Kinetics of C–H Bond and Alkene Oxidation by *trans*-Dioxoruthenium(VI) Porphyrins†

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A series of [Ru^{VI}LO$_2$] complexes (H$_2$L = *para*-substituted tetraphenylporphyrins) have been synthesised and characterized, and the kinetics and mechanism of oxidation of the C–H bond and alkenes investigated. The complexes were selective towards tertiary C–H bonds in saturated alkanes but were almost inactive towards secondary C–H bonds. However, they were reactive towards aromatic hydrocarbons and the second-order rate constants (k_2) for the oxidation of ethylbenzene and cumene by [Ru(tpp)O$_2$] (tpp = 5,10,15,20-tetraphenylporphyrinate) were 2.21 × 10^{-4} and 3.16 × 10^{-4} dm^3 mol^{-1} s^{-1} respectively. A kinetic isotope effect (k_H/k_D) of 11.7 was found for the allylic oxidation of cyclohexene by [Ru(tpp)O$_2$]. The major organic products of the oxidation of alkenes in CH$_2$Cl$_2$–MeOH mixtures were epoxides and [Ru(tpp)O$_2$] gave a monomeric product formulated as [Ru^{IV}(tpp)O]·EtOH or [Ru^{IV}(tpp)(OH)$_2$]·EtOH. Similar reactions with [Ru^{VI}(oep)O$_2$] (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate) gave [{Ru^{IV}(oep)(OH)}$_2$O] in non-co-ordinating solvents. The observed rate law for alkene oxidation was rate = k_2[Ru^{VI}][alkene]. There exists an almost linear free-energy relationship between log k_2 and $E_{\frac{1}{2}}$ (one-electron oxidation potentials of alkenes) with slope = −1.1 V^{-1} for the [Ru(tpp)O$_2$] system. Activation parameters have been determined for the oxidation of styrene, norbornene and cyclooctene by [Ru^{VI}LO$_2$]. Non-linear and U-shaped Hammett plots were observed for the oxidation of substituted styrenes. The mechanism of alkene oxidation is proposed to involve a continuum of transition states, the structures of which may change and be stabilized by different substituents.

The study of oxygen-atom transfer reactions and hydrogen-atom abstractions mediated by oxometal complexes is an important area in the functionalization of hydrocarbons.[1–4] In particular, there has been considerable interest in the oxidation chemistry of oxometalloporphyrins owing to their relevance to enzymatic reactions of cytochrome P-450. Although many reports on the oxidative reactions of oxo complexes of chromium, manganese and iron porphyrins have surfaced during the past decade,[1,3] the mechanism of alkene epoxidation by oxometalloporphyrins is still a matter of controversy.[3] Oxoruthenium complexes which are potent oxidants of organic hydrocarbons and are more substitution inert than their first-row congeners and should be good model systems for mechanistic investigation of oxygen-atom transfer reactions.[5–12] Recently, we reported the synthesis and characterization of ruthenium(VI) complexes of 5,10,15,20-tetraphenylporphyrin (H$_2$tpp) and 2,3,7,8,12,13,17,18-octaethylporphyrin (H$_2$oep).[10] In this report, the results of kinetic studies on the reactions of alkenes with both [Ru^{VI}LO$_2$] (H$_2$L = *para*-substituted tetraphenylporphyrin) and [Ru^{VI}(oep)O$_2$] are presented.

Experimental

Preparation of Compounds.—Ruthenium dodecacarbonyl [Ru$_3$(CO)$_{12}$] was purchased from Strem; *m*-chloroperoxybenzoic acid (Merck, 85%) and octaethylporphyrin (H$_2$oep, Aldrich) were used as received. *para*-X-Substituted tetraphenylporphyrins (X = H, H$_2$tpp; Cl, H$_2$tcpp; Me, H$_2$tmpp; or MeO, H$_2$tmopp) and [Ru^{II}(por)(CO)] (por = L or oep) were prepared according to literature procedures.[13] All solvents for the syntheses were of analytical grade. The compound [Ru(oep)O$_2$] has been prepared and reported elsewhere.[10]

[Ru^{VI}LO$_2$] (L = tpp, tcpp, tmpp *or* tmopp). A dichloromethane–ethanol (1:1) solution of [Ru^{II}L(CO)(MeOH)] (100 mg) was added to a well stirred ethanolic solution of excess of *m*-chloroperoxybenzoic acid (200 mg in 15 cm^3). The dark purple solid formed was filtered off and washed with EtOH (yield ≈ 70–80%).

[Ru(tpp)O$_2$]. UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm(log ε) 545(sh)(3.89), 518(4.24), 418(5.29) and 340(sh)(4.19). IR: 819 and 1017 cm^{-1}. ^{1}H NMR(CDCl$_3$): δ 9.1 (pyrrolic H, s); 8.4 (*o*-H); and 7.9 (*m*-, *p*-H, dd) (Found: C, 70.7; H, 4.15; N, 7.70. Calc.: C, 70.9; H, 3.75; N, 7.50%).

[Ru(tmpp)O$_2$]. UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm(log ε) 550(sh)(3.80), 520(4.18), 420(5.29) and 340(sh)(4.19). IR: 823 cm^{-1}. ^{1}H NMR (CD$_3$OD–CDCl$_3$): δ 9.1 (pyrrolic H, s); 8.2 (*o*-H, dd), 7.6 (*m*-H, dd) and 2.72 (*p*-CH$_3$, s) (Found: C, 70.1; H, 4.55; N, 6.95. Calc.: C, 70.3; H, 4.65; N, 6.85%).

[Ru(tmopp)O$_2$]. UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm(log ε) 552(sh)(3.79), 521(4.02), 424(5.18) and 340(sh)(4.10). IR: 821 cm^{-1}. ^{1}H NMR (CD$_3$OD–CDCl$_3$): δ 9.1 (pyrrolic H, s), 8.3 (*o*-H, dd), 7.3 (*m*-H, dd) and 4.12 (*p*-CH$_3$O, s) (Found: C, 64.9; H, 4.35; N, 6.60. Calc.: C, 64.3; H, 4.60; N, 6.45%).

[Ru(tcpp)O$_2$]. UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm(log ε) 545(sh)(3.89), 518(4.18), 418(5.24) and 340(sh)(4.10). IR: 821 cm^{-1}. ^{1}H NMR (CD$_3$OD–CDCl$_3$): δ 9.1 (pyrrolic H, s), 8.3 (*o*-H, dd) and 7.8 (*m*-H, dd) (Found: C, 59.7; H, 2.95; N, 6.35. Calc.: C, 59.4; H, 2.75; N, 6.35%).

Reaction Product of [Ru(tpp)O$_2$] *with Alkenes in Ethanol.*—An ethanolic solution of norbornene (1 g in 100 cm^3) was added to a well stirred solution of [Ru(tpp)O$_2$] in dichloromethane and then stirred for 12 h. The solution was evaporated to about 5 cm^3. The product formed was filtered off and washed with EtOH. UV/VIS (CH$_2$Cl$_2$–EtOH): λ_{max}/nm(log ε) 412(4.95) and 519(4.14). IR: 781 and 1012 cm^{-1}. ^{1}H NMR (CDCl$_3$–C$_2$D$_5$OD): δ 10.9 (*o*-H, br s), 8.5 (*p*-, *m*-H, br m) and −22.7 (pyrrolic H, br s).

Instrumentation.—Ultraviolet/visible spectral measurements and repetitive scan experiments were carried out on a Shimadzu

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† *Supplementary data available* (No. SUP 56849, 22 pp): electronic and NMR spectra, kinetic plots. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: cal = 4.184 J.

UV-240 spectrophotometer. Infrared spectra were obtained on a Nicolet 20 SXC FT-IR spectrophotometer. Cyclic voltammograms were recorded on a Princeton Applied Research model 173/179 potentiostat/digital coulometer and model 175 universal programmer. The working electrode was a glassy carbon electrode referenced to an Ag–AgNO$_3$ (0.1 mol dm^{-3} MeCN) electrode. Ferrocene was added as internal standard; the potentials were determined against the ferrocenium–ferrocene couple; scan rate 100 mV s^{-1}. The GLC analysis was performed on a Varian model 940 equipped with a flame-ionization detector and a 6 ft × $\frac{1}{8}$ in stainless-steel column with Chromosorb W (80–100 mesh) as solid support and 10% Carbowax 20 M or SE 30 as stationary phase. The oxidized products were determined by coinjection of the reaction mixture with authentic samples. Kinetic measurements were performed on a Unicam SP8000 or a Beckmann Acta III spectrophotometer, both equipped with a water-bath (model 2800, Masterline, Fourma Scientific). The former was also linked to an Apple II microcomputer *via* an AD/DA interface card. The temperature of the water-bath was recorded to the nearest 0.1 °C.

Kinetic Measurements.—The solvents dichloromethane and 1,2-dichloroethane were distilled over CaH$_2$. Methanol (GR Grade, Merck) was used as received. Alkene substrates were purchased commercially and purified by standard procedures such as column chromatography, recrystallization or fractional distillation. The rates of reduction of [Ru^{VI}(por)O$_2$] (por = tpp or oep) by alkenes were measured by monitoring the decrease in absorbance of the ruthenium complex at 418 and 540 nm respectively. The reactions were carried out with [alkene] $\gg$ [Ru^{VI}]. Plots of $\ln|A_\infty - A_t|$ *vs.* time were linear over four half-lives. The pseudo-first-order rate constants (k_{obs}) were determined on the basis of a least-squares fit by relation (1)

$$\ln|A_\infty - A_t| = -k_{obs}t - \ln|A_\infty - A_0| \qquad (1)$$

where A_∞ and A_t are the absorbance at the completion of reaction and at time t respectively; A_∞ readings were obtained for at least four half-lives. Second-order rate constants (k_2) were determined from slopes of plots of k_{obs} *vs.* alkene concentration. The activation enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) were obtained from the slope and intercept of Eyring plots of $\ln k_2/T$ *vs.* $1/T$ according to equation (2).

$$\ln(k_2/T) = [\ln(R/Nh) + \Delta S^\ddagger/R] - \Delta H^\ddagger/RT \qquad (2)$$

Stoichiometric Oxidation of Hydrocarbons by [Ru^{VI}(por)O$_2$].—The complex [Ru^{VI}(por)O$_2$] (por = tpp or oep) was stirred with a ≈20-fold excess of hydrocarbon substrate in dichloromethane under argon. The end of the reaction was monitored by the formation of [{Ru^{IV}(por)(OH)}$_2$O]. For [Ru(tpp)O$_2$] the reaction with alkenes in dichloromethane–methanol (19:1) mixture was found to produce a monomeric ruthenium(IV) porphyrin complex instead of [{Ru^{IV}(tpp)(OH)}$_2$O] and a similar amount of organic products as in dichloromethane alone. In a typical run, [Ru^{VI}(por)O$_2$] (50 μmol) was stirred with alkene (1 mmol) in solvent (2 cm^3) under argon for 24 h. After addition of internal standard, an aliquot was taken for GLC analysis.

Results and Discussion

Synthesis of [Ru^{VI}LO$_2$] (L = tpp, tcpp, tmpp *or* tmopp).—The isolation of [Ru(oep)O$_2$] has been reported previously by the oxidation of [Ru^{II}(oep)(CO)] with *m*-chloroperoxybenzoic acid in alcohol.[6,10] Here [Ru^{VI}LO$_2$] were isolated similarly in high yields as air-stable purple solids. Because of the low solubility of [Ru^{II}L(CO)] in alcohol, preparation of [Ru^{VI}LO$_2$] was carried out in CH$_2$Cl$_2$–EtOH. Again, in the presence of weakly co-ordinating solvents such as alcohol, the dioxoruthenium(VI) complexes were formed without the complication of dimerization.

It is noteworthy that the ν_{asym}(RuO$_2$) stretching frequency of [Ru^{VI}LO$_2$] is quite insensitive to the *para* substituents and occurs between 819 and 821 cm^{-1}, comparable to values found for [Ru(oep)O$_2$] (821.6 cm^{-1}) and [Ru(tmsp)O$_2$] (H$_2$tmsp = 5,10,15,20-tetramesitylporphyrin, 821 cm^{-1}).[6b] The [Ru^{VI}LO$_2$] complexes are diamagnetic solids and display well resolved ^{1}H NMR spectra which reveal the pseudo D_{4h} symmetry. The signal of the pyrrolic protons of metalloporphyrins is known to be sensitive to the electron density of the porphyrin ring. Accordingly, it shifts from δ 8.8 for [Ru^{II}(tcpp)(CO)] to 9.08 for [Ru^{VI}(tcpp)O$_2$]. However, the chemical shifts of the pyrrolic protons of [Ru^{VI}LO$_2$] are virtually the same, again suggesting that the peripheral *para* substituents have little electronic influence on the metalloporphyrins.

Cyclic voltammograms of [Ru^{VI}LO$_2$] in dichloromethane show one reversible oxidation couple and one irreversible reduction wave. According to previous studies,[6,10] the oxidation couple is assigned as the ligand-centred oxidation [Ru^{VI}(por)O$_2$] $-$ e $\longrightarrow$ [Ru^{VI}(por$^{\bullet+}$)O$_2$]$^+$ and with E° being 0.86, 0.77, 0.72 and 0.64 V *vs.* ferrocene-ferrocenium for por = tcpp, tpp, tmpp and tmopp respectively. The irreversible reduction wave is due to the reduction of Ru^{VI} to Ru^{V}. In accordance with this assignment, the potential at which electrochemical reduction of [Ru^{VI}LO$_2$] occurs (-0.76, -0.80, -0.85, -0.88 V for the above series) is less sensitive to the *para* substituents of the porphyrin ring.

Reduction of [Ru^{VI}(tpp)O$_2$] by substrates like norbornene in CH$_2$Cl$_2$–EtOH produced a monomeric ruthenium(IV) porphyrin complex, tentatively assigned as [Ru^{IV}(tpp)O]·EtOH or [Ru^{IV}(tpp)(OH)$_2$]·EtOH. The addition of alcohol here inhibits the formation of [{Ru^{IV}(tpp)(OH)}$_2$O]. Magnetic susceptibility measurement (μ_{eff} = 2.4, Evans method) suggested that the ruthenium product is paramagnetic with a $(d_{xy})^2(d_{xz},d_{yz})^2$ ground-state configuration. Similar μ_{eff} has been reported for [Ru^{IV}(tmsp)O].[14]

The ^{1}H NMR spectrum (270 MHz) of this ruthenium(IV) complex in CDCl$_3$–C$_2$D$_5$OD is given in SUP 56849. Based on the integral ratio and the spectra of similar ruthenium(IV) complexes like [Ru^{IV}(tmsp)O],[14] the resonances at δ 8.5 (br m), 10.9 (br s) and -22.7 (br s) are tentatively assigned to the *p*- and *m*-, and the pyrrolic protons respectively. A peak due to pyrrolic protons shifted upfield and other broad signals of *o*, *m*- and *p*-protons again support the paramagnetic nature of the compound. The signals due to the CH$_3$ and CH$_2$ protons of EtOH occur at normal positions, indicating that there is no co-ordinated ethanol or ethoxy ligand.

Oxidation of C–H *bonds by* [Ru^{VI}(por)O$_2$] (por = tpp *or* oep).—*trans*-Dioxoruthenium(VI) porphyrins were found to be reactive towards both alkenes and alkanes. However, both [Ru(tpp)O$_2$] and [Ru(oep)O$_2$] have limited stability and are reduced slowly in dichloromethane to [{Ru^{IV}(por)(OH)}$_2$O]. This observation would account for the low yields of the reactions of [Ru^{VI}(por)O$_2$] with alkanes. For saturated alkanes, [Ru^{VI}(por)O$_2$] are very selective oxidants as only the tertiary C–H bond is oxidized. For example, the oxidation of adamantane (tricyclo[3.3.1.1^{3,7}]decane) gave only ≈20% adamantan-1-ol in both cases (Table 1). Here the rate of oxidation is probably slow when compared with the rate of degradation of [Ru^{VI}(por)O$_2$]. Not surprisingly, only trace amounts of oxidized products were detected in the oxidation of saturated secondary C–H bonds such as those in cyclohexane. No kinetic data could be obtained for these alkane substrates since the rate of oxidation is too slow to compete with the self degradation of the ruthenium complexes. However, [Ru^{VI}(por)O$_2$] were more reactive towards aromatic hydrocarbons. Oxidation of ethylbenzene gave *sec*-phenethyl alcohol and acetophenone in good yields. Kinetic results were limited to [Ru(tpp)O$_2$], which has been found to be more reactive than [Ru(oep)O$_2$]. The

Table 1 Stoichiometric oxidation of hydrocarbons by $[Ru^{VI}(por)O_2]$ (por = tpp or oep) in dichloromethane

Substrate	Product	Yield[a] (%) $[Ru(tpp)O_2]$	Yield[a] (%) $[Ru(oep)O_2]$
Norbornene	*exo*-Norbornene oxide	77	75
Styrene	Styrene oxide	50	43
	Benzaldehyde	5	20
trans-Stilbene	*trans*-Stilbene oxide	45	22
	Benzaldehyde	—	6
cis-Stilbene	*cis*-Stilbene oxide	100	16
	trans-Stilbene oxide	—	44
	Benzaldehyde	—	7
Cyclooctene	Cyclooctene oxide	53	
Cyclohexene	Cyclohexene oxide	7	
	Cyclohexenone Cyclohexenol	109	
Ethylbenzene	*sec*-Phenethyl alcohol	37	91
	Acetophenone	18	29
Adamantane[b]	Adamantan-1-ol	21	16
Cyclohexane	Cyclohexanol Cyclohexanone	Trace	Trace
Methylcyclohexane	1-Methylcyclohexanol	25	
Cyclohexanol	Cyclohexanone	50	
Benzyl alcohol	Benzaldehyde	100	

[a] Based on $[Ru^{VI}(por)O_2]$ used. [b] Solvent: benzene.

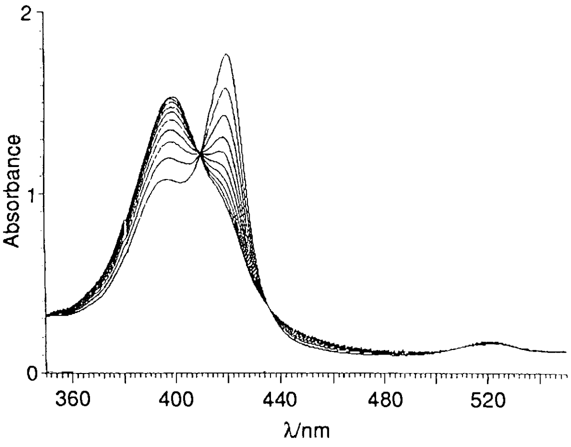


Fig. 1 Spectral changes in the reaction of $[Ru(tpp)O_2]$ (10^{-5} mol dm^{-3}) with cumene (3.6 mol dm^{-3}) in CH_2Cl_2–MeOH (19:1). Scan interval = 4 min

spectral changes in the reaction between $[Ru(tpp)O_2]$ and cumene in CH_2Cl_2–MeOH are shown in Fig. 1. The final product was identified as Ru^{IV}, either $[Ru^{IV}(tpp)O]\cdot EtOH$ or $[Ru^{IV}(tpp)(OH)_2]\cdot EtOH$ as discussed above. The second-order rate constants are 2.21×10^{-4} and 3.16×10^{-4} dm^3 mol^{-1} s^{-1} for ethylbenzene and cumene respectively. Taking the statistical factor into account, the selectivity ratio k[tertiary(C–H)]/k[secondary(C–H)] is 2.9:1. Plots of k_{obs} *vs.* [aromatic hydrocarbon] are shown in Fig. 2.

Allylic oxidation was found to be the major pathway for the oxidation of cyclohexene by $[Ru(tpp)O_2]$. Presumably, abstraction of allylic hydrogen gave cyclohexyl radical which was subsequently converted into cyclohexenone and cyclohexenol. The UV/VIS spectral changes for this reaction in CH_2Cl_2–MeOH are similar to those with cumene. The second-order rate constants for the oxidation of cyclohexene and $[^2H_{10}]$cyclohexene by $[Ru(tpp)O_2]$ were found to be 6.58×10^{-3} and 5.64×10^{-4} dm^3 mol^{-1} s^{-1} respectively. Hence, the kinetic isotope effect k_H/k_D is 11.7, indicating that the allylic oxidation proceeds *via* a H-atom abstraction pathway with a $O{=}Ru^{IV}{=}O\cdots H{-}C_6H_9$ transition state. Large kinetic isotope effects for the oxidation of cyclohexene by iron–porphyrin systems ($k_H/k_D = 4$)[15] and $[Ru(bipy)_2(py)O]^{2+}$ ($k_H/k_D = 18$)[16] (bipy = 2,2′-bipyridyl, py = pyridine) have been reported previously.

Oxidation of alkenes by $[Ru^{VI}(por)O_2]$.—Previous work showed that $[Ru^{VI}(oep)O_2]$ reacted with alkenes to give epoxides in good yields.[10] Here similar findings were observed for $[Ru^{VI}(tpp)O_2]$ and Table 1 summarizes the combined results. Both $[Ru(tpp)O_2]$ and $[Ru(oep)O_2]$ afforded good yields of epoxides. With arenes, both epoxidation and oxidative cleavage of C=C bonds were found but with the latter the minor pathway. Oxidation of *cis*-stilbene by $[Ru(tpp)O_2]$ and $[Ru(tcpp)O_2]$ gave *cis*-stilbene oxide exclusively with no *trans*-stilbene oxide and benzaldehyde, whereas for $[Ru(tmpp)O_2]$ a similar reaction gave a mixture of *cis*- and *trans*-stilbene oxides in 3:1 ratio. However, the reaction of *cis*-stilbene with $[Ru(oep)O_2]$ resulted in benzaldehyde and a 1:2.5 mixture of *cis*- and *trans*-stilbene oxides and benzaldehyde.

The spectral trace for the reaction of $[Ru^{VI}(oep)O_2]$ with styrene in 1,2-dichloroethane exhibiting clean isosbestic points has been reported before[10] and is given SUP 56849. On the basis of UV/VIS and ^1H NMR spectroscopy, the final product was $[\{Ru^{IV}(oep)(OH)\}_2O]$.[10] The observation of isosbestic points indicates no accumulation of reaction intermediate in the conversion of $[Ru^{VI}(oep)O_2]$ into $[\{Ru^{IV}(oep)(OH)\}_2O]$. We suggest that the $[Ru^{IV}(oep)O]$ complex, which is the immediate oxo-transfer product, is very unstable towards dimerization to μ-oxo-Ru^{IV}.[10] This is supported by the evidence that a monomeric Ru^{IV}–oep complex formulated as $[Ru^{IV}(oep)O]\cdot EtOH$ has been isolated and found to undergo rapid dimerization in non-co-ordinating solvents such as 1,2-dichloroethane. The dimerization of the $[Ru^{IV}(oep)O]$ intermediate would be so rapid that k_3 would be greater than k_2 (Scheme 1).

$$[Ru^{VI}(por)O_2] + \text{alkene} \xrightarrow{k_2} [Ru^{IV}(por)O] + \text{epoxide}$$

$$2[Ru^{IV}(por)O] + H_2O \xrightarrow{k_3} [\{Ru^{IV}(por)(OH)\}_2O]$$

por = tpp or oep

Scheme 1

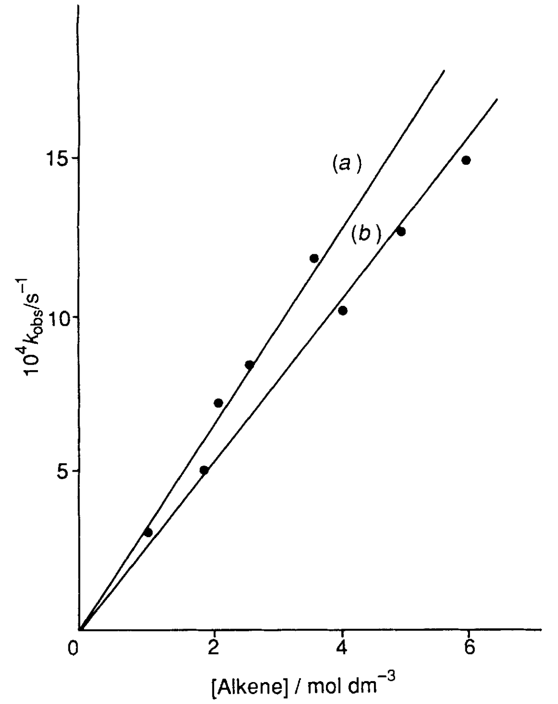


Fig. 2 Plots of k_{obs} vs. [aromatic hydrocarbon] for the oxidation of cumene (a) and ethylbenzene (b) by $[Ru(tpp)O_2]$ (10^{-5} mol dm^{-3}) in CH_2Cl_2–MeOH (19:1)

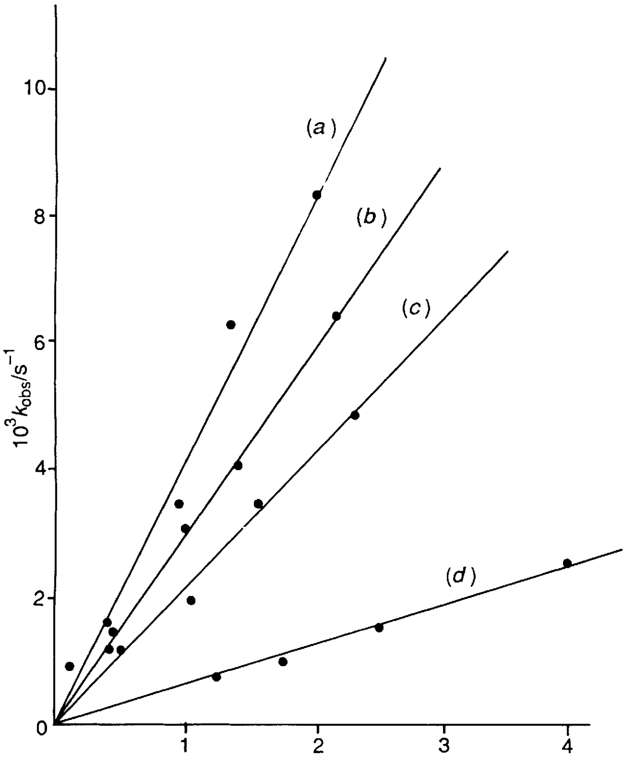


Fig. 3 Plots of k_{obs} vs. [alkene] for the oxidation of alkenes by $[Ru(tpp)O_2]$ in CH_2Cl_2–MeOH (19:1). Alkenes: (a) styrene, (b) norbornene, (c) cyclooctene and (d) hex-1-ene

Stoichiometrically, $[Ru^{VI}(tpp)O_2]$ was shown to react with alkenes to afford epoxides and $[\{Ru^{IV}(tpp)(OH)\}_2O]$ in non-co-ordinating solvents like dichloromethane. However, the dimerization of the $[Ru^{IV}(tpp)O]$ intermediate here was found to interfere with the overall kinetics. The reaction of $[Ru^{VI}(tpp)O_2]$ with styrene in CH_2Cl_2 alone (spectral changes in SUP 56849) did not follow clean pseudo-first-order kinetics probably due to the comparable rates of epoxidation and dimerization ($k_3 \approx k_2$ in Scheme 1).

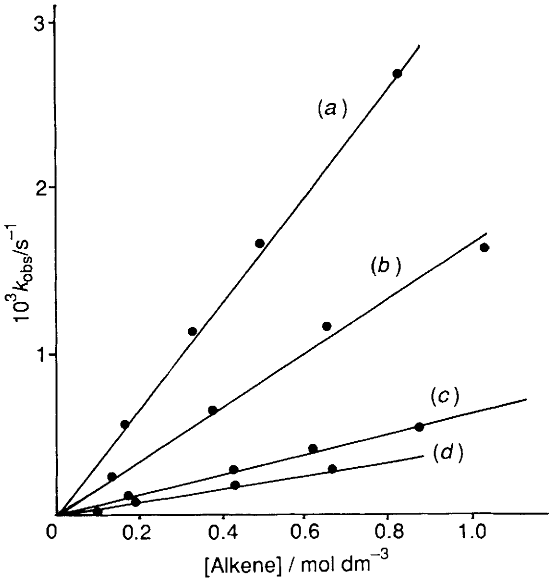


Fig. 4 Plots of k_{obs} vs. [alkene] for the oxidation of alkenes by $[Ru(oep)O_2]$ in 1,2-dichloroethane. Alkenes: (a) β-methylstyrene, (b) cyclooctene, (c) α-methylstyrene and (d) norbornene

This observation hinders the monitoring of the actual oxygen-atom transfer step. In order to follow the kinetics of the reduction of $[Ru(tpp)O_2]$ by alkenes, the addition of a small amount of methanol could overcome the problem of dimerization. The UV/VIS spectral changes in the reaction between $[Ru(tpp)O_2]$ and styrene in CH_2Cl_2–MeOH (19:1) are very similar to those shown in Fig. 1. The lack of absorption at ≈550 nm for the final ruthenium product indicates that $[\{Ru^{IV}(tpp)(OH)\}_2O]$ was not formed throughout the reaction.

In this work the rates of alkene oxidation by $[Ru^{VI}(tpp)O_2]$ were monitored spectrophotometrically by the decrease in absorbance at 418 nm (Soret band) in CH_2Cl_2–MeOH (19:1) (or about 1.2 mol dm^{-3} MeOH). For the oxidation by $[Ru^{VI}(oep)O_2]$ the reaction was monitored by the absorbance changes at 540 nm in 1,2-dichloroethane. A small amount of 2,6-dimethylpyridine which functions as a non-co-ordinating base was added since the rates of the reactions were found to be sensitive to trace amounts of acid present in the solvent. The disappearance of $[Ru^{VI}(por)O_2]$ (por = tpp or oep) with time was followed for at least four half-lives under the conditions $[alkene] \gg [Ru]$. The observed pseudo-first-order rate constants, k_{obs}, show a linear dependence on the alkene concentration (Figs. 3 and 4). The experimental rate law is as in equation (3). For both oxidants no rate saturation was observed under the conditions employed.

$$-d[Ru^{VI}]/dt = k_2[Ru^{VI}][alkene] \qquad (3)$$

The kinetic data are summarized in Table 2. The first-order rate constant of the self-degradation of $[Ru(tpp)O_2]$ in 1.2 mol dm^{-3} MeOH was estimated independently and was found to be very small, thus having little effect on the overall rate of oxidation of alkenes. The oxidation of alkenes by $[Ru(tpp)O_2]$ was found to be slightly faster than that by $[Ru(oep)O_2]$ by a factor between 2 and 10. However, the rate constants in this work are low when compared with other oxometal systems. For example, the rate of epoxidation of norbornene by $[Ru(tpp)O_2]$ is about 18 times slower than that by oxo[5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinato]chromium(V) ($k_2 = 5.4 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}).[17a]

A linear free-energy plot of $\log k_2$ vs. $E_{\frac{1}{2}}$ (one-electron potentials of alkenes) for the oxidation of various alkenes by

Table 2 Second-order rate constants for the oxidation of hydrocarbons by [Ru(tpp)O_2] and [Ru(oep)O_2]

	$10^3\ k_2$/dm^3 mol^{-1} s^{-1}	
Substrate	[Ru(tpp)O_2]	[Ru(oep)O_2]
4-Methoxystyrene	47.4 ± 2.5	29 ± 1.5
4-Methylstyrene	8.81 ± 0.2	2.69 ± 0.08
4-Fluorostyrene		2.03 ± 0.03
4-Chlorostyrene	11.4 ± 0.4	2.88 ± 0.15
Styrene	4.30 ± 0.3[a]	1.55 ± 0.09[b]
4-Nitrostyrene	16.7 ± 1.0	13.1 ± 0.9
α-Methylstyrene		0.6 ± 0.03
β-Methylstyrene		3.36 ± 0.03
cis-Stilbene	3.17 ± 0.07	
trans-Stilbene	2.12 ± 0.09	
2,3-Dimethylbut-2-ene	3.77 ± 0.04	2.90 ± 0.13
Norbornene	3.01 ± 0.09[a]	0.39 ± 0.02[b]
Cyclooctene	2.14 ± 0.20	1.69 ± 0.05[b]
Hex-1-ene	0.626 ± 0.02	
Cyclohexene	6.58 ± 0.17	
[$^2H_{10}$]Cyclohexene	0.564 ± 0.01	
Ethylbenzene	0.221 ± 0.016	
Cumene	0.316 ± 0.02	

[a] Activation parameters $\Delta H^\ddagger$/kcal mol^{-1} ($\Delta S^\ddagger$/cal K^{-1} mol^{-1}): styrene, 10 ± 1 (−35 ± 5); norbornene, 14 ± 1 (−24 ± 3). [b] Activation parameters $\Delta H^\ddagger$/kcal mol^{-1} ($\Delta S^\ddagger$/cal K^{-1} mol^{-1}): styrene, 16 ± 2 (−18 ± 3); norbornene, 14 ± 1 (−26 ± 2); cyclooctene, 9 ± 2 (−41 ± 4).

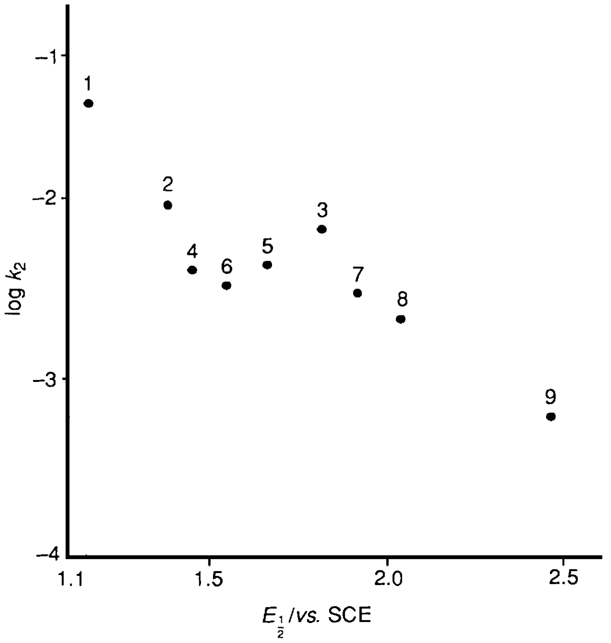


Fig. 5 Linear free-energy plot of log k_2 *vs.* $E_{\frac{1}{2}}$ (one-electron potentials of alkenes) by [Ru(tpp)O_2]. Alkanes: 1, 4-methoxystyrene; 2, 4-methylstyrene; 3, cyclohexene; 4, 2,3-dimethylbut-2-ene; 5, styrene; 6, *cis*-stilbene; 7, norbornene; 8, cyclooctene; 9, hex-1-ene

[Ru(tpp)O_2] has been found (Fig. 5). The observed slope of −1.1 V^{-1} shows that there is little degree of charge transfer in the transition state. This value can be compared with the value of −3 V^{-1} recently obtained by Bruice and co-workers[17b] in the alkene epoxidation by oxo[5,10,15,20-tetrakis(2,6-dibromophenyl)porphyrinato]chromium(V) and −1.83 V^{-1} for the catalysed epoxidation using substituted [*N*,*N*′-ethylenebis(salicylideneiminato)]oxochromium(V) complexes by Kochi and co-workers.[18] Using data for the oxidation of substituted styrenes, the ρ^+ values obtained for oxoiron(IV) porphyrinate π-cation radicals have been reported to be −1.9[19] and −0.93,[20] respectively. The second-order rate constants k_2 for the oxidation of 2,3-dimethylbut-2-ene by [Ru^{VI}LO_2] were also determined as 3.24 × 10^{-3}, 3.59 × 10^{-3}, 3.77 × 10^{-3} and 4.90 × 10^{-3} dm^3 mol^{-1} s^{-1} for L = tmopp, tmpp, tpp and tcpp respectively. Qualitatively, the rate constants increase with the reduction potential of [Ru^{VI}LO_2]. However, the span of the rate constants is very small (less than a factor of two) suggesting that the extent of charge transfer is also small in the rate-determining step of the oxidation.

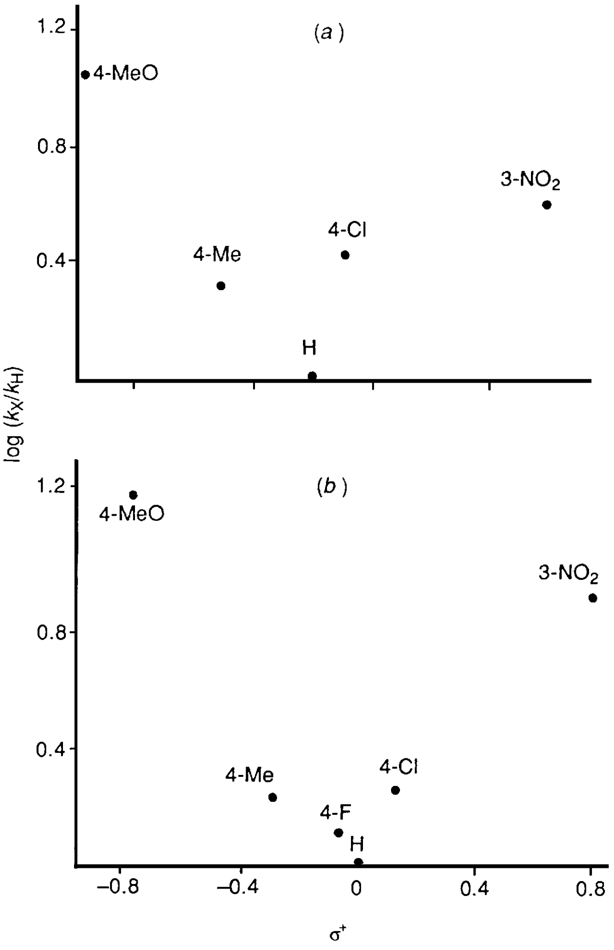


Fig. 6 Hammett plots for the oxidation of substituted styrenes by (*a*) [Ru(tpp)O_2] and (*b*) [Ru(oep)O_2]

The activation parameters for the oxidation of styrene, norbornene and cyclooctene have been studied for both [Ru(tpp)O_2] and [Ru(oep)O_2] and the results are in Table 2. Eyring plots (ln k_2/T *vs.* $1/T$) are given in SUP 56849. The $\Delta S^\ddagger$ values are large and negative and vary dramatically with the structure of the alkenes. This reflects the orientational demand of the reactants for the oxygen-atom transfer to occur and the reaction is likely to proceed *via* an associative mechanism. For the oxidation by [Ru(oep)O_2] the k_2 value for α-methylstyrene is smaller than that of styrene, again indicating the operation of steric factors.

Hammett Plots.—For the oxidation of substituted styrenes, the Hammett plots obtained for both [Ru(tpp)O_2] and [Ru(oep)O_2] are surprisingly non-linear. In fact they are U-shaped changing from *p*-MeO to *m*-NO_2 substituted styrenes [Fig. 6(*a*) and 6(*b*)]. This contrasts with the findings in oxometalloporphyrin systems like those of Fe,[19,20] Cr[17] and Mn[21] in which log k_{rel} correlates linearly with σ^+. The result may imply a shift in the structure of the transition state as the substituents change from being electron releasing to electron withdrawing. Such a non-linear relation was also observed recently in the styrene oxidation catalysed by a ruthenium-substituted heteropolyanion.[22] The reaction proceeds through two different transition states depending on the ring substituents, hence a change in mechanism when going from electron-donating to electron-withdrawing substituents.

Mechanism of Alkene Oxidation.—Previous studies[17–26] showed that there are a number of possibilities for the mechanism of epoxidation by oxometalloporphyrin (Scheme 2). None

$$\mathrm{O{=}Ru^{VI}{=}O} + \text{alkene} \xrightarrow{\text{concerted}} \text{metalloxetane} \qquad \text{(A)}$$

$$\longrightarrow \mathrm{O{=}Ru^{V}\text{–}O,alkene^{\bullet +}} \qquad \text{(B)}$$

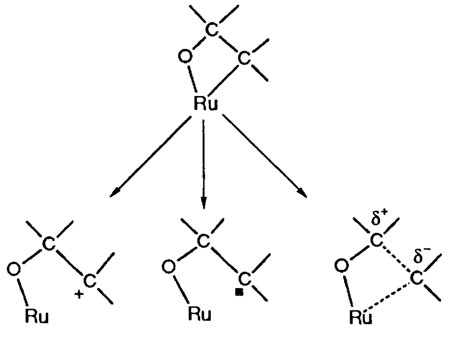
$$\longrightarrow [\mathrm{O{=}Ru\text{–}O\text{–}C\text{–}\overset{+}{C}}] \qquad \text{(C)}$$

$$\longrightarrow [\mathrm{O{=}Ru^{V}\text{–}O\text{–}C\text{–}\dot{C}}] \qquad \text{(D)}$$

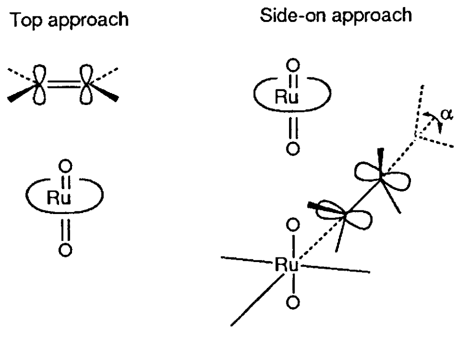
Scheme 2

of these pathways can explain the observed U-shaped Hammett plots. Pathway B could be excluded because of the substantially low one-electron reduction potential ($\mathrm{Ru^{VI}}$–$\mathrm{Ru^{V}}$) for both [Ru(tpp)O_2] and [Ru(oep)O_2] [−0.80 and −0.90 V *vs.* saturated calomel electrode (SCE)] when compared with other oxometalloporphyrins such as $\mathrm{Cr^{V}{=}O}$ and $\mathrm{Fe^{IV}(por^{\bullet +}){=}O}$. The ΔG° for the formation of [$\mathrm{O{=}Ru^{V}\text{–}O,alkene^{\bullet +}}$][17] will be too positive and hence thermodynamically unfavourable.

Here we propose a mechanism which is a continuum of transition states, the structure of which may change and will be stabilized by different substituents (Scheme 3). Our results are most readily explained if there are varying amounts of Ru–C and C–C bond cleavage during the interactions between $\mathrm{O{=}Ru^{VI}{=}O}$ and >C=C< in the transition state. There are two possible geometries of approach of a C=C bond to a Ru=O group as shown in Scheme 4.



Scheme 3



Scheme 4

Approach along the Ru–O axis (top approach) is improbable because with this geometry one would expect little non-bonded interaction between the alkene substituent and porphyrin periphery. The difference in stereospecificity in the epoxidation of *cis*-stilbene by [Ru(tpp)O_2] and [Ru(oep)O_2] argues against this pathway. With reference to previous work,[23a] it is likely that the approach of an alkene to the Ru=O group of [$\mathrm{Ru^{VI}}$(por)O_2] is at an angle (α) to the porphyrinate plane (the side-on approach) so as to optimize the steric effect and orbital overlap.[23a] Such interaction could be concerted in nature and would give rise to a transition state normally termed a metallocycle (Scheme 3), which could account for the relative insensitivity to the substituent in the oxidation of *para*-substituted styrenes by both [Ru(oep)O_2] and [Ru(tpp)O_2].

With electron-donating substituents the Ru–C bond cleavage could run ahead of the C–C bond cleavage hence giving an acyclic oxometal radical or carbocation intermediate as shown in Scheme 3. Here we would favour the radical intermediate because the degree of charge transfer was found to be small as reflected in the slope of the linear free-energy plot (Fig. 5). This pathway could account for the very large k_2 value in the oxidation of *p*-methoxystyrene. With the acyclic oxometal radical there will be rotation about the C–C bond and *cis* to *trans* isomerization will be expected. In this work the extent of isomerization was found to be sensitive to the steric bulk of the porphyrin ligand as in the case of the iron porphyrin system. The complex [Ru(oep)O_2] reacted with *cis*-stilbene to give a mixture of *cis*- and *trans*-stilbene oxides, whereas [Ru(tpp)O_2] gave *cis*-stilbene oxide exclusively. Presumably the *meso*-phenyl groups of the tpp ligand hinder free rotation of the intermediate.

In some cases partial heterolytic cleavage of the C–C bond in the metallocycle will lead to the development of negative charge at the α-carbon of the substituted styrene (Scheme 3). Stabilization of the transition state by the *m*-NO_2 group may account for the increase in k_2 for this extreme case. This pathway could explain the oxidative cleavage products of styrene by [$\mathrm{Ru^{VI}}$(por)O_2] (por = tpp or oep). However, since most of the alkenes chosen in this work are rather electron rich, the transition state will more likely be the acyclic radical or the metallocycle formed from a concerted process. This would explain why there is a linear free-energy plot of log k_2 *vs.* $E_{\frac{1}{2}}$ of alkenes (Fig. 5).

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