School of Chemistry Cardiff University



# **ExonMobil**

## Density Functional Theory study of the Selective Oxidation of Polynuclear Aromatic Hydrocarbons

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#### Abstract

Density functional theory has been used to model the selective catalytic oxidation of model polynuclear aromatic hydrocarbons, in particular pyrene. Two transition metal catalysts have been employed, ruthenium tetroxide and a peroxy tungsten complex. The B3LYP method was used in all calculations. The LANL2DZ effective core potential was used for ruthenium and tungsten atoms. The 6-31G(d,p) basis set was used for all other atoms. Selectivity studies show that catalyst-substrate adducts will form at the carbon-carbon bond of the polynuclear aromatic hydrocarbon that will give the least reduction in aromaticity. The strain induced in planar polynuclear aromatic hydrocarbon structures did not have a bearing on catalyst selectivity. Interior carbon-carbon bonds of polynuclear aromatic hydrocarbons will not be attacked, meaning that oxidative fragmentation of these compounds starts at the exposed carboncarbon bonds. For the ruthenium catalysed oxidation system, multiple catalyst attacks at similar sites on polynuclear aromatic hydrocarbons is possible but unlikely due to the catalytic amounts used. It is indicated that the presence of aliphatic functional groups at the adduct formation sites for the ruthenium catalyst will not hinder adduct formation. Water is necessary for the success of both catalysts. The pathway found for ruthenium catalysed oxidation shows a stable dione intermediate, this intermediate has been confirmed by experimental findings and the literature. For the ruthenium catalyst water is required as it is involved in the reaction mechanism, facilitating the abstraction of hydrogen atoms adjacent to the catalyst adduct formation site. Water is not as directly involved in the tungsten catalyst mechanism, taking the role of a stabilising agent for transition state structures. The reaction pathways found for both catalysts show that the final reaction intermediate before breaking the carbon-carbon bond is an organic anhydride. Each reaction type shows a different route to this structure. Both reaction mechanisms show an energetically favourable trend from reactants to products. Transition state energy barriers are not prohibitive.

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#### 1 Introduction

#### 1.1 Heavy oils, resids, bitumens

Heavy oils, residues (resids) and bitumens are characterised by their high viscosity or resistance to flow, high density and high concentrations of nitrogen, sulphur, oxygen and heavy metals. These oils can be sourced to the degraded products from the refinement of light oil, which is the residual material remaining after the refinery process of crude oil. Naturally, they may be found due to the bacterial decomposition of large deposits of oil [1]. In this thesis the terms heavy oils, resids and bitumens refer to the degraded products of the refinery process.

#### 1.2 The Refinery Process

The refinery process depends on the type of crude oil available and the product required. Crude oil is a natural resource, a mixture composed of the naturally processed remains of flora and fauna. As there is a variation in the spread of plant and animal species across the globe, so too crude oils sourced at different points will differ. The refinery process can be thought of as two processes, separation and conversion. In the separation processes, fractions are separated from the crude oil mixture. The conversion processes include reforming and catalytic cracking.

#### 1.2.1 Fractional Distillation

When crude oils first arrive at a refinery they are separated using a technique called fractional distillation. This is a relatively simple process whereby the crude oil mixture is heated until it boils. Each fraction in the crude oil mixture will boil at a different temperature, a chemical characteristic of each fraction. Each fraction will also condense at a different temperature. As the vapour from each fraction climbs the distillation column the temperature decreases. Therefore each fraction will condense at different points in the distillation column. The column is designed in such a way that the condensed fractions are then run off so that condensation can continue. This separation is dependent upon the relative sizes or molecular weights of the fractions. Light fraction such as liquid petroleum gas tend to condense at the top of the column whereas, heavier fractions such as diesel oil will condense lower down in the column. Some very heavy fractions will not boil. These fractions remain at the bottom of the column. These fractions are called the residue or resid. This is shown in figure 1-1.



Figure 1-1-1: Schematic of a fractional distillation column. Naphtha fractions are typically used in the chemical industry and kerosene is used to fuel airplanes.

#### 1.2.2 Hydroprocessing

Hydroprocessing is a conversion technique used to satisfy environmental regulations [2]. This process uses hydrogen to remove sulphur, nitrogen and oxygen in crude oil fractions. Shown as [R-S] and [R-N] in the figure below.

catalyst

 $[R-S] + H_2 \longrightarrow [R-H] + H_2S$   $300-450 \ ^{\circ}C$ 

catalyst

 $[R-N] + H_2 \longrightarrow [R-H] + NH_3$ 300-450 °C

Catalysts are generally sourced from the transition elements, many use the element tungsten and cobalt on an alumina support. Dibenzothiophene is particularly difficult to remove due to the sterically hindered site of the sulphur atom. A 2007 study found that use of a tungsten catalyst in the presence of hydrogen peroxide as an oxidant had the potential to remove up to 98.6% of the sulphur content in a model oil [3].

#### 1.2.3 Catalytic cracking

This is a conversion process used to upgrade certain low grade fractions. For example, after distillation of crude oil, petroleum naphtha can be cracked to give a high octane additive to fuel. The octane number of a fuel refers to the amount of compression a fuel can withstand in an engine combustion chamber before it ignites. High octane fuels are generally small, branched alkanes. For example, iso-octane has an octane number of 100, the highest. The structure of iso-octane is shown in figure 1-2.



Figure 1-1-2: Iso-octane, the standard used to measure the octane rating of a fuel. Iso-octane has an octane rating of 100.

Catalytic cracking is a process whereby hydrogen is introduced to a crude oil fraction and with the use of a catalyst the molecules of the fraction are 'cracked' to produce other, short chain hydrocarbons. The process was first commercialised in the late 1930s [4]. Alkanes and alkyl aromatics will be degraded to alkanes, aromatics and alkenes. Catalytic cracking is not perfect, however, as catalysts can be poisoned by the presence of sulphur and metals such as nickel, vanadium and iron in the feedstock. With a typical refinery feedstock one can expect approximately 5-8% coke formation, this will also hinder the catalyst. The amount of catalyst poisoning and coke formation will change depending on the source of the feedstock. When cracking a residue feed (residue from fractional distillation) coke formation can reach 15% [5]. Petroleum coke is a carbonisation product of high-boiling hydrocarbon fractions or heavy residues [6].

#### 1.3 Polynuclear aromatic hydrocarbons

Aromatic residues from the refinery process are a major contributor to the composition of coke found at refineries. They are composed of polynuclear aromatic hydrocarbons (PAHs). PAHs are a type of hydrocarbon. They are composed of a number of fused (not bonded) aromatic cycles. An example of a well-known single aromatic hydrocarbon cycle is benzene. The smallest cycles will have five carbon atoms while cycles of six carbon atoms are most predominant [7]. When pure they are solid and can vary in colour from colourless to a pale yellow-green. Although this type of chemical compound does exist naturally, many PAH are introduced to the atmosphere through the incomplete combustion of fossil fuels and their derivatives. PAH are hazardous and have caused tumours in laboratory conditions [8].



Figure 1-1-3: Naphthalene, molecular formula  $C_{10}H_8$  an example of a PAH. Naphthalene consists of two, six carbon aromatic cycles fused together.

Much of the world's remaining oil resources are composed of heavier fractions like PAH. As these fractions contribute to much of the coke formation in the refinery process it is worth considering new routes into conversion processes in order to upgrade these heavy fractions.

#### 1.4 Selective Oxidation

Historically, oxidation was defined as the chemical addition of oxygen to an element or compound. Oxidation may be defined as a chemical reaction where the atoms of an element or compound lose a number of their electrons, resulting in a positive charge on the valence shell of electrons. This definition can be extended to selective oxidation by specifying that the atoms of one particular element type lose a number of electrons. Selective oxidation has been used to characterise polymerised pitches [9]. A polymerised pitch is a solid polymer whose monomers are of large molecular size, like PAHs. These pitches have some common chemistry with heavy fractions, namely a high volume of PAH. This study made use of ruthenium tetroxide as a selective oxidation catalyst in an initial step in the characterisation of PAHs. Used as an oxidative catalyst, ruthenium tetroxide will convert PAH to carbon dioxide and smaller carboxylic acids. The same may be said for more isolated benzene rings, where the aromatic constituent of a hydrocarbon will be oxidised to the relevant carboxylic acid [10] as seen in figure 1-4.



*Figure 1-1-4: Ruthenium tetroxide catalysed oxidation of cyclohexylbenzene to cyclohexane carboxylic acid.* 

While osmium tetroxide had been known as an oxidation catalyst, ruthenium tetroxide was introduced as a safer alternative [11] in 1953. This paper noted that, though the oxidation of phenanthrene with osmium tetroxide could take from two to seven days, the reaction using ruthenium tetroxide was observed to occur 'rapidly'. The structure of phenanthrene is shown in figure 1-5.



Figure 1-1-5: Phenanthrene, a PAH composed of three fused benzene rings.

Further study of osmium and ruthenium tetroxide oxidations was carried out on pyrene in 1959 [12] with the aim of using ruthenium dioxide to attack double carbon-carbon bonds. This study used sodium periodate as the oxidant *in situ* and further found that increasing the amount of periodate present in the reaction vessel increased the yield of oxidised product. The use of periodate was explained due to its ability to oxidise ruthenium to ruthenium tetroxide *in situ*. Ruthenium was introduced to the reaction as ruthenium dioxide, with an oxidation state of Ru(IV), whereas the oxidation state of ruthenium tetroxide is Ru(VIII). At this stage it was known that ruthenium tetroxide would oxidise PAH rapidly and that a group one metal periodate served as an *in situ* oxidant for ruthenium dioxide. More recent studies had promised selectivity in ruthenium catalysed oxidation of PAH [13].

#### 1.5 Project Aims

This project proposes to answer the following questions:

- 1. Is there selectivity for a specific molecule within a mixture of similar molecules?
- 2. What is the selectivity for oxidation of a specific position within the PAH?
- 3. How selective is oxidation of the PAH when compared to long chain alkyl constituents?

#### 2 Theoretical Basis for Calculations

#### 2.1 Introduction

Computational chemistry may be described as the calculation of molecular properties at relevant points on the Potential Energy Surface (PES) of a reaction. The PES may be considered as a 3N-6 dimensional graph of the energy of a system related to the various geometric configurations of the system. In this case, N is the number of nuclei in the system. These configurations may be due to changes in bond lengths, rotations and dihedrals. The points principally studied here are the minima and saddle points that relate to stable reaction intermediates and the transition states between these intermediates. In order to calculate the molecular properties at these points for any system beyond the very simple one must apply approximations to the Schrödinger equation. Examples of simple systems where analytical solutions can be gained from the Schrödinger equation include the hydrogen atom, H and the helium ion, He<sup>+</sup>. The results of these analytical solutions can then be used to provide the functional forms used in the basis sets of more complex systems.

#### 2.2 The Schrödinger Equation

The Schrödinger equation allows one to calculate the energy of a system through consideration of the Hamiltonian and wave function for that system.

$$H\Psi = E\Psi \tag{2.1}$$

The Hamiltonian (*H*) contains information on the kinetic energies of the electrons and nuclei, the attraction between electrons and nuclei and the nuclear and electronic repulsions. The real wave function ( $\Psi$ ) when given as a product of itself  $|\Psi^2|$  and integrated over a region of space will give the probability of the system in question being found in that region of space. When integrated over all space, for a real chemical system the result will be one. Unfortunately the Schrödinger equation cannot be solved for any system beyond the very simple, for example the hydrogen atom. In order to perform calculations on more complex systems a number of approximations are applied to the Schrödinger equation.

#### 2.2.1 The Born-Oppenheimer Approximation

This is employed to simplify the Hamiltonian. This is achieved by considering the motion of the electrons relative to that of the nuclei. Though the nuclei are in motion, relative to the movement of the electrons this motion is very little. This is due to the size of the electrons relative to the size of the nuclei. The Born-Oppenheimer takes advantage of this and counts the motion of the nuclei of a system to be zero. This simplifies the Hamiltonian and allows the electronic structure to be calculated at a fixed nuclear geometry. The electron-nuclei attraction term is also simplified.

#### 2.3 Density Functional Theory

Even with the Born-Oppenheimer Approximation, the calculation of chemical systems remains a daunting task. To simplify this, various methods have been developed. One of these is known as Density Functional Theory (DFT). The primary focus of this method is the electron density. The Hamiltonian of a system contains information on the kinetic energies of electrons and nuclei, the attraction between electrons and nuclei and the electron-electron and nucleus-nucleus repulsions. One can see that for most systems of interest the Hamiltonian will include a large number of variables. It is the number of variables in the Hamiltonian that makes solution to the Schrödinger equation an issue. Reducing the number of variables would simplify the equation. Ideally one could replace these many variables with a simpler expression. For this reason the electron density is employed. The electron density is useful as, integrated over all space the result is the number of electrons in the system.

$$n = \int \rho(\mathbf{r}) d\mathbf{r} \tag{2.2}$$

- n is the number of electrons in the system
- $\rho(\mathbf{r})$  is the electron density of the system

Nuclear positions can also be determined from the electron density. As nuclei may be considered point charges, their positions will appear as maxima in the electron density. Even with this simplification there remains the difficulty of calculating the electron-electron interaction term of the Hamiltonian. Kohn and Sham [14] put forward a solution to this in 1965.

#### 2.3.1 Approximations to Density Functional Theory

#### 2.3.1.1 Kohn-Sham Theory

This theory considers how to account for the electron-electron interaction term in the Hamiltonian. The defining characteristic of this theory is that the Hamiltonian is initially changed to one representing a system of non-interacting electrons. Therefore there is a pretend starting point which can be adapted to have the same ground state electron density as a real system composed of interacting electrons. It is assumed that the non-interacting electron system can give the same electron density as the real system of interest with the inclusion of a potential to represent the missing electron-electron interactions. This reduces the complicating interaction terms to one term;  $E_{xc}$ . The energy functional of the Schrödinger equation is then considered as;

$$E[\rho(\mathbf{r})] = T_{ni}[\rho(\mathbf{r})] + V_{ne}[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] + \Delta T[\rho(\mathbf{r})] + \Delta V_{ee}[\rho(\mathbf{r})]$$
(2.3)

Where;

- T<sub>ni</sub> is the kinetic energy of all non-interacting electrons
- V<sub>ne</sub> is the nuclear-electron interaction
- Vee is the classical electron-electron repulsion
- $\Delta T$  is the correction to  $T_{ni}$  due to the interacting nature of the electrons

#### • $\Delta V_{ee}$ contains all non-classical corrections to electron-electron repulsion

For the pretend system the kinetic energy can be expressed as a sum of individual electron kinetic energies. When an orbital expression for the electron density is employed this can then be written as;

$$E[\rho(\mathbf{r})] = \sum_{i}^{N} \left( \left\langle \chi_{i} \right| - \frac{1}{2} \Delta_{i}^{2} \left| \chi_{i} \right\rangle - \left\langle \chi_{i} \right| \sum_{k}^{nuclei} \frac{Z_{k}}{|\mathbf{r}_{i} - \mathbf{r}_{k}|} \left| \chi_{i} \right\rangle \right) + \sum_{i}^{N} \left\langle \chi_{i} \right| \frac{1}{2} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_{i} - \mathbf{r}'|} d\mathbf{r}' \left| \chi_{i} \right\rangle + E_{xc}[\rho(\mathbf{r})]$$

$$(2.4)$$

This separates the term  $E_{xc}$ , the exchange-correlation energy of the electrons.  $E_{xc}$  accounts for the difference between the classical and quantum mechanical electron-electron repulsion and the difference in kinetic energy between the real and pretend systems. DFT functionals in use today either ignore the  $E_{xc}$  term or attempt to substitute it with experimental parameters or constructed functions. It is the manner in which this term is treated that separates the DFT methods used in this thesis.

#### 2.3.1.2 Local Density Approximation

The Local Density Approximation (LDA) is the simplest practical approach to calculating the exchange-correlation energy,  $E_{xc}$ . This is done by considering the energy density,  $\varepsilon_{xc}$  which is related to  $E_{xc}$  by

$$E_{xc}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \,\varepsilon_{xc}[\rho(\mathbf{r})] d\mathbf{r}$$
(2.5)

Here  $E_{xc}$  is exactly calculated from the value of the electron density at position **r**, hence 'local'. The Local Spin Density Approximation is an extension of the LDA where electrons of  $\alpha$  and  $\beta$  spin are treated separately where:

$$\rho(\mathbf{r}) = \rho_{\alpha}(\mathbf{r}) + \rho_{\beta}(\mathbf{r}) \tag{2.6}$$

#### 2.3.1.3 Generalised Gradient Approximation

The generalized gradient approximation (GGA) may be thought of as a correction or extension of the LDA. As the electron density is not normally uniform in a molecular system one can understand that the LDA may not be as accurate as one would wish. The GGA is typically represented as a term added to the LDA that describes the extent to which the electron density is changing. This is done by computing the first derivative or gradient of the electron density and including this in the functional to give the exchange-correlation energy.

#### 2.3.1.4 Hartree-Fock Theory

This theory simplifies a many-electron problem by treating it as a set of one-electron problems. The interaction of each electron with the effective field of all the other electrons is then averaged over their orbitals. This treatment includes the exchange effects on the Coulomb repulsion between electrons. Hence Hartree-Fock theory accounts for the electron exchange correlation. For this reason Hartree-Fock theory is sometimes incorporated into Density Functional Theory methods as outlined in section 2.3.2.

#### 2.3.2 DFT Methods Used

This thesis included use of the DFT methods BLYP, B3LYP and BHandH as implemented in Gaussian03. BLYP is a standard DFT method relying on the GGA, not the LDA. B3LYP is derived from this method and includes a certain amount of Hartree-Fock exchange in calculations.

$$E_{xc}^{B3LYP} = (1-a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^B + (1-c)E_c^{LSDA} + cE_c^{LYP}$$
(2.7)

- $E_{xc}^{B3LYP}$  is the electron exchange-correlation energy calculated according to Becke's GGA exchange and Lee, Yang and Parr's GGA correlation functional
- $E_x^{LDSA}$  is the electron exchange energy calculated using the LSDA
- $E_x^{HF}$  is the Hartree-Fock electron exchange energy
- $\Delta E_x^B$  is the change in the electron exchange energy calculated using Becke's GGA exchange
- $E_c^{LDSA}$  is the electron correlation calculated using the LSDA
- $E_c^{LYP}$  id the electron correlation energy calculated by Lee, Yang and Parr's GGA correlation functional

The three parameters, a, b and c determine the contribution of each term on the right hand side of the above equation. For the B3LYP method these three parameters are as follows, a=0.20, b=0.72 and c=0.81. One can therefore say that the electron-exchange energy used in the B3LYP method will be 11.63% pure Hartree-Fock exchange energy. The remaining exchange is calculated using the LSDA and Becke's GGA exchange.

BHandH is very similar to B3LYP but with a higher degree of Hartree-Fock energy included in the exchange-correlation calculation, 50%.

$$E_{xc}^{BHandH} = (1-a)E_{xc}^{DFT} + aE_{x}^{HF}$$
(2.8)

In the case of BHandH the constant a, has a value of 0.50.

#### 2.4 Basis Sets

A basis function is a one electron function centred on an atomic nucleus. Molecular orbitals are described by a number of these functions called a basis set. In this study the basis set employed for all calculations was the 6-31G(d,p) [15] basis set. For each atom this provides six primitive gaussians with two extra functions for each valence orbital.

#### 2.5 Effective Core Potential

Effective core potentials are employed to cater for the relativistic effects encountered when performing calculations on large atoms. In this study the LANL2DZ [16] effective core potential was used for ruthenium and tungsten atoms. This was necessary due to the large number of core electrons in each case. The effective core potential replaces the basis functions of these many core electrons with a potential.

#### 3. Ruthenium Ion Catalysed Oxidation

#### 3 Ruthenium Ion Catalysed Oxidation

#### 3.1 Introduction

The aim of this project is the selective oxidation of polynuclear aromatic hydrocarbons, (PAH). PAH are found naturally in coal and crude oil deposits around the world. Of specific interest to this project are the PAH found after the fractional distillation process carried out on crude oil in oil refineries. It is hoped that a process will be found whereby these PAH can be economically reduced in molecular size to smaller, more industrially profitable hydrocarbons. The focus here was to employ ruthenium ion catalysed oxidation (RICO) chemistry to selected model PAH. The aim of this is to isolate the partial oxidation products of RICO and to determine structure, reaction energy profiles and rates of reaction.

The RICO chemistry relies on the use of ruthenium tetroxide (RuO<sub>4</sub>) as an oxidant for the PAH. Ruthenium tetroxide is generated from ruthenium chloride (RuCl<sub>3</sub>.xH<sub>2</sub>O) and a strong oxidant, potassium periodate (KIO<sub>4</sub>). With the PAH to be oxidised in the reaction flask in either a monophasic<sup>1</sup> or biphasic system, this is how the reaction is run. The products of the reaction are generally analysed by GC – MS. The experimental work is being carried out by Ewa Nowicka, whereas this project is currently focused on the computation understanding of the RICO reaction.

In an article published by Frenking and co-workers, density functional theory (DFT) studies are done to elucidate the reaction pathway for the oxidation of ethene by ruthenium tetroxide [17]. After the initial generation of ruthenium tetroxide, a [3 + 2] cycloaddition of the ruthenium tetroxide ( $Ru^{8+}$ ) with ethene occurs resulting in the  $Ru^{6+}$  complex shown in figure 1.

Following this, three different possible routes were calculated and it was found that the addition of a second ethene molecule was most energetically favourable. This meant that the ruthenium was further oxidised to the +4 oxidation state.

In order to facilitate the breaking of the C - C bond, oxygen provided from the iodate in solution is added to the ruthenium complex twice. This reduces  $Ru^{4+}$  to  $Ru^{6+}$  and in turn to  $Ru^{8+}$ . The resulting reaction pathway with the energies calculated by Frenking and co-workers is shown in figure 3-1.

<sup>&</sup>lt;sup>1</sup> Experimental work on monophasic system carried out by Ewa Nowicka.



*Figure 3-1* Showing the lowest energy reaction pathway for the oxidation of ethene by ruthenium tetroxide adapted from reference 1. All energy values are in kcal mol<sup>-1</sup>. The energy value, 3.1 kcal mol<sup>-1</sup> refers to the energy of the ruthenium tetroxide – ethene adduct with respect to the energy of ruthenium tetroxide and ethene.

The PAH molecules under investigation in this work include naphthalene, chrysene, anthracene, perylene, phenanthrene, pyrene, ethylbenzene and 2 - ethylnaphthalene. Anthracene however, is found in coal, not oil and is not studied as intensively as the other PAH. The reason for the inclusion of anthracene was for the compilation of energy trends, when considered with increasing numbers of aromatic rings within the various PAH. Four of these PAH are shown in figure 3-2. Toluene is included as it was part of the initial study in the project, based on the results in a paper by I. Suh *et al* [18].



Figure 3-2: Examples of the PAH under study.

Menéndez *et al* produced a paper in 2000 dealing with the problem of characterising the compounds present in polymerised pitches [19]. Here, ruthenium tetroxide was used as a selective oxidant for PAH. The reasoning behind this decision was based on the fact that when used to oxidise PAH, ruthenium tetroxide results in benzene carboxylic acids and carbon dioxide only. As ruthenium oxide was a selective oxidant, this property was used to analyse the results and hence determine the structure of the original PAH. The study focused on a few specific PAH, namely 9, 10 – diphenylanthracene, triphenylene and coronene, shown in figure 3-3.



*Figure 3-3: A sample of the PAH studied by Menéndez et al. a) diphenylanthracene, b) triphenylene and c) coronene [9].* 

The most relevant result from this study shows that the selectivity of ruthenium tetroxide with respect to PAH is most favourable at the least sterically hindered sites. Also shown is that when these sites are blocked, for example in diphenylanthracene, the rate of oxidation decreases. Figure 3-4 shows the reaction pathway found in this study to the first intermediate, pyrene-4,5-dione. This intermediate was first found through the experimental work and has been found to fit with the pathway presented in this study.



Figure 3-4: Overall mechanistic scheme of work done to produce the pyrene-4,5-dione.

- 3.2 Results and Discussion
- 3.2.1 Catalyst Selectivity

The given aim of the project was the selective oxidation of polynuclear aromatic hydrocarbons, (PAH). Given that RICO chemistry has been established for some time [20], specifically in the area of carboncarbon bond cleavage [21] it was decided to begin with this chemistry. Some selectivity has already been reported, specifically for the case of the oxidation of pyrene as shown in work by Harris *et al* [20], where 2,7-disubstituted pyrenes are selectively oxidised to either 4,5 or 4,5,9,10-pyrene diones using ruthenium tetroxide with 4 to 8 parts oxidant (sodium periodate) depending on whether the dione or the tetraone was the desired product. In this case oxidative selectivity is taken to be a result of mild experimental conditions. The work reads as a continuation of that done by Oberender and Dixon in 1959 [21]. This paper deals primarily with osmium tetroxide catalysed oxidation of pyrene but also shows that the ruthenium catalysed oxidation of pyrene with sodium periodate oxidant will give the pyrene 4,5-dione as the principle product. This work also showed that an increase in the amount of oxidant used will increase the yield of major products, this is also shown by Harris *et al* where doubling the amount of oxidant required to produce the dione results in the tetraone product.

In order to determine the possible oxidation products the oxidation mechanism was studied. The first stage of this was to determine how the catalyst should attack the PAH. Prior to this study, Frenking *et al* [17] used density functional theory to probe the mechanism of ruthenium tetroxide catalysed ethene oxidation. First, the ethene – ruthenium tetroxide adduct formation was examined. Two routes were investigated, a [2+2] and a [3+2] addition and the latter was found to have a lower barrier to the

formation of the final 5 – membered ring product. In the case of the [2+2] adduct, two barriers were found, the first at 43.4 kcal mol<sup>-1</sup> related to initial adduct formation followed by a second at 19.9 kcal mol<sup>-1</sup> relative to the starting point and corresponding to the structural rearrangement necessary to give the final adduct. For the [3+2] path only one barrier was found at 5.0 kcal mol<sup>-1</sup>. The same trend was found for adduct formation using osmium tetroxide, where a [3+2] adduct was preferred. When considering any PAH it must be noted that there are a number of possible sites for catalytic attack, therefore, before the viability of the [3+2] mechanism was examined, it was important to determine the selectivity.

The first portion of the study was to determine the selectivity of the active catalytic species, RuO<sub>4</sub>, as the catalyst selectivity will determine which carbon – carbon bond will be broken. A 2004 investigation undertaken by Frenking et al [17] examined the ruthenium ion catalysed oxidation reaction between ruthenium tetroxide and ethene. This study used a similar computational approach to the one undertaken here. Frenking found that the initial reaction step was a [3+2] addition of an ethane molecule to two of the oxygen molecules bonded to the ruthenium centre. This [3+2] addition is also found in osmium tetroxide catalysed oxidation reactions. In another density functional theory study on the addition of ethene to the chromium-oxygen bonds in chromyl chloride it was found that a [3+2] addition as the initial reaction step was also favoured when osmium tetroxide is used [22]. With PAH there are three possible sites for [3+2] adduct formation, outer, inner and bridgehead, shown in figure 3-4. An outer carbon – carbon bond is associated with one aromatic ring and will have a hydrogen atom bonded to each sp<sup>2</sup> hybridised carbon atom. An inner carbon – carbon bond will not have hydrogen atoms attached, but will be bonded to other carbon atoms only, that is it should be shared by two to four aromatic rings, depending on the number of aromatic rings in the PAH. A bridgehead carbon – carbon bond will not include any carbon - hydrogen bonds and will have one carbon atom inside the PAH and one on the outside of the PAH. The works of Harris and Oberender both show a catalyst preference for the bond formed by carbon atoms 4 and 5.



*Figure 3-5: Showing examples of inner (I), outer (numbered) and bridgehead (BH) carbon – carbon bonds in pyrene. Bond types are ringed in black.* 

Initially RuO<sub>4</sub>, phenanthrene, pyrene and coronene were optimised separately. This ensured that all starting structures were of the correct geometry. All calculations were done at the B3LYP/ 6-31G(d,p) level with zero point correction included. All symmetrically distinct carbon-carbon bonds were identified for each PAH to avoid repeating calculations. For example, coronene has 30 carbon-carbon bonds. However, only the bonds I,I, I,B, B,1 and 1,2 were used in calculations as all other bonds in coronene are symmetrically equivalent to one of these four bonds. RuO<sub>4</sub> was positioned at each bond labelled in figure 3-6b with a carbon oxygen distance of approximately 1.4 Å using Materials Studio. These structures composed of the separately optimised RuO<sub>4</sub> and PAH were then optimised.



Figure 3-6: PAH studied: A) Phenanthrene, B) Coronene.

Each optimisation was calculated with singlet and triplet spin states to allow for the possibility that the highest energy valence electrons for the complex may be of equal or opposite spin. Ruthenium has eight d electrons and upon complex formation will assume an oxidation state of VI leaving two d electrons.

Due to the placement of the catalyst in an ideal position for complex formation, the end result of each calculation was the optimised [3+2] intermediate.



Figure 3-7: Relative Binding Energies at each site in phenanthrene labelled in inset in both singlet and triplet Ru states. Binding energies calculated as  $E_{Binding} = E_{Complex} - E_{Ruthenium Tetroxide} - E_{Phenanthrene}$ . Singlet states are shown as a solid line with triplet states as a dashed line. Numbering shown in fig. 3- 5. BH and I as in fig. 3-4.

Figure 3-7 shows that adduct formation at atoms 9 - 10 gives the lowest binding energy for both singlet and triplet states. This may also be said to be the most structurally isolated outer carbon - carbon bond in the phenanthrene structure. What is meant by this is that, considering adduct formation, this is the least sterically hindered site. When the adduct forms at this site the remaining two aromatic cycles retain their aromatic character. If a sterically ideal site on either of the other two aromatic rings is selected for adduct formation, all aromatic character is lost. It is also apparent that the singlet state is consistently lower in energy than the triplet state. Positions 3 - 4 and 1 - 2 are also favourable and regarded as outer carbon – carbon bonds whereas position BH - BH, that with the least favourable (highest positive value) adduct formation energy may be said to be the most sterically hindered site when the approach of the catalyst is considered. Table 3-2 gives the lowest energy result for naphthalene, phenanthrene, pyrene and coronene adducts. Figure 3-8 shows all the positions most favoured for complex formation.



Figure 3-8: Structure of coronene, pyrene, phenanthrene and naphthalene. Most favoured sites for [3+2] adduct formation are shown in red, their symmetrical equivalents in blue.



Figure 3-9: Showing the optimised  $RuO_4$  and phenanthrene complex in the singlet (left) and triplet (right) states.

DAH Bond Number Desition	Singlet Binding Energy	
1 AII Dolla Number 1 ostaon	(kcal mol <sup>-1</sup> )	
Naphthalene 2	-31.7	
Phenanthrene 6	-36.3	
Pyrene 4	-35.2	
Coronene 1	-26.0	

*Table 3-1: Giving the most favourable binding energies for each of four PAH.* 

Results for pyrene and coronene were similar, in that the most sterically unhindered sites had the most favourable binding energy and that singlet energies were found to be consistently lower than triplet energies. Figure 3-8 shows the optimised geometries for the phenanthrene complex in the singlet and triplet state. In both cases it can be seen that the position 9,10 carbon–carbon bond has moved out of the plane of the molecule.

Table 3-2 shows bond length data taken from the most favourable adduct sites for each PAH.

Bond Length	Data (Å)	Singlet	Triplet	Bond
Naphthalene	2R	1.70	1.73	$\mathbf{R} = \mathbf{O}$
Position 2				
		1.90	1.90	R - OC
		1.50	1.40	C - O
		1.53	1.10	C - C
		1.10		С - Н
Phenanthrene	3R	1.70	1.73	$\mathbf{R} = \mathbf{O}$
Position 6				
		1.90	1.90	R - OC
		1.50	1.40	C - O
		1.52	1.54	C - C
		1.10	1.10	С - Н
Pyrene 4R	Position	1.70	1.73	$\mathbf{R} = \mathbf{O}$
4				
		1.90	1.90	R - OC
		1.50	1.40	C - O
		1.52	1.54	C - C
		1.10	1.10	С - Н
Coronene	7R	1.70		$\mathbf{R} = \mathbf{O}$
Position 1				
		1.90		R - OC
		1.50		C - O
		1.52		C - C
		1.10		С - Н

Table 3-2: Showing the bond length data for both singlet and triplet states of each of the lowest energy adducts for naphthalene, pyrene and phenanthrene. Triplet state frequency data for coronene was not calculated due to the obvious trend in the data.. R refers to the number of fused aromatic rings in the structure

The data shown in table 3-2 shows that structurally, the differences in each of the lowest energy complexes is minimal regardless of number of rings per PAH. Using pyrene as an example, the carbon – carbon bond distance prior to complex formation was 1.36 Å, giving a general increase of 0.2 Å after the addition of ruthenium tetroxide across the bond. This signifies that before adduct formation the affected carbon – carbon bond has sp<sup>2</sup> (double bond) character whereas after the addition of RuO<sub>4</sub> this becomes a single (sp<sup>3</sup>) carbon – carbon bond.

Figure 3-7 shows that for phenanthrene, the singlet  $RuO_4$  binding energy is favourable. Table 3-1 shows that phenanthrene and pyrene appear especially competitive. However, apart from observing that the most energetically favoured sites appear to present less steric hindrance to complex formation the chemical reason for this has not been explored.

All PAH optimised structures were planar, due to all carbon atoms being sp<sup>2</sup> hybridised and the binding energy trend was true for results of both singlet and triplet calculated energies. With the more inaccessible carbon – carbon bonds giving less favourable binding energies it was proposed that the energetic cost of moving affected carbon atoms out of the original plane of the molecule may explain the binding results. This is observed in table 3-1 where the binding energy for coronene (7ring, 7R) is less than that for the other PAH with fewer aromatic rings and therefore less structural rigidity. In order to determine whether or not this could explain the range of binding energies, the ruthenium and oxygen atoms were removed from each optimised complex structure for pyrene and a single point calculation was performed on the remaining carbon and hydrogen atoms. As the single point calculation gives the energy of a single geometry and does not change the geometry in any way the energy difference between these strain calculations and the optimised pyrene structure gave a value for the steric strain induced in the PAH upon complex formation. Table 3-3 shows the strain energy of complex formation at each carbon – carbon bond with the singlet binding energy as comparison.

Position	Binding	Strain	Strain Angle	
	Energy	Energy	(°)	-C atom affected
	(kcal mol <sup>-1</sup> )	(kcal mol <sup>-1</sup> )		by complex formation at
1 – 2	-19.87	66.04	5.19	position 4
3 – BH	-11.83	64.52	8.73	·
<b>BH</b> – 4	3.99	67.07	9.11	
4 – 5	-35.19	65.87	6.48	
BH – I	13.87	61.65	7.13	
I - I	22.85	52.43	13.27	

Table 3-3: Comparison of binding and strain energies for pyrene, strain angles were calculated as the difference of the dihedral for one of the two carbon atoms affected at each site and a 180 °, planar dihedral. This is shown in the image to the right of table 3-3

Strain energy remains almost constant for outer carbon bonds and decreases for inner carbon bonds. The binding energy does not follow this trend, meaning that another factor also plays a role in determining the binding energy of complex formation. The dihedral angles used for the strain angle were those of one of the carbon atoms moved out of plane by carbon – oxygen bond formation due to the [3+2] adduct formation at each of the six positions in pyrene. Table 3-3 shows that the carbon atoms moved least out of the original plane of the molecule was not that of the lowest energy complex formation site, rather the second lowest. However, the adduct formation site with the least favourable energy did have the largest strain angle. This implies that the strain induced as a result of complex formation does contribute to the binding energy but is not the only factor in determining the energy. This is further shown by the least energetically favourable binding site having the lowest strain energy.

The next approach was to examine the HOMO of each complex formed and compare it with the HOMO of pyrene. Due to the highly aromatised nature of pyrene it was thought that as complex formation will disrupt aromaticity, this may show in a change of the HOMO.



*Figure 3-10: Showing pyrene and RuO*<sup>4</sup> *before and after binding. The double bond to be attacked is highlighted in red in each case. It is observed that after complex formation this is a single bond* 

Figure 3-11 shows the HOMO of pyrene and that of both the most and least favourable adducts formed.



Figure 3-11: Showing three HOMO orbitals. A; pyrene, B; phenanthrene, C; pyrene-RuO<sub>4</sub> adduct position 4,5, D; pyrene-RuO<sub>4</sub> adduct position I-I. Note that the orbital density is distributed evenly across the structure.

Within figure 3-11, that on the bottom right (D), the highest binding energy site has a HOMO similar to that of pyrene. The image on the lower left (C) is that of the lowest binding energy site (I-I). Here the HOMO has changed, where previously there had been a node across the central carbon – carbon bond there is now an orbital shared across four carbon atoms. The node has moved to the carbon – carbon bond at the RuO<sub>4</sub> attack site. This is because these two carbon atoms (atoms 4 and 5 of pyrene) have become sp<sup>3</sup> hybridised. Where the HOMO lies across the bond the atoms are sp<sup>2</sup> hybridised.

The lower left image in figure 3-11 shows the most energetically favourable adduct formed from  $RuO_4$  and pyrene. Note that the left hand side of the HOMO here is that of phenanthrene, this shows that the three aromatic rings not attacked by the catalyst remain conjugated. The HOMO of phenanthrene is shown in figure 3-11 above the least favourable [3+2] pyrene adduct HOMO.

Position	Binding	НОМО	LUMO	HOMO -
	Energy	(eV)	(eV)	LUMO
	(kcal mol <sup>-1</sup> )			Gap (eV)
Pyrene	N/A	-0.196	-0.055	0.141
1 – 2	-19.87	-0.202	-0.152	0.05
3 – BH	-11.83	-0.217	-0.15	0.067
<b>BH</b> – 4	3.99	-0.186	-0.148	0.038
4 – 5	-35.19	-0.225	-0.155	0.07
BH – I	13.87	-0.212	-0.145	0.067
I – I	22.85	-0.205	-0.145	0.06

Table 3-4: Energy values for binding ( $E_{Binding} = E_{Adduct} - E_{Pyrene} - E_{Ruthenium Tetroxide}$ ) and the corresponding HOMO and LUMO energies of pyrene and the ruthenium tetroxide adduct. Position 4-5 has the lowest HOMO energy value, with position BH-4 having the highest, followed by positions 1-2 and I-I.

The orbital images and data show that complex formation at the most energetically favourable site produces a significant change in the HOMO orbital of pyrene whereas at the highest energy site, I-I the HOMO is very similar to that of an isolated pyrene molecule. Orbital energy data gives BH-4 as that with the lowest HOMO orbital energy.

In conclusion it is believed that the reason for the low binding energy at position four is due to a combination of three effects; 1) that this position offers one of the more isolated carbon – carbon bonds in pyrene, 2) while the site does not offer the lowest strain energy it does present less steric hindrance than the inner carbon – carbon bonds and 3) that while the HOMO of pyrene is changed upon complex formation at this site, the new HOMO is low in energy relative to the other five sites and while aromaticity is sacrificed on the ring affected by adduct formation the other three aromatic rings retain aromaticity.

#### 3.2.2 Adduct Formation

With the selectivity of the catalyst satisfactorily explained, the manner in which  $RuO_4$  bonds across the carbon-carbon bond was next investigated. This was accomplished by taking the optimised structures of pyrene and  $RuO_4$  and placing the catalyst in a position favourable for approach to position four but not close enough to produce the complex upon optimisation. This was then optimised and it was found that the catalyst was in a good position for bonding at position four.



*Figure 3-12: The optimised starting structure for a scan to simulate complex formation via carbon – oxygen bond formation.* 

The optimised carbon-oxygen distance shown in figure 3-12 is 2.7 Å and it can be seen that the catalyst has assumed a position over the desired carbon – carbon bond, further identifying position four as the most favourable for binding. The object of this calculation was to determine whether the formation of the two carbon–oxygen bonds was stepwise or concerted. To that end, instead of scanning an oxygen atom directly into a carbon atom, thereby limiting the position of the oxygen atom, the scan was done by decreasing the distance between the ruthenium atom and one of the two carbon atoms at position four. This allowed for free movement (within the optimisation) of all four oxygen atoms. From the scan output the energy of the system versus the ruthenium-carbon atom distance could be viewed graphically. This was done to determine the highest energy point from the scan. The geometry of this point was then extracted from the scan calculation output and used as the starting point for a transition state optimisation.



Figure 3-13: Scan results for pyrene-RuO4 adduct formation at the position shown in fig. 3-9

Figure 3-13 shows the scan results for adduct formation. A stepwise result would be expected to show two increases in energy (two scan steps) before complex formation, namely the separate formation of two carbon-oxygen bonds. A number of attempts were made to calculate the transition state but all

failed to produce the required negative vibrational mode. From what had been read in the literature [17] and the results shown here, it was concluded that the complex was formed via a [3+2] addition of two oxygen atoms from RuO<sub>4</sub> across a carbon-carbon bond of pyrene where results shown earlier give the most likely position for adduct formation. The final point energy shown in figure 3-13 agrees with the (zero point corrected) energy given previously as -35.2 kcal mol<sup>-1</sup>.

#### 3.2.3 Oxidation State of Ruthenium

In his paper on the oxidation of alkenes by ruthenium tetroxide, Frenking *et al* [17], the lowest energy pathway found to carbon – carbon bond cleavage shows that after complex formation and prior to carbon – carbon bond breaking the catalyst (Ruthenium) was oxidised to oxidation state eight, as seen in figure 3-14.



Figure 3-14: The overall energy pathway to carbon – carbon bond cleavage in ethene as shown by Frenking et al. Note that after complex formation has occurred the metal is oxidised to its state prior to complex formation [17].

Figure 3-14 shows the oxidation of the catalyst before bond cleavage. It is noted that two ethene molecules were bound to the catalyst prior to oxidation. The addition of a second PAH was not done in this study as the steric hindrance would be great. Oxidation of ruthenium from Ru<sup>(VI)</sup> to Ru<sup>(VIII)</sup> was accomplished simply by adding an oxygen atom to the complex and optimising.



*Figure 3-15: The optimised structure of the Ru*<sup>(VIII)</sup> *pyrene complex.* 

The energy difference between the two complexes of Ru<sup>(VI)</sup> and Ru<sup>(VIII)</sup> was calculated by using half the energy of molecular oxygen. The energy difference between the two complexes was found to be 32.30 kcal mol<sup>-1</sup>, meaning that the oxidation of ruthenium brought the complex close to the staring energy prior to adduct formation. However, due to the manner in which the value was calculated (half the energy of molecular oxygen) the increase in energy given may not be relied upon.

#### 3.2.4 Direct Bond Cleavage

Applying the pathway set out by figure 3-14 to pyrene (without second PAH addition) gives direct carbon-carbon bond cleavage as the next step. The energy cost for breaking the carbon-carbon bond 4,5 in pyrene was calculated using a relaxed potential energy surface scan as for adduct formation. The two carbon atoms were specified in the input file with the optimised bond distance, this distance was then increased in increments of 0.1 Å to achieve bond cleavage. The calculation was performed for both the Ru<sup>(VII)</sup> and Ru<sup>(VIII)</sup> complexes to ensure that the reported oxidation of ruthenium was a necessary step. If the prior oxidation of ruthenium was required then the transition state and final point energy values for the Ru<sup>(VIII)</sup> calculation should be lower than those of the Ru<sup>(VI)</sup> calculation.

kcal mol <sup>-1</sup>	Transition State	<b>Final Point</b>
Ru (VI)	45.9	12.8
Ru (VIII)	9.8	-20.8

Table 3-5: Optimised results for direct cleavage of the  $sp^3$  hybridised C-C bond of the pyrene ruthenium tetroxide adduct.

Once performed, the results of the geometrical scans were analysed and the structures corresponding to the highest energy found on the scan and the lowest energy structure after this point in the scan's progress were extracted from the output and used to generate two new input files, one for the determination and optimisation of the transition state structure, here the point at which C-C cleavage is attained and another for the final point, that is the structure and energy of the C-C cleaved product of

the scan. One can immediately see that the oxidation state of the ruthenium catalyst has a large effect on the barrier to carbon bond cleavage, the higher oxidation state giving a more favourable barrier by an approximate factor of 4.5 with a very favourable, negative energy value for the result of bond breaking, as seen in table 3-5



*Figure 3-16: Optimised structures for the transition state, A and final point, B with ruthenium in oxidation state VIII at the start of the scan* 

At this point reference was made to the experimental work done on the project<sup>2</sup> and it was found that under biphasic reaction conditions the dialdehyde seen in figure 3-16B was not observed. This prompted a second look at the possible mechanistic pathways after [3+2] addition of the catalyst, [3+2] adduct formation being supported by the literature [17]. It was decided to look into the possibilities of carbon – hydrogen bond activation. The hydrogen atom in question being also bonded to one of the carbon atoms bonded to the catalyst. The initial approach was to remove one of these hydrogen atoms onto the nearest oxygen atom attached to ruthenium. This was accomplished using a scan as previously described except that the atoms specified in the calculation were the relevant hydrogen atom and the closest oxygen atom on the ruthenium centre. It was noted that as a result of the [3+2] addition of the catalyst to pyrene, the PAH was no longer planar and had therefore lost much structural symmetry, therefore scans were run for both relevant hydrogen atoms as shown in figure 3-17. Calculations were performed in both oxidation states of ruthenium, Ru<sup>(VI)</sup> and Ru<sup>(VIII)</sup>. Results quickly showed that there was no discernible difference between the abstraction of one or the other hydrogen atom from carbon.

<sup>&</sup>lt;sup>2</sup> Experimental work carried out by Ewa Nowicka, Cardiff University



Figure 3-17: Starting structure for Ru(VI) H abstraction scan with arrow indicating scan direction

kool mol-1	<b>Transition State</b>	<b>Final Point</b>	
KCal III01	Α	В	
Ru (VI)	59.2	0.8	
Ru (VIII)	36.4	-71.0	

Table 3-6: Results for H abstraction to oxygen as illustrated in figure 3-16. The starting point for the  $Ru^{(VII)}$  scan was -35.2 kcal mol<sup>-1</sup> and that of the  $Ru^{(VIII)}$  scan -2.9 kcal mol<sup>-1</sup>.

Table 3-6 gives the results for the barrier height to be overcome for C-H bond activation. Here it is again shown that the higher oxidation state of ruthenium produces a lower energy barrier. While the transition state barrier was found to be much greater than that of direct C-C cleavage, the final point was over three times as favourable. When viewing the output of the scan as a movie in Molden [23], it was reasoned that the high barrier may have been due to the fact that the hydrogen atom being abstracted moved onto the oxygen atom via a constrained 3-membered ring composed of one atom each of hydrogen, oxygen and carbon. As the reaction was known to occur in a liquid medium, of which a major component was water, it was decided to introduce two water molecules to the calculation. Thus two water molecules were placed so that there was a hydrogen bonding network established between the hydrogen atom to be abstracted, the two water molecules and the oxygen atoms on the ruthenium centre. With this initial structure it was hoped that by scanning the hydrogen atom in question to the oxygen atom of the first water molecule, a hydrogen shuttle could be established whereby C-H cleavage was attained with the hydrogen entering solution and another hydrogen atom bonding to an oxygen atom on ruthenium from the solvent medium.



*Figure 3-18: Optimised starting point for hydrogen – shuttle with arrows showing intended hydrogen – shuttle* 

Ru<sup>(VI)</sup> was not included in calculations as all previous results gave more favourable energy barriers when ruthenium was maintained at oxidation state eight. Results showed that the inclusion of two water molecules had a favourable effect by lowering the amount of energy required for C-H cleavage.

kcal mol <sup>-1</sup>	Transition State	Final Point
1st H Abstraction	9.3	-73.3

Table 3-7: Optimised transition state barrier and end point C - H cleavage via hydrogen – shuttle

The data shown in table 3-7 show a reduction in the barrier to C-H cleavage by 27.1 kcal mol<sup>-1</sup> the end point is also slightly more favourable than the data shown in table 3-6 for C-H cleavage without water present. The reduction in the barrier is due to the stabilising effect of the two water molecules which remove the strain induced by a 3-membered ring transition state as found when no water molecules were present. The result of the inclusion of water was not found to be a ring opened product but a ketone. At this point the experimental results were again referred to and it was found that the ring opened products were a mixture of aldehydes and carboxylic acids and dicarboxylic acids. However, the pyrene-4,5-dione was seen as a stable intermediate prior to ring opening. Based on this it was decided to attempt the formation of the second ketone via the same hydrogen-shuttle route as for the first. These calculations were done again with ruthenium in oxidation states 6 and 8.

1 <sup>st</sup> H Abstraction Ru(VIII)	Transition State	9.3
	Final Point	-73.6
2nd H Abstraction Ru(VIII)	Transition State	1.3
	Final Point	-53.0
2nd H Abstraction Ru(VI)	Transition State	9.5
	Final Point	-42.4

Table 3-8: C-H cleavage barriers (kcal  $mol^{-1}$ ) for both H abstractions to produce the pyrene-4,5-dione

Results given in table 3-8 show that the higher oxidation state of ruthenium is continually preferable for the production of more favourable energy barriers and better end points.



Figure 3-19: Overall mechanistic scheme of work done to produce the pyrene-4,5-dione

Figure 3-19 shows the results at this point in the search for the pathway to the ring-opened product. The data in blue describes the energetics involved in the direct production of 4,5-pyrene dione. It is also noted that the inclusion of two discreet water molecules to the calculation for direct carbon bond cleavage reduces the energetic cost by about 11.5 kcal mol<sup>-1</sup>, making it appear to be competitive with dione production. However, given the more favourable trend associated with C-H bond activation and the experimental observation of the dione as a stable intermediate it is believed that the pathway shown in blue is the principle pathway with the 9.3 kcal mol<sup>-1</sup> transition state barrier to the first hydrogen shuttle being the rate limiting step. Experimental results have shown that ring opened products are observed after the dione intermediate, therefore routes from the dione to the ring opened products were explored.

#### 3.2.5 Geminal Diols

A geminal diol is an organic functional group described by two hydroxyl groups (-OH) on one carbon atom. One could also describe a geminal diol as a 1,1-diol. The functional group may be formed through the nucleophilic addition of a water molecule to a ketone. The reaction will proceed slowly in pure water but can be either acid or base catalysed. The reaction equilibrium will favour the ketone reagent but may be presumed to occur in an aqueous environment.



*Figure 3-20: Acid (left) and base (right) catalysed cyclohexanone hydration to produce the geminal diol* 

The base catalysed reaction is driven by the nucleophilic hydroxide ion attacking the carbonyl carbon which leaves the carbonyl oxygen atom with a negative charge. This then in turn attacks a water molecule to give the 1,1-diol product with a hydroxide ion to balance the equation. The acid catalysed reaction is initiated by the hydroxonium ion protonating the ketone to make it more electrophilic. This is followed by the sequential attack of two water molecules which again results in the 1,1-diol product, this time balanced by a hydroxonium ion. Both routes are shown in figure 3-19. As there is an excess of water in the reaction mixture it is assumed that both paths are followed.


Figure 3-21: Simplified representation of the hydration of cyclohexanone, note the equilibrium is biased towards the ketone and not the geminal diol product

While experimental results for the oxidation of pyrene have shown pyrene-4,5-dione as an intermediate and not the equivalent geminal diol, pyrene-4,4,5,5,-tetraol. It is not unreasonable to assume that a small amount of the tetraol is present. The hydration equilibrium for the geminal diol would also favour experimental results where the dione is always observed before any ring opened products. It is also easy to see that oxidation of the geminal diol to the observed acid aldehyde product should be facile.



Figure 3-22: Illustration of the sequential hydration of pyrene-4,5-dione to pyrene-4,4,5,5,-tetraol

The first step in the investigation of this route was to determine the energy barriers between pyrene-4,5-dione and each subsequent geminal diol. In order to do this, pyrene-4,5-dione was optimised with two explicit water molecules. Though the hydration reactions were to be calculated separately and each only require one water molecule, it was decided to use two explicit water molecules for continuity. Consideration was also given to the fact that a second water molecule would likely stabilise any transition states found, more accurately representing experimental conditions and reducing energy barriers. As there was to be no ruthenium present at this stage no effective core potentials were used, the 6-31G(d,p) basis set was applied to all atoms with the B3LYP functional as formerly. In order to produce the structure, the optimised pyrene structure was imported to Materials Studio where the hydrogen atoms on carbons 4 and 5 were changed to oxygen atoms. Two water molecules were drawn and placed within 3.0 Å of the new ketone groups. This was done in order to have the two water molecules in good proximity to the dione for the hydration reaction without putting a bias on any hydrogen bonding network which may form during optimisation. The result in figure 3-23 shows that the two water molecules do adapt a hydrogen bonding network. One molecule sits above the dione with

each hydrogen atom hydrogen-bonded to a carbonyl oxygen atom. The oxygen of this first water molecule lies above (out of the page) the two hydrogen atoms and is hydrogen bonded to one of the hydrogen atoms of the second water molecule which lies above and parallel to the plane of the molecule. The second hydrogen atom of the second water molecule is not involved in hydrogen bonding. Its closest possible acceptor is the right hand carbonyl oxygen at a distance of 3.341 Å, outside the tolerance for a hydrogen bond, set at 2.500 Å in order to avoid assigning undue precedence to relatively weak interactions.



Figure 3-23: Optimised structure of pyrene-4,5-dione with two explicit water molecules. The hydrogen bonding network is visible as dashed light blue lines with figures showing the lengths in Å.

There are two possible approaches to simulate the hydration of one of the ketone groups of the dione. The first approach attempted pushed the hydrogen atom of the second water molecules towards the oxygen of the second water molecule by decreasing the 1.83 Å distance between them along the hydrogen bond.



Figure 3-24: Results of relaxed PES scan for the hydration of one carbonyl group on pyrene-4,5-dione

Results show that the energy barrier develops once the reaction coordinate reaches approximately 1.5 Å. After this point the energy of the system increases steadily with the reduction in distance between the hydrogen atom of the second water molecule and the oxygen atom of the first water molecule. This reaches a peak at the transition state where the imaginary vibrational mode shows this hydrogen atom jumping between the two water molecules. The hydrogen atom involved in the 0.97 Å hydrogen-bond in figure 3-25 is also shown to jump, this time between the oxygen atom it is bonded to and the oxygen atom it is hydrogen bonded to. This transition state thus shows the formation of the first alcohol group of the geminal diol, with the second hydroxyl forming from the second water molecule.



Figure 3-25: Optimised transition state (left) and final point (right) of relaxed PES scan for the hydration of pyrene-4,5-dione

A summary of the zero point corrected data for these calculations is shown in table 3-9. While the results show that the energy barrier is not unreasonable, nonetheless it is greater than those found previously

for the carbon-carbon and carbon-hydrogen cleavage events. This agrees with the hydration information shown in figure 3-19, that the reaction is biased towards the carbonyl reactant rather than the geminal diol product. This in turn ties in with the aforementioned observation that the pyrene-4,5-dione is consistently observed in experimental analysis. If the reaction does proceed via a geminal diol intermediate after the production of the dione then a lag between the observation of the dione and any ring opened products would be expected.

	Zero Point	Free
	Corrected	Energy
	(kcal mol <sup>-1</sup> )	(kcal mol <sup>-1</sup> )
Pyrene-4,5-dione	0	0
2 Water Molecules		
Transition State	20.4	22.7
5,5-dihydroxypyren-4(5H)-one	1.6	3.2
2 Water Molecules		

Table 3-9: Relative energies for the transition state and final point structures of the hydration of pyrene-4,5-dione with zero point and free energy corrections

The next step in this investigation was to produce the pyrene-4,4,5,5,-tetraol shown to the right in figure 3-21. In order to do this the final point structure for the first hydration event shown at the right in figure 3-24 above was imported to Materials Studio where an extra water molecule was added to give a total of two. As before, this was done to stabilise the water molecule involved in the hydration reaction via a hydrogen bonding network.



Figure 3-26: Starting point structure for the hydration of the second carbonyl group of pyrene-4,5dione, hydrogen bond distances are shown in Å

Figure 3-26 shows this structure after a geometry optimisation. As expected a hydrogen bonding network has formed linking the geminal diol via the two water molecules to the carbonyl carbon. The approach used for the previous scan was again employed here. This was executed by scanning along the 1.788 Å hydrogen-bond shown in figure 3-25. The distance between the two atoms was set to decrease in steps of 0.1 Å. The aim of the calculation was to produce a geminal diol functional group on each of carbon atoms 4 and 5 with a view to seeing the diacid product upon carbon-carbon bond cleavage.



Figure 3-26: Hydration of remaining carbonyl group on intermediate 5,5-dihydroxypyren-4(5H)-one

Figure 3-26 shows the results of the relaxed PES scan for this calculation. The aim of the calculation was the production of pyrene-4,4,5,5,-tetraol. However, this structure was not found on the sampled reaction coordinate. The approach to this calculation was the same as for the generation of the first geminal diol group. Instead of seeing pyrene-4,4,5,5,-tetraol as the final point structure it was observed that the geminal diol functional group had "hopped" from carbon atom 5 to carbon atom 4. Furthermore, multiple attempts at the optimisation of a transition state structure proved fruitless and no negative mode was found. Table 3-10 shows the net difference in energy between the structure in figure 3-25 and that in figure 3-26 with corrections for the zero point and free energies.

Correction	ZPE	Free
		Energy
Total Energy	Change -1.04	-0.56
(kcal mol <sup>-1</sup> )		

*Table 3-10: Energy difference between 5,5-dihydroxypyren-4(5H)-one and 4,4-dihydroxypyren-5(4H)-one, calculated with two explicit water molecules* 

As can be seen, the difference in energy between the starting and end points is negligible. Any perceived difference can be set as the difference in the observed hydrogen bonding networks in figures 3-27 and 3-28.



Figure 3-27: Optimised final point structure of second relaxed PES scan showing new hydrogen bonding network distances in Å

For example, the hydrogen bond formed between a hydrogen atom of a water molecule and the oxygen atom of the carbonyl in the starting point structure is 1.87 Å. The same hydrogen bond in the final point structure is 2.23 Å. The difference in hydrogen bond distance and optimised energy may be explained by the high degree of freedom experienced by the water molecules during the calculation. That is, there is no difference between the two systems.

	5,5-dihydroxypyren-4(5H)-one	4,4-dihydroxypyren-5(4H)-one
	Starting Structure	End Structure
	(Å)	(Å)
Carbonyl	1.225	1.224
C=O		
C-OH a	1.448	1.459
C-OH b	1.375	1.372
C4-C5	1.555	1.553
COH  a	106.342	106.623
COH  b	108.722	111.969

Table 3-11: Comparison of the relevant distances for the starting and end point structures 5,5dihydroxypyren-4(5H)-one

As there was no energetic or structural difference of any meaning found between the starting and final point structures and any barrier height found was assigned to energy costs of the rearrangement it was determined not to follow this reaction coordinate any further.

## 3.2.6 Pyrene Hydroxylation

In order to determine the likelihood of carbon-carbon bond cleavage via a hydroxylated carbonyl carbon route the viability of the hydroxylation step had to be found. To this end the optimised final point structure of the second hydrogen shuttle was employed. For the hydroxylation calculations one of the water molecules was removed in order to reduce calculation time as two were sufficient. Hydroxylation was then attempted through pushing the oxygen atom of the water molecule closest to a carbonyl carbon towards that carbon atom. Thus the water molecule would be the hydroxyl source with the second explicit water molecule and the RuO<sub>3</sub> group used to stabilise the remaining H atom formerly of the water molecule.



Figure 3-28: Start point for carbonyl carbon hydroxylation scan.

The relaxed PES scan followed the coordinate shown by the blue arrow in figure 3-28. The scan was performed in increments of 0.1 Å as usual. Once complete, the results were analysed to find a good starting point structures for the transition state and final point optimisations. Table 3-12 shows the zero point corrected energies for the hydroxylation following the reaction coordinate specified in figure 3-28.

	ZPE	Free
		Energy
Transition	2.57	4.24
State		
<b>Final Point</b>	-20.9	-19.98

*Table 3-12: Zero point (ZPE) corrected and free energy for transition state and final point optimised structures in kcal mol*<sup>-1</sup>

At this point the hydroxylation of one carbonyl carbon looks favourable, with a low, positive transition state value and high, negative final point energy. The final point structure shows that the coordination between the unaffected carbonyl group and the ruthenium centre has been lost. The carbonyl oxygen of the affected carbon atom retains its coordination to the ruthenium centre. This carbon atom now displays functionality close to that of an acid group, although the removal of the ruthenium and cleavage of the carbon-carbon bond would be necessary to make this formal.



Figure 3-29: Optimised final point structure for the hydroxylation of one carbonyl centre. Possible acid group circled

From this point there are a number of possible ways forward. A second hydroxylation could be started from the structure in figure 3-29. The second hydroxylation could also be attempted following oxidation of the ruthenium centre, the addition of another water molecule could also be used to effect hydroxylation.

### Pyrene Hydroxyl Intermediates

With the resolution of a plausible reaction pathway to the pyrene-4,5-dione intermediate the next question was to achieve the experimentally observed ring-opened products. As the geminal diol approach had not yielded satisfactory results another approach had to be adapted. Figure 3-30A gives the Mulliken atomic charges associated with the final point structure of the second hydrogen shuttle.



Figure 3-30: Illustration of the final point structure of the second hydrogen shuttle showing the associated Mulliken atomic charges, 3-30A and the optimised structure, 3-30B

The oxygen atom (i.e.  $H_2O$ ) in figure 3-30A displaying a charge of -0.578 is found at a distance of 2.4 Å from the ruthenium atom (top water molecule). The distances between the ruthenium atom and the carbonyl oxygen atoms are 1.26 Å and 1.27 Å. Therefore one may assume that there is a certain degree of coordination of these three oxygen atoms about the ruthenium atom. The reason for this may be inferred from the fact that the formal oxidation state of the ruthenium atom at this point is VI, RuO<sub>3</sub>. When viewed in Molden the ruthenium atom appears bonded to each of the carbonyl oxygen atoms with the top water molecule in figure 3-30A seen to coordinate to the ruthenium atom also. A route to carbon-carbon cleavage was examined whereby the carbonyl carbon atoms were hydroxylated to provide a starting point structure for carbon-carbon cleavage. This would also point towards the diacid product. Once optimised a relaxed PES scan was performed where the distance between the two functionalised carbon atoms was increased in increments of 0.1 Å.



Figure 3-31: Relaxed PES scan of C-C cleavage to give diacid product, starting structure shown on right

The zero-point corrected transition state energy for this cleavage event was found to be 4.76 kcal mol<sup>-1</sup>, with the final point optimised at -74.63 kcal mol<sup>-1</sup>. The data therefore indicates that this pathway to cleavage is energetically favourable and initially would agree with experimental findings. That is, the presence of a pyrene-4,5-dione intermediate before the observation of any ring-opened products.

This approach was further tested in the presence of two water molecules. This was achieved by adding two water molecules to the starting structure in Materials Studio. Once optimised the same relaxed PES scan was performed. It was hoped that the final point structure of the previous scan would be stabilised by the water molecules.



Figure 3-32: Relaxed PES scan for C-C cleavage of hydroxylated pyrene-4,5-dione with 2 explicit water molecules. The optimised final point structure is shown on the right. The reaction coordinate followed was the C-C distance.

In this case the transition state and final point energies were found to be 1.80 kcal mol<sup>-1</sup> and -72.12 kcal mol<sup>-1</sup>, respectively. This shows a small decrease in the energy barrier for carbon-carbon dissociation, 2.96 kcal mol<sup>-1</sup>.



Figure 3-33: Optimised structure of pyrene-4,5-diol.

The right of figure 3-32 shows the starting point for one possible carbon-carbon cleavage event. This structure could be described as the reduced form of the dione intermediate, i.e. pyrene-4,5-diol with the Ru<sup>(VIII)</sup> attached. Once the ruthenium and associated oxygen atoms were removed and the resulting structure optimised this was seen to be the case. As shown in figure 3-32, pyrene-4,5-diol displays the full aromaticity of pyrene. At this point a route to the adduct structure shown in figure 3-30B was

investigated. This was done by again making use of relaxed PES scan. The reaction coordinate used was the distance between one of the two symmetrically indistinct functionalised carbon atoms, atom numbers 4 and 5 and the closest oxygen atom of the  $Ru^{(VIII)}$  catalyst. The 2.63 Å distance between the two atoms was reduced in steps of -0.1 Å. The resultant data is shown in figure 3-34. One can see that, similar to the [3+2] adduct formation data, the relaxed PES scan gave no indication as to the presence of a transition state and, once beyond a threshold distance of approximately 2.3 Å the graph becomes steeply negative leading to a good final point guess. The final point shows a favourably negative binding energy. Allowing for zero point corrections this came to -47.95 kcal mol<sup>-1</sup>. There is no transition state shown as there was no barrier found. Overall the addition of  $RuO_4$  to pyrene-4,5-diol was found to be very similar to the addition of  $RuO_4$  to pyrene. This similarity may be explained by the fact that pyrene-4,5-diol has the full aromaticity of pyrene. The pyrene/RuO<sub>4</sub> adduct binding energy was calculated at -35.2 kcal mol<sup>-1</sup> implying that the pyrene-4,5-diol/RuO4 adduct is a more favourable end result at -47.95 kcal mol<sup>-1</sup>.



Figure 3-34: Adduct formation scan for the attack of pyrene-4,5-diol by RuO<sub>4</sub>. The reaction coordinate used was the C-O distance.

So far this route has presented itself quite favourably. It does however depend on the presence of pyrene-4,5-diol in solution. From experimental observations it is known that pyrene-4,5-dione is present. Calculations were therefore performed to determine whether the alcohol or ketone form would be more stable in solution. The reaction conditions imply a great excess of water so this was the solvent chosen for the model. The model compounds were pyrene-4,5-diol and pyrene-4,5-dione. Calculations were done using two explicit water molecules or through the PCM model. All calculation were done using the same basis set as used throughout, 6-31G\*\* and repeated with the larger 6-311G+\*\*. The larger basis set was employed due to the small differences in results from the model compounds. This is because the larger basis set should better define the solvent hole used in the PCM model. In addition to this, due to the difficulty in getting some of the energy values to converge the Opt=VeryTight option was used in the calculation input. This helped to ensure a full set of data.

System	Basis Set	ΔEzpe	ΔЕрсм
Model Compound	6-31G**	-48.10	-48.24
	6-311G+**	-46.27	-46.40
Model Compound plus 2 explicit H <sub>2</sub> O	6-31G**	-6.71	-5.14
	6-311G+**	-9.09	-7.76

Table 3-13: Results showing relative stability of pyrene-4,5-dione vs. pyrene-4,5-diol in water. Energy difference calculated as E(pyrene-4,5-diol) - E(pyrene-4,5-dione). All values shown in kcal mol<sup>-1</sup>

Results in table 3-13 show that the pyrene-4,5-diol structure was favoured both with and without the PCM model. Although the inclusion of two explicit water molecules was found to narrow the difference significantly.

However, there is a problem with the initial assumption in this pathway. The hydroxylation of the carbonyl carbon atom is deemed highly unlikely. Although many references may be found for the hydroxylation of the carbon atom  $\alpha$ - to a carbonyl group there was no evidence found to support the above. Also, not all possibilities had been tested. The final approach attempted to achieve ring-opening was both direct and simple.

# 3.2.7 Direct C-C Cleavage

As has been shown, the proposed route to the 4,5-pyrene dione intermediate has a favourable, overall negative energetic pathway. However, once the dione intermediate is reached further reaction proved difficult with attempts being made. After numerous attempts to cleave the bond between carbon atoms 4 and 5 of the 4,5-pyrene dione intermediate a more straight forward approach was attempted. This amounted to a relaxed potential energy surface scan where carbon atoms 4 and 5 were pulled apart in increments of 0.1 Å.



Figure 3-35: Relaxed PES results for cleavage of carbon atoms 4 and 5 of 4,5-pyrene dione. The relative optimised SCF energy is also shown for transition state and final point structures. The start and final points of the scan are illustrated to the right. The C-C distance was used as the reaction coordinate.

Figure 3-35 shows the results of the relaxed potential energy surface scan. Interestingly, three steps into the scan the energy has decreased by approximately 30 kcal mol<sup>-1</sup>, this implies that the equilibrium carbon – carbon bond distance for the final point of the second hydrogen shuttle may be 0.3 Å longer than the optimised value. This would put the bond length at approximately 1.7 Å. The optimised bond length for the final point of the second hydrogen shuttle was found to be 1.483 Å. The optimised distance between carbon atoms 4 and 5 in pyrene was calculated at 1.361 Å. The increase by 0.122 Å between pyrene and the final point of the second hydrogen shuttle, that is the 4,5-pyrene dione intermediate with the reduced Ru<sup>(VI)</sup> catalyst and three water molecules present is as one would reasonably expect from the loss of the localised electron giving a single carbon – carbon bond. However, the reduction in energy from a 0.3 Å increase in bond length implies that bond cleavage in this case is facile with the reasonable barrier associated with the formation of new carbon – oxygen bonds.

From the starting point a low barrier is observed leading to a favourably negative final point structure. The end point (shown in figure 3-36) displays the type of functionality one might expect from the results of a Baeyer – Villiger type oxidation. This type of oxidation is discussed in chapter 4.



*Figure 3-36: Optimised transition state, left and end point structures for the relaxed PES scan of 4,5 cleavage of the second H shuttle final point.* 

Figure 3-36 shows the optimised transition state and final point structures taken from the output of the relaxed potential energy surface calculation. The negative vibrational mode which occurs at the saddle point was found at 2.533 Å along the specified reaction coordinate. After this point the energy along this coordinate becomes sharply negative. This negative part of the graph in figure 3-36 also describes the insertion of an oxygen atom originally seen as an oxo – ligand on the ruthenium centre. This is seemingly facilitated by the stabilisation effect of a coordinating water molecule on the reduced  $Ru^{(IV)}$  shown in figure 3-36, right. It is presumed that, in the reaction conditions this would be rapidly oxidised to  $Ru^{(VIII)}$ . As a result of the scan the 4,5-pyrene dione intermediate has been oxidised to phenanthro[4,5-*cde*]oxepine-4,6-dione. While the final point structure shown in figure 3-36 was not observed through experimental analysis, this data is believed to be representative of the carbon – carbon bond cleavage event. The difference in the final products between experiment and modelling may be explained by the fact that the modelling can only describe one reaction coordinate at a time. It is believed that, in the experimental conditions used the Baeyer – Villiger product will not be observed but rather the acid – aldehyde product mix seen in experiment. Regarding the final structure, consideration of the reaction conditions allows one to presume the regeneration of  $Ru^{(IV)}$  to  $Ru^{(VIII)}$ .

#### 3.2.8 Multiple Catalyst Attack

A likely route to the pyrene-4,5-dione has been shown for a single ruthenium tetroxide catalyst molecule attacking a single pyrene substrate molecule. The route found is energetically feasible and produces the experimentally observed intermediate. The tetraone equivalent, pyrene-4,5,9,10-tetraone, was also observed through product analysis. Using the route already found (figure 3-9) there were still two possibilities for the production of the tetraone product. The first being that two catalyst molecules attacked the pyrene substrate, the second being a sequential catalytic attack, first at the 4,5 position then at the 9,10 position as seen in figure 3-37. This is possible due to the fact that the favoured adduct formation site, 4,5, has a symmetrically equivalent site, 9,10. Although possible this was not particularly likely due to the catalytic amounts of ruthenium tetroxide present. The second route was sequential in

that, once the first dione was formed, the catalyst went on to attack carbon atoms 9 and 10 on 4,5-pyrene dione.



*Figure 3-37: Top; catalyst [3+2] adduct formation at pyrene-4,5,9,10. Bottom; second catalyst [3+2] adduct formation at 9,10 site of pyrene-4,5-dione.* 

With respect to the "double-attack" approach where both positions 4,5 and 9,10 are simultaneously attacked by two ruthenium tetroxide molecules, it was not deemed necessary to repeat all steps in the route to 4,5-pyrene dione. Given the previously observed favourable energetic trends the double adduct and subsequent oxidation step would be repeated for comparison.

Structure	<b>Double Adduct</b>	<b>Double Adduct</b>	
	Ru <sup>(VI)</sup>	Ru <sup>(VIII)</sup>	
Formation Energy (kcal mol <sup>-1</sup> )	-76.97	-10.21	

Table 3-14: Zero point corrected formation energies for 4,5,9,10  $RuO_4$  pyrene adduct calculated for  $Ru^{(VI)}$  and  $Ru^{(VIII)}$ 

Table 3-14 shows the results of these calculations. The formation energy for the ruthenium tetroxide double adduct, pyrene positions 4,5,9,10 is energetically favourable. The formation energy for a single ruthenium tetroxide pyrene adduct at the 4,5 position was found to be -35.19 kcal mol<sup>-1</sup> (table 3-3). This result implies that, in the presence of two catalyst molecules the substrate pyrene will be oxidised to the tetraone in favour of the dione. One may note that the formation energy for the pyrene-4,5,9,10 adduct is approximately twice that of the single pyrene-4,5 adduct. This implies that there is no real energetic reason for the formation of the pyrene-4,5,9,10 adduct to occur in favour of the pyrene-4,5 adduct. Indeed, the likelihood of this pyrene-4,5,9,10 adduct occurring is low due to the catalytic quantities of ruthenium tetroxide employed in the experiments. As the tetraone had been observed the next step was to examine the feasibility of pyrene-4,5-dione oxidation. That is, ruthenium tetroxide attack at the 9,10 position of pyrene after the formation of the dione intermediate at the 4,5 position.

Calculations were performed by taking the optimised structures for the [3+2] adduct with the ruthenium atom in oxidation states  $Ru^{(VI)}$  and  $Ru^{(VIII)}$  and replacing the hydrogen atoms at carbons 9 and 10 with oxygen atoms each bonded to  $sp^2$  hybridised carbon atoms. This structure is equivalent to the pyrene-4,5-dione intermediate forming a [3+2] adduct with the regenerated ruthenium tetroxide catalyst.

	Ru <sup>(VI)</sup>	Ru <sup>(VIII)</sup>
	Adduct	Adduct
Formation Energy (kcal mol <sup>-1</sup> )	-31.87	1.11

Table 3-15: Formation energies of the [3+2] Ruthenium VI and VIII adducts with pyrene-4,5-dione

The formation energies of these two structures were calculated as the energy of the optimised adduct minus that of pyrene-4,5-dione, minus ruthenium tetroxide and minus half the energy of one oxygen molecule in the case of the Ru<sup>(VIII)</sup> adduct. The geometry of both structures was found to be similar to that of the pyrene adducts with the exception of the two ketones which adopted an expected planar geometry to the main body of the molecule. The formation energy of the Ru<sup>(VII)</sup> pyrene-4,5-dione adduct is in agreement with that of the pyrene adduct and the double adduct discussed above.

	Ru <sup>(VI)</sup>	Ru <sup>(VIII)</sup>
	(kcal mol <sup>-1</sup> )	(kcal mol <sup>-1</sup> )
Pyrene-4,5 Adduct	-35.19	-2.89
Pyrene-4,5,9,10 Adduct	-76.97	-10.21
Pyrene-4,5-dione-9,10 Adduct	-31.87	1.11

Table 3-16: Summary of data for multiple catalyst attack on pyrene, that for the pyrene-4,5 adduct and the pyrene-4,5-dione-9,10 adduct are similar while the more favourable pyrene-4,5,9,10 double adduct may be considered in line with the others.

This data is summarised in table 3-16. The increase in the favourable energy value with the increase in the number of catalyst molecules can be said simply to be due to the number of catalyst molecules. This is because the favourable energy value appears to increase linearly with a relevant increase in catalyst numbers.

## 3.2.9 Effect of Aliphatic Side Chains

Thus far all results have been reported with respect to pyrene. Pyrene was chosen as a good, though idealised representative of crude oil. It is a large molecule with a variety of different sites for carbon-carbon bond cleavage. However, if the chemistry is going to work on real fractions some effort must be made to examine the applicability of RICO chemistry to a sample more representative of the actual conditions. An aromatic hydrocarbon with an aliphatic side-chain was employed for this purpose. Due to computational restraints this has been limited to 4-butylpyrene. This was chosen as there are sufficient results for pyrene for comparison. The aliphatic chain has been limited to four carbon atoms in order to ensure that geometry optimisation is not a protracted affair due to the freedom of movement in the aliphatic chain.



Figure 3-38: Optimised structure of 4-butylpyrene.

The optimised structure is shown in figure 3-38. Note that the aliphatic side-chain is extended away from the aromatic structure. If the number of carbon atoms in the side-chain were to be increased one would find structural optimisation difficult due to the high degree of freedom of the  $sp^3$  hybridised carbon atoms in the aliphatic chain. Four carbon atoms allow one to determine the impact of an aliphatic substituent on the RICO chemistry without large computational cost. As has been previously shown, once [3+2] addition of the RuO<sub>4</sub> catalyst to the substrate molecule occurs, reaction to the dione-type intermediate is facile. Therefore it was reasoned that if the presence of aliphatic side-chains were to inhibit the reaction, this would occur at the initial adduct-formation stage. To this end two structures were optimised. Using the previously optimised 4-butyl-pyrene, a RuO<sub>4</sub> adduct was optimised at the 4,5 position and at the 9,10 position, directly opposite the aliphatic chain. The 9,10 position was not investigated when studying pyrene as the 4,5 and 9,10 positions of pyrene are symmetrically indistinct.



*Figure 3-39: 4-butylpyrene and ruthenium tetroxide adduct, at position 4,5 top and position 9,10 bottom.* 

The optimised structures shown in figure 3-39 are similar. The only obvious difference, aside from the catalyst position is the slight buckle in the aliphatic chain displayed when ruthenium tetroxide forms an adduct at the 9,10 position. From the results of the structural optimisations it was possible to determine the energy difference between the two sites for adduct formation. The energy was calculated as that of the 4,5 adduct minus the 9,10 adduct. This resulted in a zero point energy corrected value of -2.77 kcal

mol<sup>-1</sup>. This indicates that the 4,5 position was more favourable for adduct formation. It had been expected that the 9,10 position would be more favourable due to the lack of steric hindrance caused by the presence of the four carbon aliphatic chain at position 4. In order to gain a more accurate insight two relaxed PES scans would have to be performed, one each for adduct formation at the 4,5 and 9,10 positions on 4-butyl pyrene. Unfortunately this was not possible as movement of the aliphatic chain made the calculation too time-intensive. Therefore it must be concluded that, from the data at hand adduct formation at the aliphatic chain is marginally more favourable than formation at another site.

Adduct Formation Energy (kcal mol <sup>-1</sup> )		
Position 4,5	-35.68	
Position 9,10	-32.92	

Table 3-17: Adduct formation energies for 4-butyl pyrene and ruthenium tetroxide with the catalyst tested at positions 4,5 and 9,10

The figures quoted in table 3-17 are in good agreement with those found for adduct formation using unsubstituted pyrene (table 3-3). In that case the favoured catalyst attack site was 4,5. This agrees with the slight bias found for this position in the butyl substituted pyrene. The results also appear to tie in with those found experimentally as aliphatic carboxylic acids were found in product analysis.

#### 3.3 Conclusions

From the research conducted into the reaction pathway for the oxidation of pyrene by ruthenium tetroxide the following conclusions may be drawn.

The selectivity of the catalyst is determined by the relative retention of aromaticity. That is, that the catalyst will attack a site where there will be least loss in aromaticity in the PAH. This is shown in figure 3-11 where the top left structure is the HOMO of phenanthrene. The bottom left structure is of the HOMO of the most favourable pyrene-RuO<sub>4</sub> adduct. One can see that this HOMO orbital is very similar to the HOMO of phenanthrene. Therefore one can say that upon adduct formation, pyrene loses 25% of its aromaticity. The least favourable pyrene-RuO<sub>4</sub> adduct HOMO is shown in the bottom right of figure 3-11. One can see here that 100% of aromaticity is lost. One of the stated aims of the project was to selectively oxidise each PAH from the centre out. It was believed that this would facilitate PAH breakup in fewer steps. However, it was consistently found that the most favourable site for catalyst attack was on the outer edges of each PAH studied (table 3-2).

Adduct formation was found to be a spontaneous process after numerous failed attempts at a stepwise approach no energetic barrier was found for the spontaneous addition of the catalyst to the PAH. The

pathway followed was that of a [3+2] addition as described by Frenking *et al* [17]. That is, once RuO<sub>4</sub> was close enough to the C-C bond indicated by selectivity studies, bond formation was facile.

After a number of attempts to initiate carbon-carbon bond cleavage at the [3+2] adduct site it was found that the cleavage process involved more steps. The incorporation of two explicit water molecules was found to better simulate the reaction conditions. This allowed for the possibility of the hydrogen shuttle in the pathway. A hydrogen shuttle was then performed which resulted sequential in hydrogen abstraction from carbon atoms 4 and 5 in pyrene. The hydrogen shuttle removed a hydrogen atom from the carbon atom of the PAH bonded to an oxygen atom of the catalyst. This hydrogen atom then pushed another hydrogen atom from one of the water molecules onto a catalyst oxygen atom thus far uninvolved in the pathway. The result of this two-step process was a dione intermediate.

It was found that maintaining the ruthenium atom in an oxidation state of  $Ru^{(VIII)}$  throughout the steps outlined above reduced energetic barriers to reaction. When the oxidation state of ruthenium was allowed to fall to  $Ru^{(VI)}$  the reaction did proceed but with a higher energetic cost. It was reasoned that, as the reaction occurs in an excess of oxidant ( $IO_4^-$ ) the oxidation of ruthenium between reaction steps would not hinder the reaction. Thus it is possible that even if the  $Ru^{(IV)}$  was not oxidised, the reaction would continue.

The dione intermediate was found to be very stable. A number of different approaches were employed to induce carbon-carbon cleavage but to no avail. These approaches include the exploration of geminal diol intermediates and pyrene hydroxylation. Analysis of experimental results also found that the dione appeared to be a stable intermediate. It was also found that the tetraone was a stable intermediate. This means that oxidation was possible at multiple PAH C-C sites.

Carbon-carbon bond cleavage was found to occur through direct cleavage of the pyrene-4,5 carboncarbon bond with the catalyst still present after the second hydrogen shuttle, that is the dione intermediate with the catalyst in close proximity. The results of the cleavage showed an ester-type intermediate. Due to the aforementioned abundance of oxidant in the reaction medium and the lack of experimental evidence for this structure, it is believed that rapid oxidation of the structure produces the observed acid/ aldehyde ring-opened products.

#### 4 Peroxy Tungsten Catalysed Oxidation

#### 4.1 Introduction

Epoxidation of sp<sup>2</sup> hybridised carbon-carbon bonds by hydrogen peroxide with tungstic acid has been considered in the literature as a route to the breakdown of cyclic hydrocarbons [24]. The method was introduced in 1983 by Venturello *et al* [25]. This procedure uses hydrogen peroxide in excess as the oxidant and tungstic acid as the oxidation catalyst. The reaction is a homogeneous catalytic reaction with two liquid phases, one aqueous and one organic. Due to this a phase transfer catalyst is employed. Venturello examined the use of both phosphate and arsenate ions as phase transfer catalysts. The reaction was found to be selective for oxidising olefins to epoxides with selectivity in the range of 80-90%. It was also found that the pH value of the aqueous phase had a bearing on the yield. As the pH decreased, the reactivity of the system increased. It was found that a pH of 1.6 in the aqueous phase gave the best results for the epoxidation of nine to ten carbon atom aliphatic hydrocarbons.



Figure 4-1: Hydrogen peroxide, A and tungstic acid, B.

As molybdenum appears directly above tungsten in the periodic table, one would expect that molybdenum would show similar activity. Indeed, knowledge of this effect gave rise to the RICO chemistry previously discussed [26]. Both tungsten and molybdenum catalysts were examined for their efficiency in oxidising alcohols to carbonyl compounds in 1985 [27]. This work found that molybdenum performed better as an oxidation catalyst than tungsten for the epoxidation of olefins, while the opposite was found to be true for the oxidation of alcohols. Again it was found that the reaction (for both catalysts) was dependent on pH. In this instance a pH of 1.4 was found to give the highest yields in the shortest amount of time using a tungsten catalyst. The molybdenum catalyst performed best in a pH of 3.0. The phase transfer catalyst used was aliquot 336, methyl trioctyl ammonium chloride. Since this time (mid 1980s) researchers have concentrated on the use of a tungsten catalyst for the epoxidation of olefins.



Figure 4-2: Proposed scheme of Ishii et al [1] with cyclohexane-1,2-diol as the intermediate in the oxidation of cyclohexene to adipic acid.

The first reference to a possible reaction mechanism appeared in 1989 where Ishii *et al* proposed a diol intermediate for the oxidation of cyclohexene to adipic acid [24]. In this case 5 wt.% of tungstic acid was used in conjunction with aqueous hydrogen peroxide, 35% in excess. The pH was again found to influence the reaction, this time a weak acidity was found favourable (pH 4-5). Adipic acid was generated with a 74% yield following the proposed reaction scheme illustrated in figure 2.

Regarding the study of the reaction mechanism, research has been done into the structure of the transition state of the epoxidation reaction. A 'butterfly' transition state structure was found for the epoxidation of alkenes with peroxy acids and a spiro transition state structure has been proposed [28]. 'Spiro' refers to the fact that the structure is a bicycle compound with the two rings connected through a single atom. 'Butterfly' refers to the shape, being similar to a butterfly with open wings if one were to consider the body of the insect to be the atoms connecting the two rings. This structure is illustrated in figure 4-3. This work explains the epoxidation of alkenes as an  $S_N2$  substitution reaction. A spiro structure may be described as a bicyclic organic compound with rings connected through just one atom. A computational study in 1997 employing B3LYP DFT with the 6-31G\* basis set [29] employed a number of different oxidants. The oxidants used were performic acid, dioxirane, oxaziridine and peroxynitrous acid. In all cases it was found that where the calculated energies found were related to structures with the oxygen-oxygen bond centred perpendicular to the double carbon-carbon bond. Other, less favourable transition states showed that the oxygen-oxygen bond.



*Figure 4-3: Transition state structure of the epoxidation of ethene with dioxirane as calculated by Houk et al [29].* 

One of the prime considerations when seeking an efficient oxidation system is oxidant efficiency. Full oxidant efficiency refers to the use of 100% of oxidant in oxidation without any redundant side products. Ideally, processes would be carried out in  $O_2$  or air where oxygen efficiency is close to 100%. Realistically, this is not possible for many processes. Therefore, one must look elsewhere for an oxidant. Another consideration is the environment. With emission restrictions and environmental targets becoming increasingly limiting one should strive for "green" chemistry. To that end, much work has been done with hydrogen peroxide. This oxidant has an oxidation atom efficiency of 50% with the

added benefit of water being the only reaction by-product generated by the oxidant. Having considered the oxidant in this manner one should give consideration to the oxidation catalyst. For this study a peroxy tungsten catalyst is proposed [25]. The use of a peroxy tungstate catalyst has been described a number of times in the literature.

### 4.2 Results and Discussion

### 4.2.1 Catalyst

When using tungstic acid as the catalyst for the oxidation of alkenes by hydrogen peroxide it is believed that the tungstic acid acts as an oxygen carrier to facilitate the oxidation of the substrate [30]. Therefore one may assume that the hydrogen peroxide in fact directly oxidises the tungstic acid which then carries the oxygen to the substrate for a further oxidation event. Tungstic acid may be described as a hydrated form of tungsten (VI) oxide (tungsten trioxide). It is commonly assumed that the tungstic acid becomes an oxygen carrier by becoming a tungsten peroxo complex. This means that at least one of the three oxo- ligands is changed to a peroxy- ligand. As there are three oxo ligands present in tungstic acid there are three possible peroxo complexes. A study is made here as to which peroxo complex is most likely formed from the oxidation of tungstic acid with hydrogen peroxide.



Figure 4-4: Showing the oxidation of tungstic acid by hydrogen peroxide to the tungsten peroxo catalyst structure as displayed in the literature

As no other tungsten peroxo complex was found in the literature a study was made of the three possible structures, shown in figure 4-5. Table 4-1 gives the relative energy of each structure. The energy values were calculated relative to the mono-tungsten (VI) pentaoxide used in literature studies. Half the energy of a single oxygen molecule ( $O_2$ ) was used to balance the calculations.





monotungsten(VI) pentaoxide monotungsten(VI) hexaoxide

Figure 4-5: Three possible catalyst structures resultant from the oxidation of tungsten (VI) oxide (shown top left) by hydrogen peroxide

Monotungsten(VI)	Monotungsten(VI)	Tungsten(VI)	Monotungsten(VI)
pentaoxide	tetroxide	oxide	hexa oxide
0	1.71	-10.3	-23.6

Table 4-1: Relative energies kcal mol<sup>-1</sup> of different possible catalyst structures, also included is Tungsten (VI) oxide (dehydrated tungstic acid)

There are many literature references to peroxy tungsten as a catalyst for hydrogen peroxide as an oxidant. However, in the references which give special attention to the tungsten catalyst, only one structure is presented [30] [31], that of the monotungsten (VI) pentaoxide. The calculations carried out here would indicate that the monotungsten (VI) hexaoxide is the more energetically favourable structure by at least 13.3 kcal mol<sup>-1</sup> as shown in table 4-1. In a 2000 study by Valentin et al [32] the catalyst structure is explored. Values are then given for the activation barrier to epoxidation via three different transition state structures, one for each catalyst.



*Figure 4-6: Catalyst structures as studied by Valentin et al. With the exception of the ammine ligands these structures are very similar to two of those shown in figure 4-5.* 

The structures given by Valentin were used as the basis for the determination of the most likely catalyst structure in this thesis. Of the two structure types studied by Valentin, 1A and 1B, monotungsten (VI) tetroxide gave a positive (unfavourable) value in the calculation summarised in table 4-1. Tungsten (VI) oxide resulted in geometry lower in energy than either monotungsten (VI) tetroxide or monotungsten (VI) pentaoxide. However, this tungsten complex does not possess any bidentate oxygen ligands meaning that it cannot be employed as a catalyst for alkene oxidation. All calculations in this thesis have shown that it is one of the two peroxy oxygen atoms coordinated to the tungsten centre that provide the oxygen for epoxidation. Studies of the mechanism have confirmed this, favouring a spiro transition state structure [29]. Monotungsten (VI) hexaoxide gave the most favourable for oxidation. The lack of information about this structure and its use as a catalyst gave pause [33] and it was decided to use the structure monotungten (VI) pentaoxide as the catalyst as it would be more comparable to the available literature.

## 4.2.2 Ethene Epoxidation as a Model of Cyclohexene Epoxidation

Upon the proposal of tungsten as a possible catalyst for the selective oxidation of PAH, a literature search was performed to determine the current knowledge of the efficacy of tungsten catalysts and to find all relevant knowledge of the mechanism of oxidation. The most promising initial reference was published by Noyori *et al* in 2003 [30]. This paper focuses on the environmental benefits that come from using tungsten as a catalyst for the oxidation of cyclohexene to adipic acid with aqueous hydrogen peroxide as the oxidant.



*Figure 4-7: Mechanism proposed by Noyori et al [30] for the tungsten catalysed hydrogen peroxide oxidation of cyclohexene to adipic acid* 

Figure 4-7 shows the proposed mechanism starts with the epoxidation of the double carbon – carbon bond of cyclohexene, this is performed by hydrogen peroxide through the intervention of the tungsten catalyst as described in figure 4-1. The epoxide is then converted to a 1,2-diol through hydrolysis. From this point three separate oxidation events are shown to give the oxidised product of a Baeyer – Villiger type oxidation, oxepane-2,7-dione. This then undergoes ring opening via a second hydrolysis event to give the aliphatic diacid product, adipic acid.

In this work initial calculations were done using the structures shown by Noyori *et al* for the tungsten catalysed oxidation.



*Figure 4-8: Tungsten catalysed epoxidation occurring in the organic phase as shown by Noyori et al* [30]

Noyori *et al* made use of a biphasic reaction system where catalyst regeneration (via oxidation by hydrogen peroxide) occurred in the aqueous phase and the catalysed oxidation of the organic substrate occurred in the organic phase. The tungsten catalyst was taken across the phase boundary by means of a phosphoric acid ester phase transfer catalyst. Throughout the reaction the oxidation state of tungsten is maintained at (VI), this is achieved by alternating peroxy and oxo oxygen groups as shown in figure 4-5. For the epoxidation of the substrate hydrogen peroxide provides the catalyst with two peroxy groups in the aqueous phase, the phase transfer catalyst then brings the tungsten catalyst into the organic phase where the oxygen atom provided by the hydrogen peroxide, show in blue, (figure 4-8) oxidises the double carbon – carbon bond of the substrate to an epoxide. The catalyst now with only one remaining peroxy group returns to the aqueous phase where it is regenerated by hydrogen peroxide. Due to catalyst regeneration the hydrogen peroxide is reduced to water, the only by-product of the reaction, thus a "green" oxidation.

The initial calculations of this work used ethene as the substrate in order to decrease computational time. The tungsten catalyst was reproduced according to figure 4-8 In order to achieve epoxidation both ethene and the tungsten catalyst, with the phase transfer catalyst were optimised in one calculation to provide a starting point. The phase catalyst modelled was not exactly that given by Noyori *et al* but was simplified from a phosphoric ester, phenyl phosphoric acid to phosphoric acid, the R group replaced by an –OH group to reduce the size of the calculation. A relaxed potential energy surface scan was then completed by stepping an oxygen atom from the peroxy group closest to the ethene molecule into one of the carbon atoms of ethene.



Figure 4-9: A) showing the starting point for the epoxidation scan. Distances are shown in units of Å and the double headed arrow shows the decreasing atom distance specified in the scan. B) Final point for ethene. Tungsten atoms are shown in purple and phosphorus atoms are blue.

Results show complete separation of epoxide and catalyst after epoxidation has occurred, (figure 4-9B) this would support the scheme of Noyori *et al* [30] which indicates catalyst regeneration takes place directly after epoxidation.

After epoxidation the substrate is expected to be converted from an epoxide to a diol via hydrolysis. This was modelled using two water molecules, two molecules were chosen as the second may stabilise the first during hydrolysis. The process was attempted with six water molecules forming a cluster about the epoxide. A similar geometric scan was then attempted. Unfortunately, after numerous attempts it was found that this consistently lead to rearrangement of the water cluster and not hydrolysis. The calculation set-up was similar to that shown in figure 4-10. As the oxygen atom (water) was stepped into the carbon atom of the epoxide (as an –OH group) the remaining hydrogen atom was picked up by a neighbouring water atom. Thus hydrogen atoms were 'passed on' until the cluster had returned to six discreet water molecules, leaving the epoxide unchanged.



Figure 4-10: Conversion of epoxide to diol with two water molecules

#### 4.2.3 Baeyer-Villiger Oxidation

For the tungsten catalysed oxidation of PAH the Baeyer – Villiger oxidation is regarded as an important step in the route to ring opening. Jin *et al* [34] showed the mechanism for the tungsten catalysed oxidation of  $\alpha$ -hydroxyl-cyclohexanone through application of the Baeyer-Villiger mechanism. Computationally, the restricted B3LYP functional was used with the LANL2DZ ECP for the tungsten atom with other atoms described by the 6-31G(d,p) basis set.



Figure 4-11: Proposed scheme of Jin et al [34] for the oxidation of  $\alpha$ -hydroxyl-cyclohexanone via two intermediates with two corresponding transition states. Catalyst regeneration occurs via  $H_2O_2$  leaving  $H_2O$  as a reaction by-product

Figure 4-11 shows the reaction scheme presented by Jin *et al.* Starting with a fully regenerated catalyst, W<sup>(VI)</sup> and the appropriately functionalised intermediate, that is the previously doubly bonded carbon atoms converted to one alcohol and one ketone group. The Baeyer-Villiger proceeds with the lone pair of electrons on the oxygen atom of the ketone group coordinating to the tungsten atom of the catalyst. This leads to the first transition state which is a four membered ring consisting of the tungsten atom, the carbon and oxygen atoms of the ketone group and one of the peroxy oxygen atoms of the catalyst. From this transition state the peroxy group of the catalyst opens up to move towards a second, five membered ring transition state which displays an epoxide-like group using the peroxy oxygen involved in the four membered-ring first transition state. As the remaining oxygen atom from the peroxy group reverts to a single atom oxo ligand on the tungsten metal centre, the other oxygen is inserted into the carbon-carbon bond giving the Baeyer-Villiger oxidation product and the tungsten catalyst remains in oxidation state W<sup>(VI)</sup>. Initial calculations were performed to reproduce the results of Jin *et al.* Structures

based on those presented by Jin *et al* were duplicated as close as possible using Materials Studio, with geometeric data matched as closely as possible. All structures were then appropriately optimised with the aim of achieving energetic data as close as possible to that published. Unfortunately, the transition state structures were not quite close enough to find the correct vibrational mode. Therefore in order to acheve the desired results two relaxed potential energy surface scans were done.



Figure 4-12: Optimised structures for Baeyer-Villiger starting point, first intermediate (M3) and end point. Arrows shown in first intermediate give scan direction for each of the two scans required to present the final point shown.

Both the geometry and energetic data from the results based on the two relaxed potential energy surface scans were in reasonable agreement with that shown by Jin *et al* [34].

Energy Comparison (ZPE included (kcal mol <sup>-1</sup> ))			
	Jin 2011 [11]	This work	
C1 + R1	0	0	
M3	-46.5	-41.43	
TS3	-28.86	-16.77	
M4	-32.28	-31.42	
TS4	-19.58	-19.27	
P1 +C2	-46.87	-54.86	

Table 4-2: Comparison of zero - point energy corrected data for the Baeyer-Villiger oxidation of a - hydroxyl - cyclohexanone. Differences in values (TS3 and P1 + C2) are due to slight geometric differences (table 4-3).

Table 4-2 shows that in the main, results were in good agreement with those published. The final point calculations gave the calculated products as lower in energy than those of Jin *et al*. The main difference is shown in the value for the first transition state far this was calculated to be higher than the value given by Jin *et al* [34]. As the vibrational mode corresponded to that of Jin *et al* it is presumed that this difference is due to the slight difference in structure geometry as shown in table 4-3.

Geometry Comparison(Å)				
	Atom Nos	Jin 2011 Å	This work Å	Difference Å
M3	1,2	1.240	1.244	0.004
	2,8	2.169	2.152	-0.017
	8,4	1.975	1.941	-0.034
TS3	1,2	1.360	1.345	-0.015
	2,8	1.998	2.007	0.009
	8,4	2.123	2.074	-0.049
	4,1	1.677	1.798	0.121
M4	1,2	1.421	1.431	0.01
	2,8	1.907	1.914	0.007
	8,9	1.962	1.942	-0.02
	9,4	1.474	1.488	0.014
	4,1	1.432	1.472	0.04
	1,7	1.541	1.550	0.009
TS4	1,2	1.373	1.379	0.006
	2,8	1.981	2.005	0.024
	8,9	1.850	1.853	0.003
	9,4	1.834	1.868	0.034
	4,7	2.331	2.332	0.0001
	1,7	1.730	1.736	0.006
P1	1,2	1.208	1.207	-0.0001
	4,7	1.450	1.441	-0.009
C2	8,9	1.716	1.717	0.001

Table 4-3: Comparison of geometric data for the Baeyer-Villiger oxidation of a-hydroxylcyclohexanone. Difference calculated as 'this work' result minus the result of Jin et al [34] and are quoted in Å. Atom numbers as shown in figure 4-11.

Tables 4-2 and 4-3 show the very good agreement obtained by reproducing the calculations presented by Jin *et al*. As before mentioned, a discrepancy was found in the energy results for the first transition state structure (TS3), this is matched in the geometric data, with the largest bond length difference shown for the same structure that is the distance between atoms 4 and 1. Labels 4 and 1 refer to the

oxygen and carbon atoms in the bond forming transition state mode prior to the first intermediate. As the distance between these two atoms is different in each study one would expect a difference in transition state energy.

The initial calculations performed were done using a PAH with the same functional groups as R1 of Jin *et al* [34] however results were not as expected due to the presumption that there would only be one transition state barrier to overcome. The calculations were then extended to the case of a PAH using phenanthrene as an example.



Figure 4-13: Initial approach to Baeyer – Villiger oxidation via relaxed PES scans A and B.

Figure 4-13 shows the starting structure for the first two attempts at the Baeyer-Villiger oxidation. Phenanthrene was used as the first model compound due to the lower degree of structural rigidity in comparison to pyrene, it was hoped that this would reduce the computational time required. The starting point shows that the PAH has both the alcohol and ketone functional groups corresponding to that of the initial R1 structure of Jin *et al*. The tungsten catalyst has been regenerated following the first few reaction steps. Both scan routes, A and B were computed, scan route A refers to moving the peroxy oxygen atom of the catalyst closest to the carbon-carbon bond of interest to the nearest carbon atom of said carbon-carbon bond. Scan route B moves the same oxygen atom as for scan route A except in this instance the oxygen atom is moved to the further carbon atom of the carbon-carbon bond.



Figure 4-14: Results of relaxed PES scans A and B in attempting to produce the Baeyer – Villiger oxidation with phenanthrene. C\* in scan B denotes a different C atom specified in the scan input. The same O atom was referred to in both cases.

The starting point for both scans is shown in figure 4-13. The results of scan A were obtained over a total scan of 1.9 Å, while the results for scan B cover 2.5 Å. In each case all scans were completed with a step distance of 1.0 Å.

The results of calculations along scan route A show two transition states accompanied by one intermediate followed by the final point of the calculation which is the ring opened product with one aldehyde group formed and the catalyst still attached to what could reasonably become an aldehyde group. The first transition state relates to carbon – oxygen bond formation along the axis of the scan that is a new bond is formed on the imposed reaction coordinate. The starting value of the reaction coordinate was 3.15 Å which is then reduced to 1.83 Å at the first transition state, this structure was then optimised to the intermediate with the reaction coordinate measuring 1.52 Å. Further along the reaction coordinate at 1.35 Å a second transition state was found, unlike the first transition state the negative vibrational mode was not along the reaction coordinate but rather relates to carbon – carbon bond cleavage. This bond breaking event includes the carbon atom identified in the scan and the second, functionalised carbon atom. Shortly after this event, the final point structure was found at a carbon – oxygen distance of 1.23 Å. This relates to the newly formed double carbon – oxygen bond of the presumed aldehyde group.



Figure 4-15: Ring opening transition state (left) and final point structures for scan route A.



Figure 4-16: Showing a molecular graphic of the end point of scan A with a possible route to the dialdehyde product represented as a pictorial representation.

Scan B presents a very different profile to that of scan A, despite the same starting point and similar route as shown in figure 4-13 The scan itself shows very high energies to be overcome, of the order of 50 kcal mol<sup>-1</sup> whereas the actual calculated transition state values are very similar, both being approximately 16 kcal mol<sup>-1</sup>. The reasoning behind this scan was that in the process of bringing the oxygen atom in to the carbon atom as indicated in figure 4-13 the oxygen atom would at some point be close to equidistant to the functionalised carbon atoms. It was hoped that a structure provided by this scenario would give oxygen insertion as desired. Unfortunately this was not the case, the input structure for the first transition state search (red) was taken as that given by the scan at a O-C\* distance of 3.3 Å, C\* denoting a different carbon atom than that specified in scan A. This was related to the apparent movement of the hydrogen atom bonded to the alcohol group towards the carbonyl group. The input for the second transition state search came from the highest energy structure from the scan data at a O-C\* distance of 1.7 Å. The transition state search based on this structure optimised to the same negative vibrational mode as found in the first transition state search. The final point of the scan optimised to an

energy close to that of the starting point. It is therefore concluded that scan B resulted in the movement of a hydrogen atom from one functionalised C\* atom to the second C atom with the O atom from the catalyst specified in the scan input stabilising the dehydrogenated C\* atom. No potential Baeyer-Villiger or ring opened type structures were observed.

At this point in the calculations no actual Baeyer-Villiger type structure had been observed although it had been modelled in the literature with a cyclohexene-based substrate [34]. Therefore it was decided that the results of Jin *et al* should be reproduced in order to determine exactly how the reaction should be modelled. The initial attempt was to submit structures based on those presented in the paper and constructed using Materials Studio [35]. Structures were created based on those given for the reactants, all intermediates and transition states and products and then optimised, with a transition state search where appropriate. For the simple reactant and product structures this approach was successful, however in the case of both transition states and the intermediates the technique did not give the desired results. Hence scans were executed to produce the structures shown in the publication.


Figure 4-17: A showing the structures as reported by Jin et al [34]. B showing structures as calculated in the reproduction done as part of this thesis. All distances are given in Å and scan paths shown using small arrows with scan distance shown in inset fig. 17B.

The overall path shown in the insert to figure 4-17 shows that two separate scans were required to obtain the desired Baeyer-Villiger product. The first scan brought the peroxy oxygen indicated in the figure 4-16 insert 1.7 Å closer to the carbonyl carbon. The second scan moved the same oxygen atom from this point in to the alcohol-functionalised carbon atom. The two scans together resulted in the insertion of

the oxygen atom between the two carbon atoms. The energetic and geometric data produced were comparable with that published, as discussed earlier in tables 4-2 and 4-3.

Phenanthrene was selected for the first application of the two relaxed PES scan approach due to it having a less rigid structure than pyrene. The starting point was possessed of two functionalised carbon atoms as for the previous calculations and the two-step scan route was applied as previously.



Figure 4-18: Starting and end points for the calculation of the Baeyer – Villiger oxidation of phenanthrene. The two scan vectors are shown for the starting structure.

For the oxidation of phenanthrene, two explicit water molecules were retained with the structure in order to provide continuity with previous calculations that is the use of water when oxidising phenanthrene to the starting point of the Baeyer – Villiger oxidation. The pathway was then applied to pyrene with carbon atoms 4 and 5 appropriately functionalised. These calculations did not include the two explicit water molecules; this was done to determine whether the inclusion of water made any appreciable difference to the results.



*Figure 4-19: Comparison of transition states, intermediate and Baeyer – Villiger oxidised structures including the differences resulting in the inclusion and exclusion of water with a PAH substrate.* 

Results indicate that the procedure shown by Jin *et al* is applicable to PAH and that the inclusion of two explicit water molecules makes the energetic pathway more favourable due to hydrogen bonding effects. The oxygen atoms labelled 2 and 9 in figure 4-11 are stabilised in the transition states by hydrogen bonding effects. It appears that this effect influences TS3 more than TS4. TS3 shows a carbonyl carbon atom (atom 1, figure 11) without four bonding partners. It is believed that the hydrogen bonding structure helps to stabilise this transition state in order for the reaction mechanism to proceed to intermediate structure M4.

## 4.3 Conclusions

While this study was unable to elucidate the pathway from carbon-carbon double bond epoxidation to the starting ketone-alcohol structure for the Baeyer-Villiger oxidation it has been shown that the Baeyer-Villiger oxidation is facile. The ring-opened Baeyer-Villiger oxidation product shows a favourable end point energy as seen in figure 4-19. Three separate possible routes for oxygen insertion in the Baeyer-Villiger oxidation were explored. These attempts show that a two-step computational approach was required to achieve the desired reaction intermediate. In order to fully determine the lowest energy reaction pathway for the oxidative cleavage of PAH using a tungsten catalyst the reaction steps prior to the Baeyer-Villiger oxidation need to be found. Extending the model PAH from phenanthrene to pyrene increased the energy of the second transition state structure and the final product. It may be that with a continued increase of the number of fused aromatic rings in the reaction substrate, these energies will continue to increase. However, there is not enough data to state this with any certainty.

The tungsten catalysed oxidation system has not been fully elucidated in comparison to the RICO oxidation. In both cases the inclusion of water molecules in the calculations have stabilised structures though water does not appear to be as involved in the tungsten catalysed oxidation system. Results

indicate that the final steps of both pathways involve the insertion of an oxygen atom between the two  $sp^2$  hybridised carbon atoms initially attacked by the catalyst. It is proposed that in both cases, this anhydride functional group dissociates to carboxylic acids.

## 5. Conclusions and Future Work

5 Conclusions and Future Work

The aim of this thesis was threefold:

1. Is there selectivity for a specific molecule within a mixture of similar molecules?

Table 3-2 shows that, for the four PAH selected to determine catalyst selectivity within a mix of PAH, naphthalene, phenanthrene, pyrene and coronene, the addition of the catalyst to phenanthrene was most favourable by 1.1 kcal mol<sup>-1</sup>. Coronene was found to be least favourable with a catalyst binding energy of -26.0 kcal mol<sup>-1</sup>, a difference of 10.3 kcal mol<sup>-1</sup> compared to phenanthrene. Selectivity of RuO<sub>4</sub> to each PAH was calculated separately. In any future work it may be of interest to test a mix of PAH. This is due to the observation that coronene has six symmetrically indistinct sites favoured for adduct formation whereas phenanthrene has but one.

2. What is the selectivity for oxidation of a specific position within the PAH?

Figure 3-7 and table 3-2 show that the oxidation catalyst (RuO<sub>4</sub>) most explored was selective. Figure 3-7 shows the structures of the range of PAH studied for selectivity. The catalyst was found to be selective with respect to the bonds shown in red. The symmetrically equivalent bonds are shown in blue. Given that it was found that multiple, simultaneous catalyst attacks were possible it may be presumed that these sites, for all PAH would also be attacked. Future work should include the application of the reaction pathway found to all positions on all PAH, individually and simultaneously. The selectivity of the catalyst to the sites shown in figure 3-7 was investigated. Two approaches were taken. The first was to measure the strain on the planar, sp<sup>3</sup> hybridised PAH. The results from these calculations did not further the understanding of the catalyst selectivity. The second approach was to find out the effect of adduct formation on the aromaticity of the PAH. To this end the HOMO of the PAH and the adduct structures were examined. It was found that the retention of as much aromaticity in the PAH structure after adduct formation directed the site of catalyst attack.

3. How selective is oxidation of the PAH when compared to long chain alkyl constituents?

It was found that the addition of a four-carbon alkyl chain did not affect the catalyst selectivity. This lack of effect is shown in table 3-17, the structure used is illustrated in figure 3-38 with the resulting structures shown in figure 3-39. As a longer alkyl chain would have increased the computational time a considerable amount due to the high degree of freedom of the sp<sup>3</sup> hybridised alkyl carbons, then inclusion of such chains is unwarranted. However, a longer alkyl chain could indeed have some effect if it were long enough to 'wrap' itself about the PAH. In future work it would be interesting to find the effect of a longer alkyl chain. To keep the computational time less than considerable it would be advisable to undertake this type of calculation using a QM/MM type method.

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