

In order to meet the increasing demands for fuels and petrochemical materials, it is essential to make better use of crude oil, especially heavy oils and residues.[1] These heavy fractions mainly consist of alkylated polynuclear aromatic hydrocarbons and heteroaromatics, which in order to upgrade to valuable compounds requires high energy input to reduce aromaticity.[2] Three major methods of heavy oil upgrading are currently employed: deep oil fluid catalytic cracking, thermal cracking and hydrocracking with desulfurization, which usually result in total or partial fragmentation of the molecules. The first two methods require extremely high temperatures, which convert high molecular weight compounds into coke.[3] The third process, hydrocracking, is often combined with thermal cracking. Hydrocracking has the possibility to transform ≥ 4-ring aromatic cores into smaller fragments, but requires *expensive* high pressure hydrogen. Moreover, over-cracking and formation of low value gas during this process is a major disadvantage.[4] In addition, many of the fused-aromatic cores of multi-ring heteroaromatics are resistant to hydrocracking as they are already electron rich molecules and reactions with hydrogen involve adding more electrons to the system. Consequently it is only accomplished under highly forcing conditions *i.e.* high temperature and pressure, and often leads to side products from non-selective reactions. It is noteworthy that coking wastes valuable carbon through formation of materials that cannot be further processed. Hydrocracking can also squander carbon and hydrogen, as these are transformed into low value gaseous products. Therefore, it is highly desirable to develop chemical processes which can selectively reduce aromaticity in a controlled manner, whilst maintaining a high degree of carbon and hydrogen in the target products.

Oxidation of the heavy oils and residues has been proposed as an alternative to high energy demanding processes, as it appears to display the reactivity required to activate electron rich aromatics. However, controlling oxidation can be challenging due to the thermodynamic end

points of CO_2 and water also leading to undesired loss of carbon. It is important that any oxidative reaction of polyaromatic compounds gives a gradual reduction of aromaticity, targeting one ring at a time, and does not result in complete combustion or coke formation.[5] This also means that polyaromatics with a greater number of rings should be oxidized at a greater rate than those with smaller ring systems.

Among many oxidation systems proposed for the upgrading of heavy oils, ruthenium ion catalyzed oxidation (RICO) is potentially an attractive approach, as selectivity in this reaction can be easily controlled by the reaction time, substrate: oxidant ratio, pH of the solution and type of solvent used.[6] Consequently, RICO is exceptionally versatile, and it has been reported to be effective for many reactions, including the dihydroxylation of olefins,[7] selective mono-oxidation of vicinal diols, keto-α-hydroxylation,[8] oxidative cyclization of polyenes,[9] oxidative cleavage of double and triple bonds,[10] oxidation of heteroatoms[11] and oxidation of saturated hydrocarbons and aromatic hydrocarbons.[12] The cost of RICO chemistry is relatively high, due to the use of ruthenium and the oxidant. However, the ruthenium is employed at low concentrations, and the versatility of the chemistry means it is attractive on a small scale.

In addition, RICO has been reported for many years to be useful for characterising aliphatic side chains in multi-ring heteroaromatics in the petroleum and coal industries. [13] For these reactions, it is hypothesized that RICO proceeds by following the steps:

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

2) Attached aliphatic chains are only likely to be oxidized at benzylic positions.

3) The aliphatic chain is not further oxidized.

Based on the above methodology, it is postulated that RICO could also be applied to the upgrading of ''bottom of the barrel'' compounds, as these consist of complex mixtures of substituted polyaromatic compounds.

When using RICO for selective polyaromatic oxidation, it is important to first understand the behaviour of model compounds, and hence simpler polyaromatic hydrocarbons should be studied. Recently we showed that 2-ethylnaphthalene can be used as a model alkylated polyaromatic compound, and it can be oxidized in either a conventional biphasic (dichloromethane, acetonitrile, water) or in a monophasic (acetonitrile, water) solvent system.[14] In both cases the reaction rate and product distribution were similar. However, this may not be the same for higher molecular weight polyaromatic hydrocarbons, as it is known that solubility in different solvents may affect the substrate reactivity. [15]

Here we have systematically studied the oxidation of polyaromatics with varying numbers of fused aromatic rings. These are naphthalene, phenanthrene and pyrene in both solvent systems, using the ruthenium ion catalyst with a focus on the product distribution. In the further studies reported here, we have performed kinetic investigations using compounds with increasing numbers of fused aromatic rings (from 2 to 5), in order to understand how the extent of the ring system affects the reactivity in RICO chemistry. This is extremely important, as moving toward the real residuals, molecules of lower molecular weight should be preserved, while larger molecules should be oxidized preferentially at a greater rate.

Results and discussion

Effect of monophasic and biphasic solvents systems

In our earlier work, it was shown that oxidation of the simplest alkylated polynuclear aromatic compound, 2-ethylnaphthalene, did not depend on the solvent system used. Reaction in a monophasic solvent system resulted in the same product distribution as a biphasic solvent system.[14] Therefore, we decided to carry out systematic studies on the oxidation of a range of non-alkylated polynuclear aromatic hydrocarbons in both solvent systems to understand whether the choice of solvent affects product distribution for larger ring systems.

First, we performed the studies using naphthalene (**1**) as a substrate in the monophasic solvent system (acetonitrile and water). GC-MS analysis of the product mixture revealed that the products include phthaldialdehyde (**2**), phthalic anhydride (**3**) and isobenzofuran 1(*3H*)-one (phthalide) (**4**) as shown in Scheme 1 (SI-Figure S1). It is worth mentioning that phthalic anhydride, observed as a product during GC-MS analysis, was probably formed via the dehydration of phthalic acid in the GC injector, as was previously reported.[16] Another compound which is formed in a similar way, by the dehydration of 2-hydroxymethyl-benzoic acid is isobenzofuran 1(*3H*)-one (**4**).[17] Based on GC-MS analysis, 57% of all reacted naphthalene was transformed into isobenzofuran 1(3H)-one (major product), 39% to phthaldialdehyde and 12% to phthalic acid. In all of the observed products, only one aromatic ring was oxidized, while the second was unreactive.
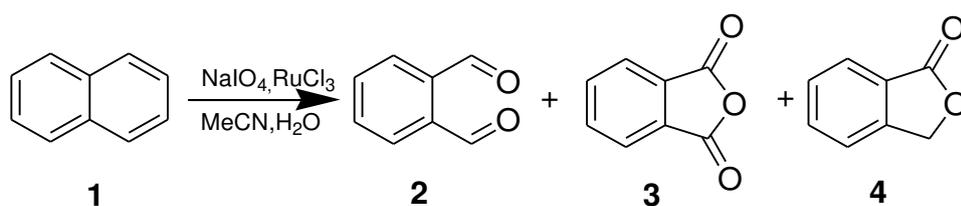
Scheme 1: Products of naphthalene oxidation in a monophasic solvent system. Reaction conditions: Naphthalene 0.164 mmol, $NaIO_4$ 1.312 mmol, $RuCl_3$ 0.012 mmol, MeCN 20 ml, H_2O 10 ml, T=295 K, stirring speed 500 rpm.

We also performed naphthalene oxidation in a biphasic solvents system. After analyzing samples from both aqueous and organic layers using GC and GC-MS, phthaldialdehyde (**2**), phthalic acid (identified as phthalic anhydride) (**3**) and isobenzofuran 1(3H)-one (phthalide) (**4**) were detected (SI-Figure S2).

In the literature, phthalic acid has always been observed as the main product of naphthalene oxidation.[18] Spitzer and Lee observed 70% selectivity to phthalic acid even when acetonitrile was not present in the reaction mixture. [19] In this study isobenzofuran 1(3H)-one has been

identified as one of the main products, and this can be explained by the shorter reaction time and milder reaction conditions that we have applied when compared to the work of Spitzer and Lee. However, comparing the products obtained in the oxidation of naphthalene in a biphasic solvent system with the one from the oxidation performed in a monophasic solvent system, it is clear that naphthalene is transformed into exactly the same products and the change of solvent composition does not significantly affect product selectivity. A similar observation was made in the oxidation of 2-ethylnaphtalene.[14]

The next polyaromatic compound probed using RICO chemistry was phenanthrene (**5**), consisting of 3 aromatic rings. GC-MS analysis of the product mixture from oxidation in the monophasic solvent system showed that the main product was 9,10-phenanthrenequinone (**6**) (selectivity 82%), along with biphenyl-2,2'-dicarbaldehyde (**7**), (selectivity 18%) (Scheme 2, SI-Figure S3). Product **7** is obtained by the oxidative C-C bond cleavage, which is crucial for the oxidative valorisation of high molecular weight multi-ring residues.
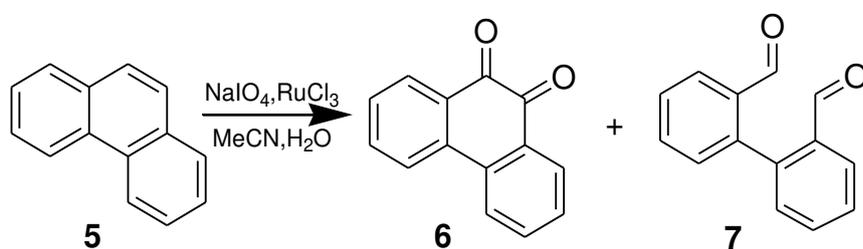

Scheme 2: Products of phenanthrene oxidation in the monophasic solvent system. Reaction conditions: Phenanthrene 0.164 mmol, NaIO$_4$ 1.312 mmol, RuCl$_3$ 0.012 mmol, MeCN 20 ml, H$_2$O 10 ml, T=295 K, stirring speed 500 rpm.

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 for phenanthrene during RICO chemistry. However, using ultrasonic-irradiation they obtained the second oxidation product, 9,10-phenanthrenequinone with an 88% yield. [20] The main

differences between the literature reports and the monophasic catalytic system employed in this study is the use of ultrasonification and a biphasic solvent system.

This suggests that the product distribution could be influenced by the choice of the solvent system. When we performed oxidation of phenanthrene using a biphasic solvent system, the major product identified by GC and ^{1}H NMR analysis in the organic layer was indeed 9,10-phenanthrenequinone (**6**) and diphenic anhydride (**8**) (2:1 ratio based on ^{1}H NMR analysis), as originally reported by Tabatabaeian *et al.* (SI-Figure S4).[20] Diphenic anhydride is considered to be a result of the diphenic acid dehydration in the GC injector.

Phthalic acid (**9**) was detected in the aqueous layer from phenanthrene oxidation. Products formed are presented in Scheme 3.
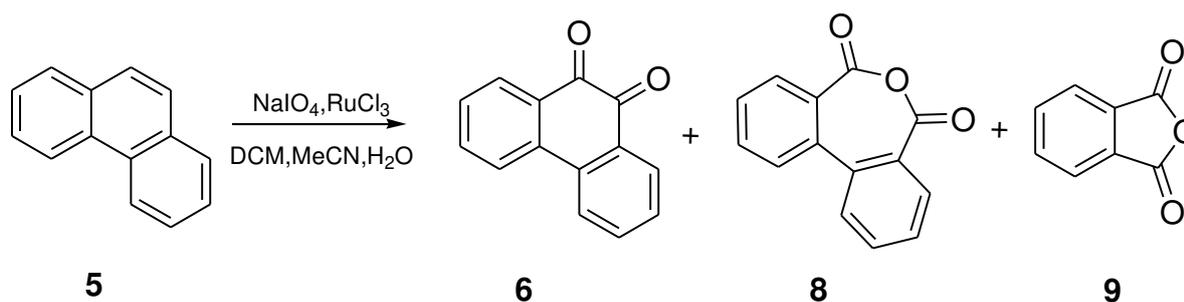

Scheme 3: Products of phenanthrene oxidation in the aqueous phase of a biphasic solvent system. Reaction conditions: Phenanthrene 0.164 mmol, NaIO$_4$ 1.312 mmol, RuCl$_3$ 0.012 mmol, DCM 16 ml, MeCN 7 ml, H$_2$O 7 ml, T=295K, stirring speed 500 rpm.

These findings are different from those previously reported by Menendez *et al.* [21] who observed 8 products, but similar to the findings of Stock and Kwok-Tuan, who observed 3 of the same major products.[22] In both cases, diphenic acid was observed, with Stock reporting 91% selectivity towards this product, while Menendez *et al.* only mentioned its presence. Kasai and Ziffer, in addition to Djerassi, found that diphenic acid is the major product for this oxidation.[6a, 23] However, it must be noted that the RICO reaction conditions applied to the oxidation of phenanthrene, varied significantly between studies. In our work, the product distribution found in a biphasic solvent differs from that obtained in the 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 than observed for the monophasic case. The differences between products in each solvent system suggests that the choice of solvent and relative solubility has an important role in determining oxidation products.

The next PAH in the series to be studied was pyrene (**10**). Oxidation was carried out under the same conditions as described in the experimental section, but the mass of reactants was increased by a factor of 3 to ensure high concentration of product in the reaction mixture. Oxidation in a monophasic solvent system resulted in two products: pyrene-4,5-dione (**11**) and phenanthrene 4,5-dialdehyde (**12**), identified by ^{1}H NMR and HPLC-MS (Scheme 4).
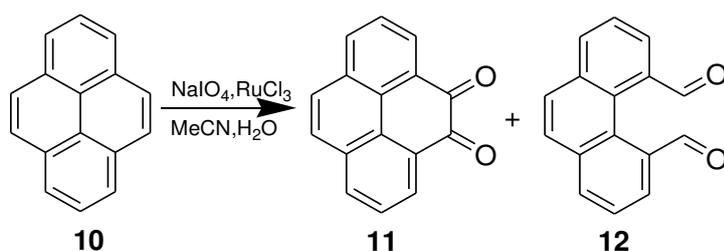
Scheme 4: Products of pyrene oxidation in the monophasic solvent system. Reaction conditions: Pyrene 0.495 mmol, NaIO$_4$ 3.936 mmol, RuCl$_3$ 0.036 mmol, MeCN 60 ml, H$_2$O 30 ml, T=295 K, stirring speed 500 rpm.

The minor product, phenanthrene-4,5-dialdehyde (**12**), 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 biphasic solvent systems are pyrene-4,5-dione and pyrene-4,5,9,10-tetraone.[24] In these products, either one or two aromatic rings have been oxidized, but under our experimental conditions only one aromatic ring has reacted and undergone ring opening to the dialdehyde.

However, it is worth noting that concentration of phenanthrene-9,10-dialdehyde was low, as only by employing High Resolution Mass Spectrometry (HR-MS), were we able to detect a signal at m/z 233 corresponding to this compound (SI-Figure S5). As stated earlier, the second major product of pyrene oxidation was pyrene-4,5-dione. Its presence was identified by ^{1}H NMR, where pyrene-4,5-dione nuclei gave characteristic signals at 8.50 ppm, 8.19 ppm, 7.85 ppm and 7.75 ppm (SI-Figure S6).[12]

Pyrene oxidation was also performed in a biphasic solvent system with the objective of understanding the differences in product distribution as a result of a change in the solvent system. From previous studies it is known that the carbon position 4,5 and 9,10 in the pyrene molecule are more susceptible to attack by the RuO_4 complex formed during RICO chemistry.[25] This means that the location of ketone, aldehyde or acid group may be expected at position 4,5 and/or 9,10. After analyzing the reaction mixture using ^{1}H NMR, signals corresponding to pyrene-4,5-dione were identified in the organic layer. Moreover, a number of additional peaks in the aromatic region, as well as signals indicating the presence of CHO species, suggests the formation of additional products (Figure 1).
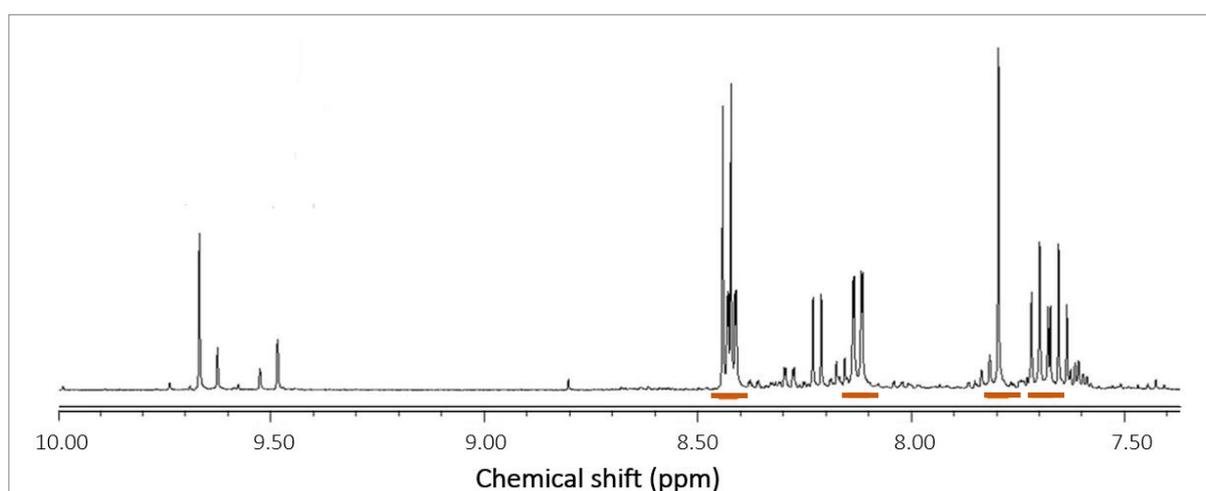

Figure 1: ^{1}H NMR spectrum of pyrene oxidation products in the organic layer. Marked signals from pyrene-4,5-dione (δ 8.44 ppm (2H, d,d), 8.13 ppm (2H, d,d), 7.80ppm (s, 1H) and 7.70 ppm (t, 3H). Reaction conditions: Pyrene 0.131 mmol, $NaIO_4$ 1.048 mmol, $RuCl_3$ 0.01 mmol, DCM 16 ml, MeCN 7 ml, H_2O 7 ml, stirring speed 500 rpm, T = 295 K.

^{1}H NMR analysis of the aqueous layer suggests the presence of a product containing at least one -CO$_2$H group. These products gave a doublet at 8.07 ppm and a triplet at 7.58 ppm, which are characteristic of products of pyrene oxidized at the 4,5 and 9,10 positions (Figure 2). What is more, the presence of aldehyde or acid groups was also observed (9.52 ppm). This finding suggests that the carbon atoms, most likely in positions 4, 5, 9 and 10, were oxidized to products with a C=O functionality.
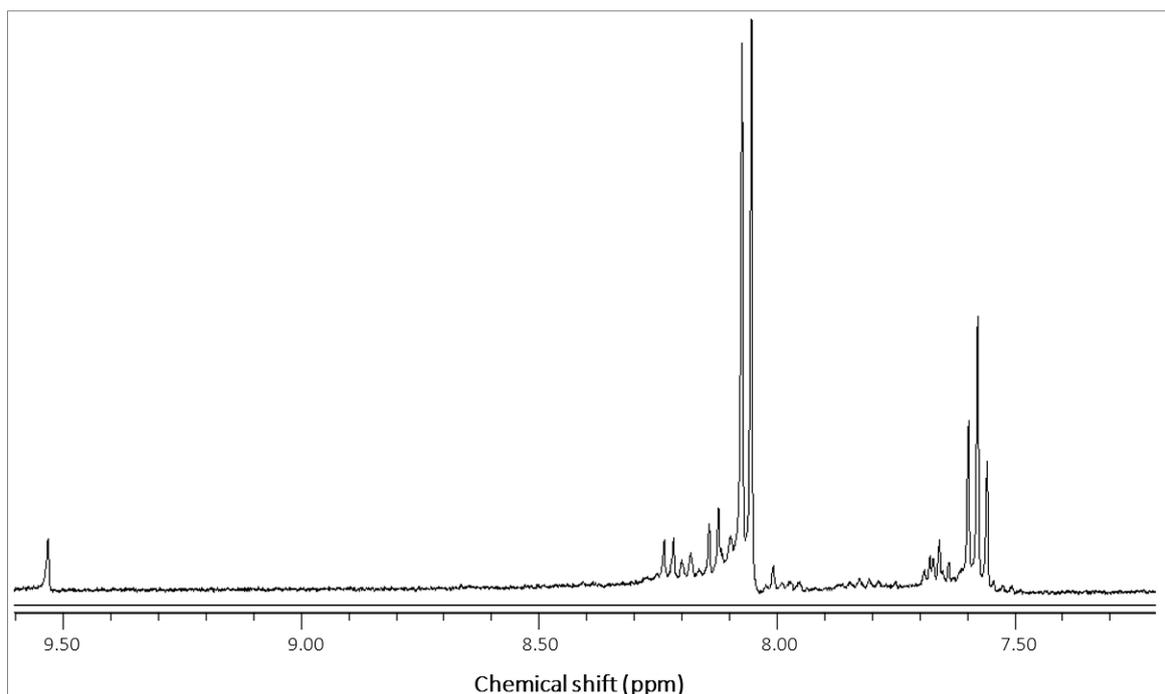
Figure 2: ^{1}H NMR spectrum of products from pyrene oxidation (aqueous layer). Reaction conditions: Pyrene 0.131 mmol, NaIO$_4$ 1.048 mmol, RuCl$_3$ 0.01 mmol, DCM 16 ml, MeCN 7 ml, H$_2$O 7 ml, stirring speed 500 rpm, T=295 K.

HRMS was used to identify these products and the following were present: pyrene 4,5-dione (**11**)**,** pyrene dione-diacid (**14**), and pyrene tetra-acid (**15**) (SI-Figure S7 and S8). No other products were observed in the organic layer, even using a Negative Electrospray technique.

Further analysis using LC-MS of 30, 60, 90, 120, 180, 240 minutes reaction time samples from the organic layer showed a number of products, with the major one being pyrene-4,5-dione (**11**) (reaction time = 9.45 min) as shown in Figure 3.
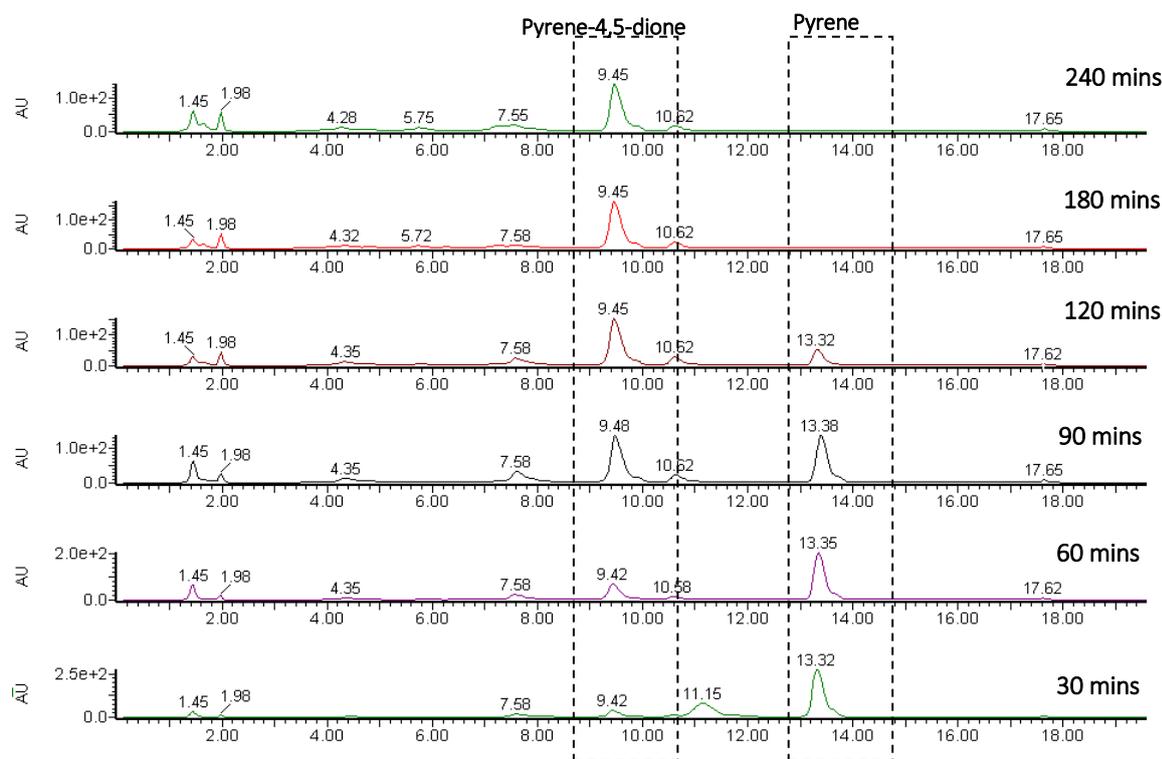
Figure 3: LC-MS analysis of pyrene oxidation in a biphasic solvent showing products in the organic layer as a function of time. Reaction conditions: Pyrene 0.131 mmol, NaIO$_4$ 1.048 mmol, RuCl$_3$ 0.012 mmol, DCM 16 ml, MeCN 7 ml, H$_2$O 7 ml, stirring speed 500 rpm, T = 295 K.

Mass spectral analysis of the peak with retention time of 7.58 min gave a molecular ion at m/z 263, which can be assigned to pyrene dione dialdehyde (**13**). LC-MS analysis did not show any significant peaks in the aqueous layer apart from the peak corresponding to pyrene-4,5,9,10-tetraacid (**15**). This incompatibility with findings from HRMS analysis, where more products in addition to pyrene-4,5,9,10-tetraacid were obtained, is considered to be a result of the lower sensitivity of the LC-MS technique. To summarize, a number of products were detected from oxidation of pyrene in the biphasic solvent system (Scheme 5), which suggest that the higher pyrene solubility resulted in higher conversion and also a greater number of oxidation products.
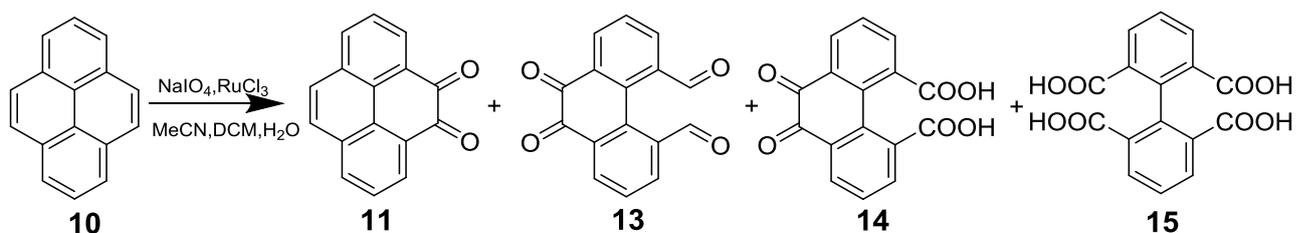
Scheme 5: Products of pyrene oxidation in the biphasic solvent system. Reaction conditions: Pyrene 0.131 mmol, $NaIO_4$ 1.048 mmol, $RuCl_3$ 0.012 mmol, DCM 16 ml, MeCN 7 ml, H_2O 7 ml, T=295 K, stirring speed 500 rpm, reaction time: 4 h.

The difference in product distribution from the oxidation of pyrene in a monophasic and biphasic solvent system clearly showed that the role of the solvent influences product selectivity. In a monophasic solvent system, the oxidation is milder and therefore more selective towards products with one opened ring.

Kinetic studies of non-alkylated PAHs

For the potential valorisation of heavy petroleum resids it is very important to selectively oxidize aromatic molecules, preferably with controlled reduction of aromaticity by opening one ring at a time. It is also crucial to maintain a higher reaction rate for molecules with larger ring systems than for those with fewer aromatic rings. Thus, kinetic studies were performed to assess the rate of reaction for molecules containing different numbers of aromatic rings.

We first recorded the time required to achieved full conversion of substrates used in the previous studies detailed above, where we concentrated on the nature of products formed. By analysing the conversion of the starting substrate it was clear that the substrates reacted with different rates. These rates are summarized by presenting the time taken for each substrate to reach full conversion in the monophasic and biphasic solvent systems (Table 1).

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Table 1. The time required for full conversion of individual polyaromatic substrates in reactions performed in monophasic and biphasic solvent systems.

Substrate	Time for full conversion (min)	
	Monophasic	**Biphasic**
Naphthalene	45	260
Phenanthrene	30	180
Pyrene	15	150

As can be observed from data presented in Table 1, the time required to achieved full conversion of the substrate in both monophasic and biphasic solvent systems follows the order:

naphthalene > phenanthrene > pyrene.

Here the effect of the number of aromatic rings on the rate of conversion is clear, as pyrene with 4 aromatic rings reacts faster than the 3 ring system, which is faster than 2. In more detailed kinetic studies, we firstly investigated the rate of oxidation of substrates with different numbers of aromatic rings for individual substrate reactions in a monophasic solvent system and compared it against the reaction carried out in a biphasic system. The time on line plots presenting substrate consumption for naphthalene, phenanthrene and pyrene oxidation performed in 3 separate experiments are shown in Figure 4.
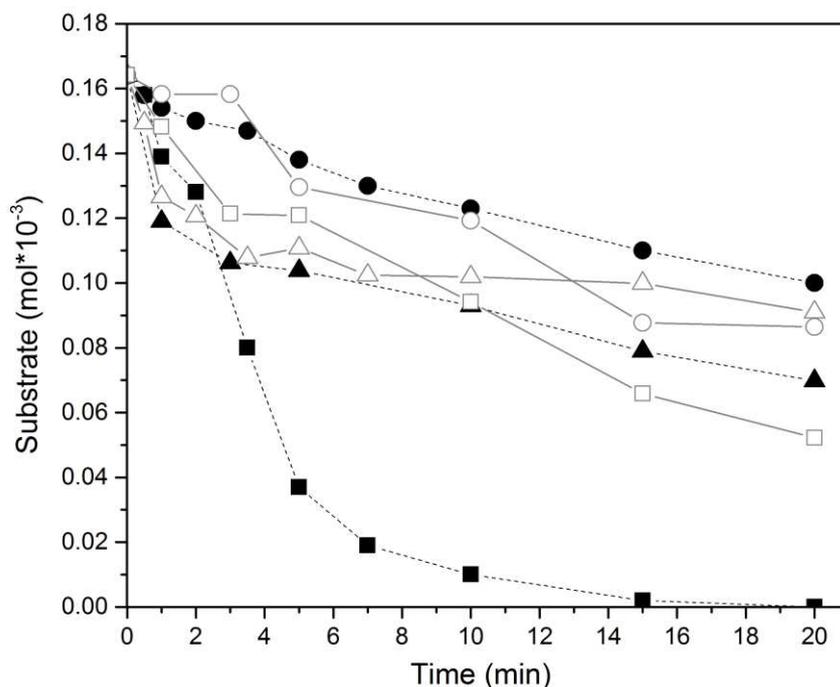
Figure 4: Comparison of the individual rates of oxidation of PAHs in a monophasic (closed symbols) and biphasic (opened symbols) solvent system: naphthalene (●), phenanthrene (▲) and pyrene (■). Reaction conditions: Substrate 0.164 mmol, NaIO$_4$ 1.312 mmol, RuCl$_3$ 0.012 mmol, T = 295 K, stirring speed 500 rpm, (monophasic solvent, MeCN 20 ml, H$_2$O 10 ml; biphasic, DCM 7 ml, MeCN 16 ml, H$_2$O 7 ml).

Oxidation of the individual PAHs in a monophasic solvent system showed a substantial difference in the rate of oxidation between pyrene, phenanthrene and naphthalene. The order of reactivity was again: *pyrene > phenanthrene > naphthalene.*

This is an important observation for the oxidative valorisation of petroleum resids, because RICO oxidizes the aromatics with a greater number of rings faster than those with fewer aromatic rings. Although a direct comparison has not been reported previously, the observation is in agreement with literature reports, which suggest that reactivity increases with the number of fused aromatic rings. This observation can be a result of the stabilization of the carbocation

intermediate of the aromatic ring.[26] However, it is also known that aromaticity plays a role, since the more π electrons that are lost, then the faster the reaction.

By carrying out individual oxidations of naphthalene, phenanthrene and pyrene in a biphasic solvent system, it was possible to compare the data for rate of reaction with that when a monophasic solvent system was used, and consequently observe how the solvent composition affects the rate of reaction.

Comparing the initial reaction rates for the first 5 minutes of reaction the rate of oxidation is similar for all three molecules in the biphasic solvent (Table 2, SI-Figure S9), in contrast to the quite different rates found with a monophasic solvent.

Table 2: Reaction rate for substrates oxidized individually in monophasic and biphasic solvent systems, and rates for competitive reactions with substrates present simultaneously in biphasic solvent measured during thr first 5 min of reaction.

Substrate	Reaction rate $\times$ 10^{-3} (mmol min^{-1})		
	Individual		Competitive
	Monophasic	Biphasic	Biphasic
Naphthalene	3.56	4.15	0.0016 (2.88)[*]
Phenanthrene	4.81	5.47	0.0052 (4.69)[*]
Pyrene	11.14	6.07	0.0076 (6.77)[*]

Note: [*]Measured over 10 min

The difference in the reaction rate of pyrene between the two solvent systems is significantly different when it is present as a single component. Whilst naphthalene and phenanthrene reaction rates only increased by 0.6 μmol min^{-1} changing from a monophasic to a biphasic solvent system, pyrene reacted at approximately half the rate. A possible explanation for this behaviour is the solubility of the reactant which affects its availability. In the monophasic

solvent the substrate, as well as oxidant and $RuCl_3$, are in the same phase, therefore there is no induction period for the reaction to commence. In the biphasic system the reactants are distributed between two phases, thus the contact between them is limited. This effect is even more apparent during the competitive oxidation between naphthalene, phenanthrene and pyrene in the biphasic solvent system; there is a clear induction period, as the rate measured during the first 5 and the first 10 min is significantly lower. It is considered that the substrates compete for binding of the RuO_4 oxidant, and then start to react with a rate similar to the one observed for individual substrates. It is worth noting that the rate of oxidation in the biphasic system is slower in the competitive reaction than in an individual reaction for all components.

Pyrene is a four ring system and the next PAH in the series is perylene containing five rings, which is insoluble in acetonitrile, and hence a comparison between oxidation in monophasic and biphasic solvent systems could not be performed. For substrates with more than 4 aromatic rings RICO chemistry was investigated only in a biphasic solvent system. Initially, the substrate : oxidant molar ratio was kept at 1:8. Figure 5, shows the competitive reaction between naphthalene, phenanthrene, and the new substrates of chrysene and perylene with larger fused rings systems. The relative oxidation rates follow the trend 5R > 4R > 3R > 2R (R = number of fused aromatic rings).
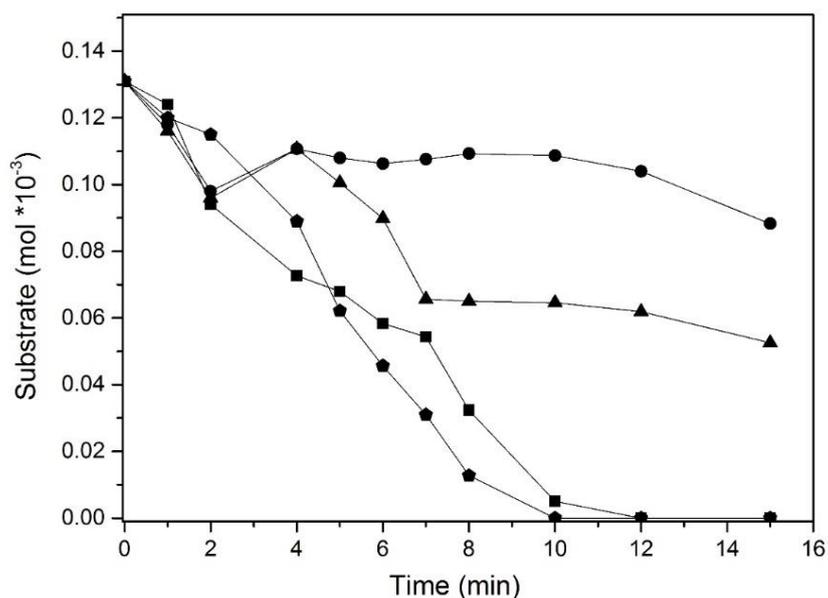
Figure 5: Comparison of competitive rates of oxidation in a biphasic solvent system, all substrates were oxidized simultaneously in a single experiment: (●: Naphthalene; ▲:Phenanthrene; ■:Chrysene; ☐:Perylene). Reaction conditions: Substrate 0.131 mmol, NaIO$_4$ 4.215 mmol, RuCl$_3$ 0.035 mmol, DCM 16 ml, MeCN 7 ml, H$_2$O 7 ml, T = 295 K, stirring speed 500 rpm.

It is again confirmed that the rate of oxidation depends on the number of fused aromatic rings (indicated by nR), and the rate of oxidation consistently follows the trend:

$$5R > 4R > 3R > 2R$$

We also investigated the influence of substrate to oxidant ratio, and lowered it from a 1: 8 to a 1: 5 ratio. Since the reaction proceeded with a much slower rate we decided to measure the rate during the first 40 min, instead of 10 min as in the case of the reaction where substrate to oxidant ratio was 1:8. Based on the data obtained, we noticed that decrease in mass of oxidant did not influence the trend, as larger ring systems reacted faster than those with fewer aromatic rings, which was consistent when less oxidant was used (Table 3).

Table 3: Initial reaction rate in competitive oxidation reactions in a biphasic solvent system.

Compound	Reaction rate × 10^{-3} (mmol min^{-1})	
	Ratio 1:5*	Ratio 1:8**
Naphthalene	0.04	2.88
Phenanthrene	0.31	6.26
Chrysene	0.77	10.67
Perylene	1.24	11.23

*measured over 40 min

**measured over 10 min

Kinetic studies of alkylated PAHs

Valorisation of crude oil residues requires molecules with larger aromatic systems to react faster than those with smaller ones. As shown in the previous section, RICO chemistry fulfils this requirement. However, the question remains if this trend is also true for compounds containing aliphatic chains attached to the aromatic ring systems, as alkylated PAHs are major components of heavy resids. Moreover, it is preferable to direct the selectivity of the reaction towards oxidation of aromatic species rather than aliphatic ones. Naphthalene and 1-decylnaphthalene were used to determine reactivity differences due to the presence of a long alkyl chain in competitive oxidation reactions. Figure 6 shows that the alkylated naphthalene reacts faster than naphthalene, however, the difference in rate is minor. This behaviour was somewhat expected due to the electron donating character of the aliphatic chain attached to the ring.[19, 27] The product analysis of the oxidation of 1-decylnaphthalene suggested that at a conversion of 42%, 60% of the product spectrum preserved the aliphatic chain attached to the aromatic ring system. GC-MS analysis further confirmed that the main product was 4-decyl phthalic acid, with 7-decylisobenzofuran-1*(3H)*-one and 4-decyl-*1H*-indene-1,3 (*2H*) dione as

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minor products. When the product distribution following the oxidation of 1-decylnaphthalene was analyzed in further detail most of the products had the alkyl chain preserved.[14]
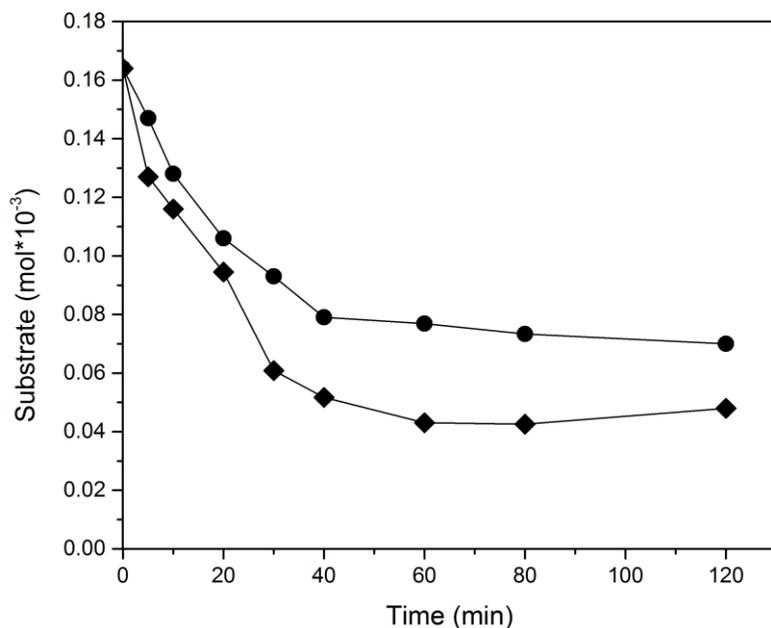

Figure 6: Competitive oxidation of naphthalene and 1-decylnaphthalene, (◆) naphthalene, (●) 1-decylnaphthalene. Reaction conditions: Substrate 0.164 mmols, ratio 1:1, NaIO$_4$ 2.624 mmol, RuCl$_3$ 0.024 mmol, DCM 16 ml, MeCN 7 ml, H$_2$O 7 ml, T = 295 K, stirring speed 500 rpm.

In order to see if the oxidation rate for alkylated PAHs also increased as the number of rings in the aromatic system increased a competitive reaction with 1-decylnaphthalene, 2-nonylphenanthrene and 1-octadecylpyrene was performed (Figure 7). The rate of oxidation of 1-octadecylpyrene was higher than the rate of 2-nonylphenanthrene. 1-decylnaphthalene exhibited the lowest oxidation rate of the molecules tested. This sequence of rates is the same as that measured for non-alkylated PAHs, and it can be concluded that the rate of reaction depends on the extent of the aromatic ring system and not the presence of an alkyl chain.

By using compounds with different alkyl chain lengths it was possible to partially investigate the influence of the aliphatic chain on product 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 that phenanthrene in competitive reaction with naphthalene in a biphasic solvent system reacted faster as well. The electron donating effect of the alkyl chain only increases from C_1 to C_4; above C_4 there is no further increase, hence pentyl and larger side chains will have equivalent effects.[28] Consequently, for the data presented in Figure 7, there is no significant differences in the inductive effect of the alkyl chain, and the difference of reaction rate that we observed is only a result of the different number of aromatic rings for each substrate.
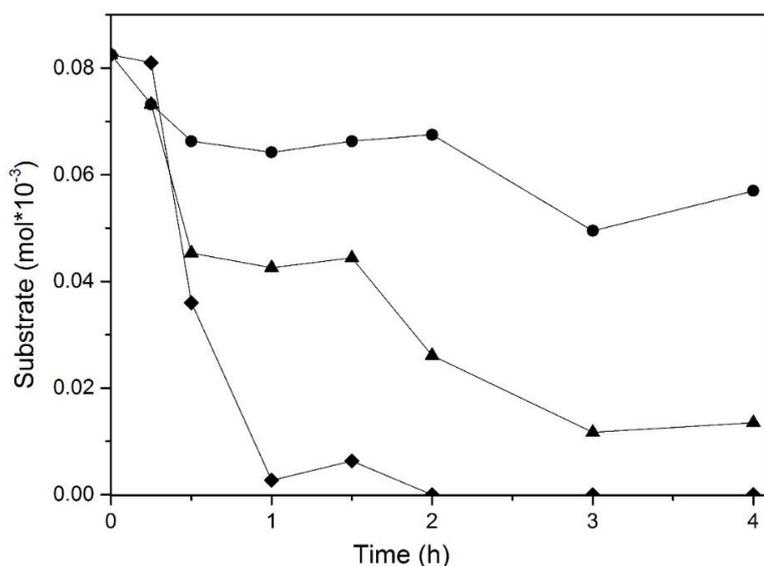

Figure 7: Competitive oxidation of alkylated polyaromatics, (●) 1-decylnaphthalene, (▲) 2-nonylphenanthrene, (♦) 1-octadecylpyrene). Reaction conditions: Substrates 0.0825 mmol (molar ratio 1:1:1), $NaIO_4$ 0.7 mmol, $RuCl_3$ 0.006 mmol, DCM 16 ml, MeCN 7 ml, H_2O 7 ml, T = 295 K, stirring speed 500 rpm.

Conclusions

It has been shown that Ruthenium Ion Catalyzed Oxidation can be used in selective oxidation of aromatic compounds. It reduces the aromaticity of the polyaromatic core of the molecule in a controlled manner by selective oxidative ring opening. Moreover, the nature of the solvent system determines the product type and distribution, for molecules with more than 2 aromatic

rings. Kinetic studies of molecules with differing numbers of aromatic rings in the molecular core showed that larger molecules reacted faster than smaller ones. This was also validated for alkylated polyaromatic hydrocarbons, and it is shown that alkylated PAHs follow the same oxidation trend as non-alkylated ones. We consider that this *proof-of-concept* investigation will provide new insight into selective oxidation chemistry for resids and bitumens upgrading, which offers an alternative to current expensive and energy demanding processes.

Experimental Section

Monophasic and biphasic oxidation reactions of PAHs (0.164 mmols or 0.131 mmols) were carried out at 295 K in a water-jacketed reactor (thermostatic water bath, Julabo F25-ME Refrigerated/Heating Circulator) using an aqueous solution of $NaIO_4$ (280 mg, 1.312 mmol dissolved in 10 ml H_2O or 1.048 mmol dissolved in 7 ml H_2O) and $RuCl_3 \cdot xH_2O$ (2.5 mg, 0.012 mmol or 2 mg, 0.01 mmol) as catalyst, always maintaining the substrate : oxidant:catalyst molar ratio 1:8: 0.07. Solvent compositions of acetonitrile (20 ml) and H_2O (10 ml) were used to give the monophasic system and acetonitrile (7 ml), dichloromethane (16 ml) and H_2O (7 ml) were used for the biphasic solvent system. Stirring speed was set to 500 rpm. During the course of the reaction, small aliquots of the reaction mixture (0.5 ml) were withdrawn at regular times and immediately quenched by the addition of an aqueous s solution of Na_2SO_3 (0.1 ml, 1.403 mmol in 6 ml H_2O) and quantitatively analyzed by gas chromatography (GC). 0.1 μl of the solution was injected into the GC fitted with a VF-5ht (30 m, 0.25 mm) column. For HPLC-MS analysis the reaction was quenched after the desired time and the organic and aqueous layers separated. The organic layer was evaporated to dryness, and the resultant solid was redissolved in 1 ml of acetonitrile and added to the external standard: benzophenone (0.1 ml, 0.01 M). For the aqueous layer, a portion of sample (0.6 ml) was combined with acetonitrile (0.4 ml) and benzophenone to make a total volume of 1.1 ml prior to analysis.

Gas Chromatography-Mass Spectrometry (GC-MS) analyses were performed using a Waters GCT premier instrument fitted with an Agilent HP-5MS column (30 m × 0.25 µm), carrier gas was He (1 ml min^{-1}) and temperature was programmed from 313 K to 553 K.

High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS) analyses were carried out using a Waters HPLC system fitted with reverse phase C18 column (4.6 × 17.5 mm) and a UV detector (λ = 254 nm) coupled to a ZQ mass spectrometer. The mobile phase was 95% H_2O/5% MeCN changing to 95% MeCN and 5% H_2O over a 20 mins period. The flow rate was set to 1 ml min^{-1}.

High Resolution Mass Spectrometry (HRMS) analyses were performed using a Waters LCT Premier XE (ES), while EI data was generated using Waters GCT Premier (EI) instrument.

^{1}H NMR spectra were recorded on a Bruker 400 MHz instrument using CD_3CN (monophasic reaction), $CDCl_3$ (biphasic reaction: organic layer) or D_2O (biphasic reaction: aqueous layer) as solvent.

Acknowledgements

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