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Stoichiometric enantioselective alkene epoxidation with a chiral dioxoruthenium(VI) D_4-porphyrinato complex

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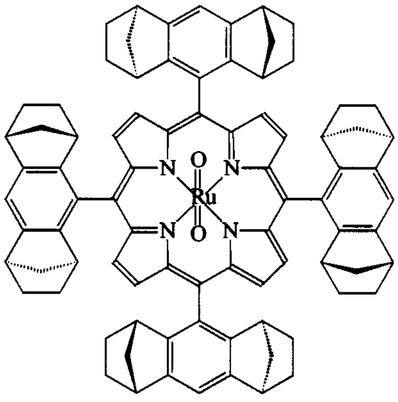
A dioxoruthenium(VI) complex containing a D_4-porphyrinato ligand por* {H_2por* = 5,10,15,20-tetrakis-[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl]porphyrin} has been prepared by oxidation of its ruthenium(II) carbonyl precursor with *m*-chloroperoxybenzoic acid and characterised by spectroscopic methods. The [Ru^{VI}(por*)O_2] complex undergoes enantioselective epoxidation of alkenes and the highest enantiomeric excess (ee) attainable is 77%. In the presence of pyrazole the complex transforms to [Ru^{IV}(por*)$(pz)_2$] when reacting with alkenes. The kinetics of the epoxidation of *para*-substituted styrenes has been studied. The experimental rate law is $-d[Ru^{VI}]/dt = k_2[Ru^{VI}][alkene]$. The second order rate constants k_2 at 25 °C fall in a narrow range, 2.1×10^{-3}–9.7×10^{-3} $dm^3\ mol^{-1}\ s^{-1}$. Comparison of the Hammett plot (log k_{rel} *vs.* $\sigma^\bullet$) with those for achiral analogues [Ru^{VI}(tpp)O_2] (H_2tpp = 5,10,15,20-tetraphenylporphyrin) and [Ru^{VI}(oep)O_2] (H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin) suggests the formation of a radical intermediate for the alkene epoxidations. Both [Ru^{II}(por*)(CO)(EtOH)] and [Ru^{VI}(por*)O_2] were examined for enantioselective catalysis. Enantioselectivities of the stoichiometric and catalytic reactions showed good correlation. There is no solvent dependence on enantioselectivity when changing the solvent from dichloromethane to benzene.

Functionalization of hydrocarbons *via* epoxidation with transition metal catalysts has continued to receive great attention.[1,2] In particular, there has been considerable interest in the oxidation chemistry of metalloporphyrins owing to their biological relevance to enzymatic reactions mediated by cytochrome P-450. Owing to the periodic relationship of ruthenium to iron, ruthenium porphyrins have been of recent interest. They have been shown to be active catalysts for epoxidation,[3] aziridination[4] and cyclopropanation[5] of alkenes and hydroxylation of alkanes.[6] More importantly, reactive oxo,[7] imido[8] and carbene[5a,b] ruthenium porphyrinato complexes have been isolated and/or spectroscopically characterized. This renders direct measurement of rates of group and atom transfer reactions feasible. Although oxometal species are tacitly agreed to be the active intermediates in many discussions of asymmetric alkene epoxidations,[1b] their characterization is elusive. Indeed, in some of the reported metalloporphyrin catalysed organic oxidations, more than one reactive intermediate has been suggested.

We anticipated that isolation of highly reactive and chiral oxometal porphyrin complexes and examination of their reactivities towards asymmetric alkene epoxidations should partly provide a clue to the factors affecting enantioselectivity. In our laboratory, a chiral monooxoruthenium(IV) complex supported by a C_2-chiral meridional ligand has been found to epoxidize styrene-type substrates stoichiometrically with enantioselectivity up to 57% enantiomeric excess (e.e.).[9] Here, we report a detailed study of enantioselective epoxidation with a chiral dioxoruthenium(VI) complex, [Ru^{VI}(por*)O_2], containing a D_4-porphyrin ligand, H_2por*{5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl]-porphyrin}. Its use in stoichiometric asymmetric epoxidations and the kinetics of its reactions with *para*-substituted styrenes are also presented. The Hammett plots of the achiral [Ru(tpp)O_2] (H_2tpp = 5,10,15,20-tetraphenylporphyrin) and [Ru(oep)O_2] (H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin) complexes are compared with that for this chiral analogue. Interpretation of these kinetic data provides a new picture for understanding the mechanism of asymmetric epoxidation by oxometal species. In this work the results of catalytic epoxidation of alkenes with PhIO as a terminal oxidant will be presented and compared with the stoichiometric ones.[10]


[Ru^{VI}(por*) O_2]

Experimental

Preparation of compounds

Ruthenium dodecacarbonyl [$Ru_3(CO)_{12}$] was purchased from Strem, *meta*-chloroperoxybenzoic acid (Merck, 85%) was used as received and H_2por* was prepared according to the literature method.[11] All solvents for the syntheses were of analytical grade.

[Ru^{II}(por*)(CO)(EtOH)]. A mixture of H_2por* (100 mg) and [$Ru_3(CO)_{12}$] (120 mg) in decalin (50 cm^3) was refluxed under an inert atmosphere for 36 h. After cooling, the orange solution was chromatographed on a silica gel column. The product was eluted by dichloromethane as an orange band. Removal of the solvent and recrystallization of the crude product using CH_2Cl_2–EtOH gave a red crystalline solid. Yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ −2.56 (s, 2 H), 1.05 (m, 8 H), 1.32 (m, 24 H), 1.85 (m, 8 H) 2.00 (d, 8 H, $J = 8.0$ Hz), 2.77 (s, 8 H), 3.56 (s, 8 H), 7.36 (s, 4 H) and 8.72 (s, 8 H). IR (KBr): 2969, 1942 and 1918 cm^{-1}. UV: 414 and 529 nm. FAB MS: *m*/*z* 1270 (M^+) and 1242 ($M^+ - CO$).

[Ru^{VI}(por*)O$_2$]. A dichloromethane solution of [Ru^{II}(por*)(CO)(EtOH)] (50 mg) was added to a well stirred solution of *m*-chloroperoxybenzoic acid in dichloromethane (100 mg in 15 cm^3). After 3 min the solution was chromatographed on a short alumina column. The product was eluted by dichloromethane. The solution obtained was evaporated to dryness by rotatory evaporation. A dark purple residue (35 mg) was obtained. Yield 70%. IR (KBr): 2960vs, 2867s, 1684m, 1559s, 1292vs, 1106m, 1076m, 1019m, 965w, 948w, 822s, 797s, 754m and 705s cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 (m, 8 H), 1.35 (m, 24 H), 1.88 (m, 8 H), 2.05 (m, 8 H), 2.88 (s, 8 H), 3.62 (s, 8 H), 7.44 (s, 4 H) and 8.96 (s, 8 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 27.183, 27.565, 42.417, 44.403, 49.339, 113.988, 118.923, 127.908, 130.780, 141.533, 144.272 and 148.062. UV/VIS: 424 nm (log ε 5.38). FAB MS: *m*/*z* 1274 (M^+), 1258 ($M^+ - O$) and 1242 ($M^+ - 2O$).

Instrumentation

Ultraviolet-visible spectra were recorded on a HPUV 8452 spectrophotometer, infrared spectra as KBr discs on a Bio-Rad FTIR spectrophotometer. The GLC analyses were performed on a HP GC instrument equipped with a flame ionization detector. The NMR spectra were recorded on a DPX300 spectrophotometer. The chiral columns for separation of enantiomers were J & W cyclodex-B (30 m) and G-TA (30 m). The enantiomeric excesses of 3-nitrostyrene oxide and 4-methylstyrene oxide were determined by ^{1}H NMR in the presence of the chiral shift reagent {[Eu(hfc)$_3$] = tris[3-(heptafluoropropylhydroxymethylene)-D-camphorato]europium(III)} (Aldrich). The temperatures of kinetic measurements were stabilized with a thermostat (±1.0 °C).

Stoichiometric oxidation of alkenes by [Ru^{VI}(por*)O$_2$] and isolation of [Ru^{IV}(por*)(pz)$_2$]

Alkene (0.2 g) and pyrazole (0.05 g) were dissolved in dichloromethane (5 cm^3). The [Ru^{VI}(por*)O$_2$] complex (50 mg) was added with stirring and the resulting solution stirred for 12 h. Organic products were obtained through column chromatography with Et_2O–light petroleum (1:10) as eluent and [Ru^{IV}(por*)(pz)$_2$] was eluted with dichloromethane. The organic products were analysed by ^{1}H NMR and/or GC. The complex [Ru^{IV}(por*)(pz)$_2$] was characterized by UV/VIS, IR, MS and magnetic moment measurements. Yield 72%. IR (KBr): 2957vs, 2865vs, 1639m, 1518w, 1469m, 1445m, 1293s, 1193m, 1106s, 1064m, 1009s, 948m, 862w, 796s, 755m and 710m cm^{-1}. FAB MS: *m*/*z* 1376 (M^+) and 1242 ($M^+ - 2pz$). UV/VIS (CH_2Cl_2): λ_{max} 414 and 512 nm. μ_{eff}(solid sample, r.t.): 2.9 μ_B.

Alternatively, [Ru^{VI}(por*)O$_2$] was generated *in situ*. A mixture of PhIO (0.1 g) and [Ru^{II}(por*)(CO)(EtOH)] (0.1 g) in CH_2Cl_2 was stirred for 10 min. The complete conversion of [Ru^{II}(por*)(CO)(EtOH)] into [Ru^{VI}(por*)O$_2$] was confirmed by electronic absorption spectroscopy. The solution was then injected into a solution of alkene containing 3 equivalents of pyrazole. The yield of organic product was calculated on the assumption of a $Ru^{VI} \longrightarrow Ru^{IV}$ transformation.

Kinetic measurements

Dichloromethane was distilled over CaH_2. Alkenes were from commercial sources and purified by distillation or chromatography. The rates of reduction of [Ru^{VI}(por*)O$_2$] by alkenes were measured by monitoring the decrease in absorbance of a 1,2-dichloroethane solution of the complex in the presence of 2% pyrazole at 424 nm. The reactions were carried out with [alkene] $\gg$ [Ru^{VI}] (at more than 1000 fold). Plots of ln $|A_\infty - A_t|$ *vs.* time were linear over at least three half-lives. The pseudo-first order rate constants (k_{obs}) were determined on the basis of least squares fits using eqn. (1) where A_∞ and A_t are the absorbance at the completion of reaction and at time t respectively; A_∞ readings were obtained after at least four half-lives. Second order rate constants (k_2) were determined from plots of k_{obs} *vs.* [alkene].

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

Oxidation of alkenes by PhIO catalysed by [Ru^{VI}(por*)O$_2$] or [Ru^{II}(por*)(CO)(EtOH)]

A mixture of substrate (100 mg), PhIO (50 mg) and catalyst (2 mg) in dichloromethane (4 cm^3) was stirred with strict exclusion of air. The reaction was completed when all PhIO solid dissolved. The GC analysis of the reaction mixture was carried out with halogenated aromatics such as 1-bromo-4-chlorobenzene as internal standard. The yields were calculated using PhIO as the limiting reactant.

Results and discussion

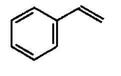
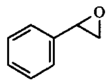
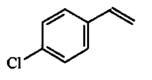
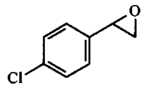
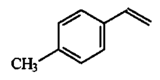
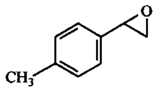
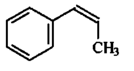
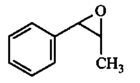
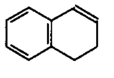
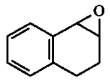
Synthesis of [Ru^{VI}(por*)O$_2$]

Preparation of dioxoruthenium(VI) porphyrin through oxidation of its ruthenium(II) carbonyl precursor by PhIO or *m*-chloroperoxybenzoic acid in CH_2Cl_2 or CH_2Cl_2–alcohol has previously been reported.[3b] The literature method works for a variety of porphyrin ligands. For the non-bulky octaethylporphyrin alcohol is needed to suppress the μ-oxo dimer formation.[3c] The H$_2$por* ligand used in this work is bulky and hence dimerization *via* Ru–O–Ru formation is not favored. Therefore only dichloromethane was used as the solvent for the synthesis. The [Ru^{VI}(por*)O$_2$] complex was obtained in a high yield by treating *m*-chloroperoxybenzoic acid with [Ru^{II}(por*)(CO)(EtOH)]; the structures for both [Ru^{VI}(por*)O$_2$][12] and [Ru^{II}(por*)(CO)(EtOH)][6] have been determined by X-ray crystallography. The [Ru^{VI}(por*)O$_2$] complex is air stable, diamagnetic and shows no manifest spectroscopic changes when dissolved in purified CH_2Cl_2 for hours at room temperature. It can be stored as a solid at −20 °C for months. It was characterized by ^{1}H, ^{13}C NMR, IR and UV/VIS spectroscopy. The ν_{asym} (O=Ru=O) occurs at 822 cm^{-1} which falls into the range reported for other achiral *trans*-dioxoruthenium(VI) porphyrins and the oxidation marker of [Ru^{VI}(por*)O$_2$] at 1019 cm^{-1} is in accordance with the ruthenium(VI) formation.[13] Comparing the ^{1}H NMR spectra of [Ru^{II}(por*)(CO)(EtOH)] with [Ru^{VI}(por*)O$_2$], the double doublet of the pyrrolic protons of the former converge to a singlet signal in the latter, as expected for the change of symmetry of the molecule from C_4 to D_4.

Stoichiometric oxidation

Oxygen atom transfer from [Ru^{VI}(por*)O$_2$] to alkenes occurs readily at room temperature with the organic epoxides being the major products. Results of stoichiometric alkene epoxidations are summarized in Table 1. The reactions were carried out in two solvents, CH_2Cl_2 and benzene, with higher product yields found in the latter solvent. Lowering the temperature was found to lower the epoxide yield. The enantiomeric excess (e.e.) of the epoxides ranged from 40 to 77% with the highest value for 1,2-dihydronaphthalene oxide obtained in the reaction of [Ru^{VI}(por*)O$_2$] with 1,2-dihydronaphthalene in dichloromethane at −15 °C. To our knowledge, this is the highest e.e. attainable in stoichiometric alkene epoxidation using well characterized

Table 1 Stoichiometric epoxidation of alkenes by [Ru^{VI}(por*)O$_2$].

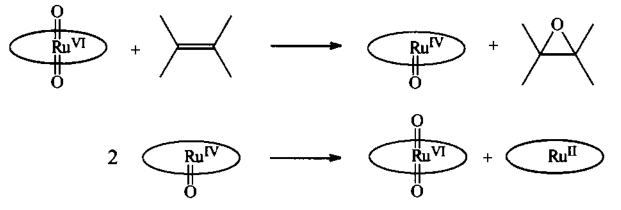
Entry	Substrate	Product	Solvent	Temperature	% Yield	% e.e.
1			CH_2Cl_2[a]	r.t.	43	59 (*R*)
			C_6H_6[a]	r.t.	61	65 (*R*)
2			CH_2Cl_2	r.t.	32	50 (*R*)
			C_6H_6[a]	r.t.	71	45 (*R*
3			CH_2Cl_2	r.t.	35	41
			C_6H_6	r.t.	41	40
4			CH_2Cl_2	r.t.	72 (*cis*/*trans* = 9.9)	67 (1*R*,2*S*)
			CH_2Cl_2	−15 °C	68 (*cis*/*trans* = 11)	70 (1*R*,2*S*)
			C_6H_6	r.t.	70 (*cis*/*trans* = 8.3)	67 (1*R*,2*S*)
			C_6H_6[a]	r.t.	64 (*cis*/*trans* = 11)	72 (1*R*,2*S*)
5			CH_2Cl_2	r.t.	32	71
			CH_2Cl_2	−15 °C	30	77
			C_6H_6	r.t.	41	72

[a] In the presence of 20 mg pyrazole.

chiral oxometal complexes.[9] The enantioselectivity shows little solvent dependence while lowering the reaction temperature tends to give higher e.e. values. In general, addition of pyrazole to the reaction mixture has little effect on the enantioselectivity except for the epoxidation of styrene to styrene oxide. In the epoxidation of *para*-substituted styrenes the side products were benzaldehydes and arylacetaldehydes. Changing the substrate from styrene to *p*-chlorostyrene lowered the e.e. from 65 to 45%. The absolute configurations of styrene and chlorostyrene epoxides were determined to be (*R*). In the reaction with *cis*-β-methylstyrene, *cis*-β-methylstyrene oxide was obtained in a high yield and with good % e.e. Besides, the epoxidation was highly stereospecific with a stereoretention of more than 90%. The absolute configuration of *cis*-β-methylstyrene epoxide was determined to be (1*R*,2*S*), thus, the configuration of the carbons bearing the phenyl group are the same for both styrene and *cis*-β-methylstyrene.

Kinetics of the reduction of [Ru^{VI}(por*)O$_2$] by alkenes

When [Ru^{VI}(por*)O$_2$] reacted with styrene in dichloromethane in the absence of pyrazole the spectral trace did not exhibit isosbestic points. This can be attributed to the accumulation and/or disproportionation of the [Ru^{IV}(por*)O] intermediate formed during the oxidation (Scheme 1). Indeed, Groves and co-workers[13] had reported that [Ru^{IV}(tmp)O] (H_2tpm = 5,10,15,20-tetramesitylporphyrin) is unstable and undergoes disproportionation in solution at room temperature. However, in the presence of pyrazole, isosbestic spectral changes for the reaction of [Ru^{VI}(por*)O$_2$] with styrene in dichloromethane were found (Fig. 1). The final ruthenium product was [Ru^{IV}(por*)(pz)$_2$] when the reaction was carried out in the presence of 3 equivalents of pyrazole. As expected for paramagnetic ruthenium(IV) complexes, the μ_{eff} of [Ru^{IV}(por*)(pz)$_2$] was found to be 2.9 μ_B. Similar reaction of [Ru^{VI}(dpp)O$_2$] (H_2dpp = 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphyrin) with alkenes in the presence of pyrazole was also found to give [Ru^{IV}(dpp)(pz)$_2$], the structure of which was determined by X-ray crystallography.[14] The observation of isosbestic spectral traces indicates no accumulation of intermediate in the conversion from [Ru^{VI}(por*)O$_2$] to [Ru^{IV}(por*)(pz)$_2$]. We propose that [Ru^{IV}(por*)O] was the immediate product of the oxygen atom transfer from [Ru^{VI}(por*)O$_2$] to alkene, which rapidly reacted with pyrazole to give [Ru^{IV}(por*)(pz)$_2$] (Scheme 2). The k_{obs} values, however, are independent of the pyrazole concentrations. Under the condition [alkene] ≫ [Ru^{VI}] and [alkene] ≤ 2 mol dm^{-3}, pseudo-first order decay of



Scheme 1

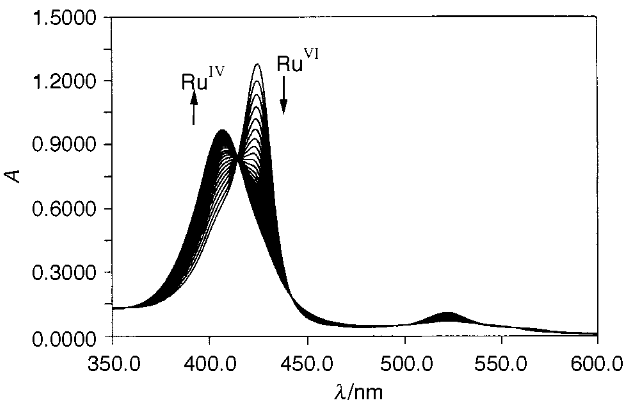
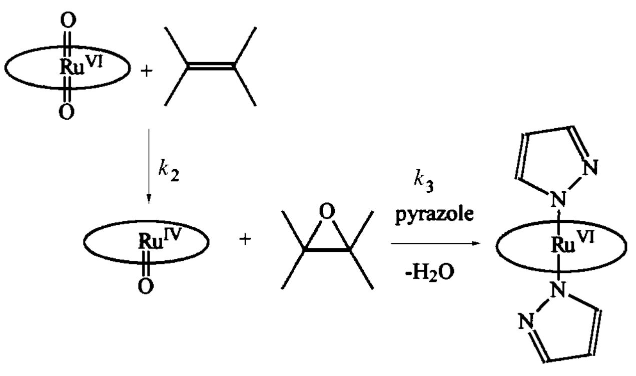
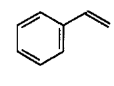
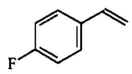
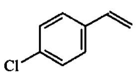
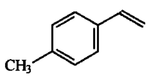
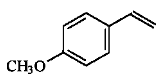
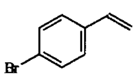
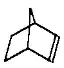
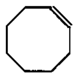
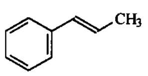
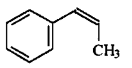
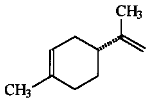
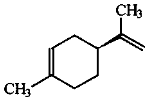


Fig. 1 Spectral trace of the reaction of styrene (0.20 mol dm^{-3}) with [Ru^{VI}(por*)O$_2$] in the presence of pyrazole (3.0%) in 1,2-dichloroethane at 298 K; scan interval 90 s.



Scheme 2

Table 2 Second order rate constants for the oxidation of alkenes by [Ru^{VI}(por*)O$_2$] in 1,2-dichloroethane at 298 K.

Entry	Alkene	k_2/dm^3 mol^{-1} s^{-1}	log k_{rel}	σ^+	TE
1		0.00219	0	0	0
2		0.00262	0.0779	−0.0073	0.16
3		0.00459	0.3214	0.114	0.23
4		0.00361	0.2171	−0.311	0.42
5		0.00965	0.6441	−0.778	1.08
6		0.00720	0.5169		
7		0.000340			
8		0.00173			
9		0.00289			
10		0.00560			
11		0.0012			
12		0.0016			

$k_{rel} = k_2$(*para*-substituted styrene)/k_2(styrene) and k_2 is the rate of oxidation of various alkenes by the dioxo complex.

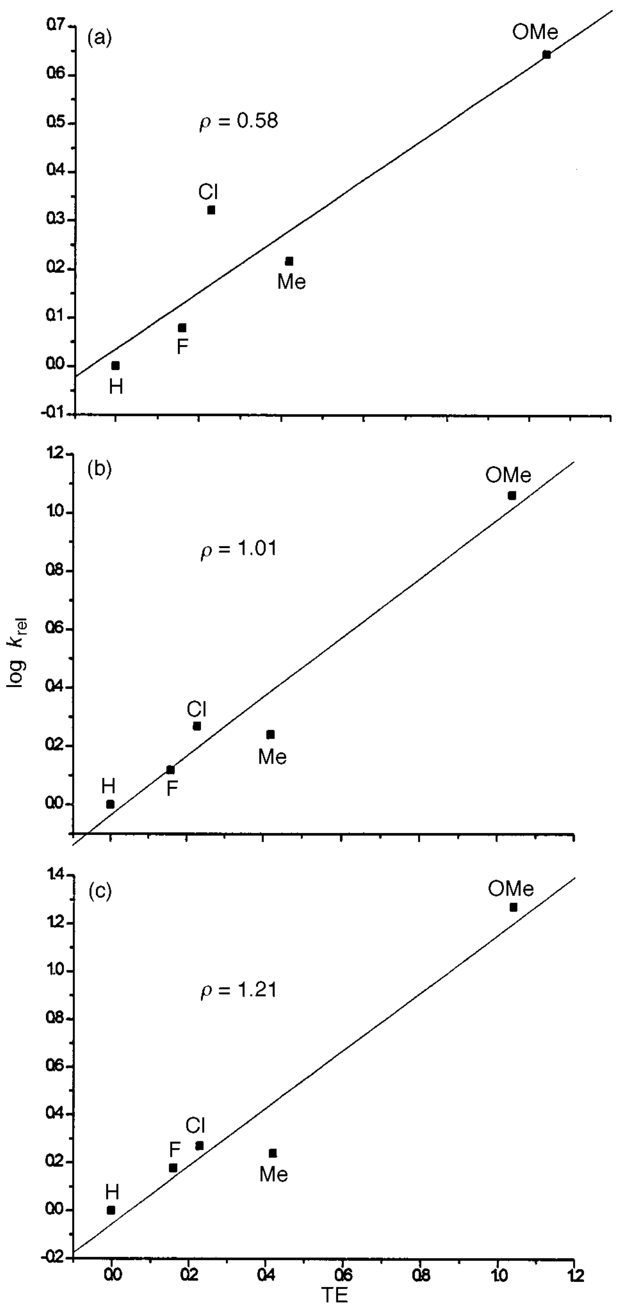


Fig. 2 Hammett plots for the oxidation of *para*-substituted styrenes by (a) [Ru^{VI}(por*)O$_2$], (b) [Ru^{VI}(tpp)O$_2$] and (c) [Ru^{VI}(oep)O$_2$].

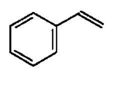
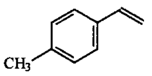
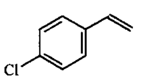
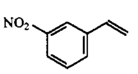
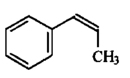
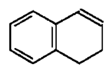
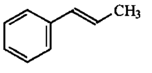
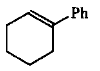
the absorbance at 424 nm (Soret band) was observed. The observed first order rate constants, k_{obs}, display a linear dependence on [alkene] and the rate law (1) was established.

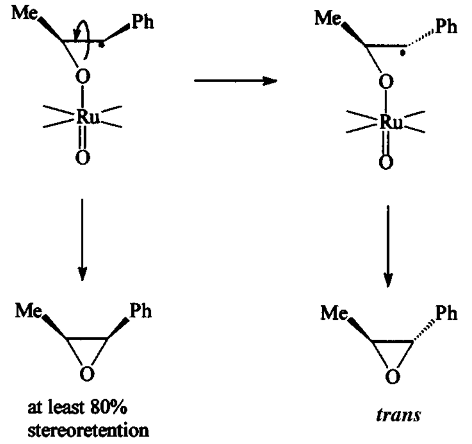
$$-d[Ru^{VI}]/dt = k_2[Ru^{VI}]\,[alkene] \qquad (1)$$

The second order rate constants (k_2) were determined by measuring the slope of the plots of k_{obs} *vs.* [alkene]. The kinetic data are summarized in Table 2. The k_2 for the oxidation of styrene is 2.19 × 10^{-3} dm^3 mol^{-1} s^{-1}. It is comparable to that by [Ru^{VI}(oep)O$_2$] (k_2 = 1.55 × 10^{-3} dm^3 mol^{-1} s^{-1}) and [Ru^{VI}(tpp)O$_2$] (k_2 = 4.30 × 10^{-3} dm^3 mol^{-1} s^{-1}). With the exception of *p*-bromo- and *p*-methoxy-styrenes, the k_2 values for the oxidation of *para*-substituted styrenes by [Ru^{VI}(por*)O$_2$] fall into a narrow range. Similar observations have previously been reported for the two achiral [Ru^{VI}(oep)O$_2$] and [Ru^{VI}(tpp)O$_2$] systems.[7] Previous studies showed that oxidation of alkenes by the achiral dioxoruthenium(VI) porphyrin [Ru^{VI}(tpp)O$_2$] exhibited a linear free-energy plot of log k_2 *vs.* $E_{\frac{1}{2}}$ (one electron potential of alkenes) with a slope of −1.1 V^{-1}. Furthermore, the oxidation of substituted styrenes by [Ru^{VI}(tpp)O$_2$] and [Ru^{VI}(oep)O$_2$] exhibited U-shaped Hammett plots. These observations were attributed to little degree of charge transfer in the transition state and a mechanism involving a continuum of transition states was suggested.

In this report, we adopt the (TE = total substituent effect parameter) values developed by Wu *et al.*[15] to construct the Hammett plots. Hammett plots for three *trans*-dioxoruthenium(VI) porphyrin complexes are shown in Fig. 2(a)–(c). The data for the [Ru^{VI}(tpp)O$_2$] and [Ru^{VI}(oep)O$_2$] complexes were taken from the literature paper. For each case, reasonable obedience to a linear correlation is obtained. The best linear fit is found for the [Ru^{VI}(oep)O$_2$] system probably due to minimum steric complication. Thus, we propose that the rate-determining step of the oxygen atom transfer involves a loosely bound radical intermediate as depicted in Scheme 3. The involvement

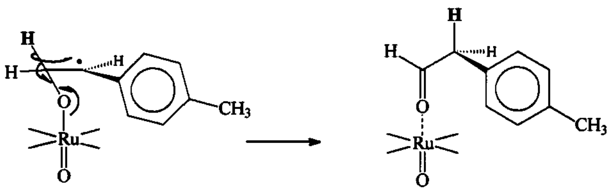
Table 3 Catalytic epoxidation of alkenes by PhIO with [Ru^{II}(por*)(CO)(EtOH)] (A) and [Ru^{VI}(por*)O$_2$] (B) as catalyst.

				Yield (%)			
Entry	Substrate	Catalyst	Solvent	Arylacetaldehyde	Benzaldehyde	Epoxide	% e.e.
1		A	CH_2Cl_2	5.5	21	71	55 (*R*)
		A	C_6H_6	3	42	57	63 (*R*)
		B	CH_2Cl_2	4	23	52	51 (*R*)
2		A	CH_2Cl_2	7	30	51	40
		A	C_6H_6	20	40	35	40
		B	CH_2Cl_2	11	42	41	38
3		A	CH_2Cl_2	Trace	32	51	41 (*R*)
		A	C_6H_6	Trace	38	66	51 (*R*)
		B	CH_2Cl_2				
4		A	CH_2Cl_2	Trace	35	53	54
		A	C_6H_6	0	38	40	52
5		A	CH_2Cl_2	—	12	59 (*cis*/*trans* = 9.9)	58 *cis* (1*R*,2*S*)
		A	C_6H_6	—	19	52 (*cis*/*trans* = 6.3)	52 *cis* (1*R*,2*S*)
		B	CH_2Cl_2	—	21	53 (*cis*/*trans* = 11)	55 *cis* (1*R*,2*S*)
6		A	CH_2Cl_2	—	—	62	30
		A	C_6H_6	—	—	46	62
7		A	CH_2Cl_2	—	47	45	16 *trans*
		A	C_6H_6		52	41	17 *trans*
		B	CH_2Cl_2		61	31	13 *trans*
8		A	CH_2Cl_2	—	—	55	8
		B	CH_2Cl_2	—	—	61	7



Scheme 3

of this radical intermediate can be used to explain the production of *trans*-β-methylstyrene oxide in the epoxidation of *cis*-β-methylstyrene as bond rotation of this carbon center radical can lead to loss of stereochemistry (Scheme 4). Its existence can also explain the rearrangement product, 2-arylacetaldehyde, in the epoxidation of styrene-type substrates through a hydrogen-atom 1,2-shift process (Scheme 3). A radical mechanism has recently been suggested to be involved in the Mn(salen) catalysed epoxidation reaction.[16]



Scheme 4

The oxidation of (+) and (−)-limonenes by [Ru^{VI}(por*)O$_2$] were studied to see if this chiral oxidant is capable of differentiating a pair of chiral substrates (Table 2, entries 11 and 12). In this work the rate constant for the reduction of [Ru^{VI}(por*)O$_2$] by (−)-limonene was found to be higher than that by (+)-limonene by a factor of ≈1.3.

Catalytic epoxidation using iodosylbenzene as oxidant

Both [Ru^{II}(por*)(CO)(EtOH)] and [Ru^{VI}(por*)O$_2$] were examined as catalysts for enantioselective alkene epoxidation using PhIO as a terminal oxidant. Both catalysts showed enantioselectivity for a wide range of alkene substrates. The best e.e. values were observed with styrene (63% e.e.) (Table 3). In the epoxidation of *para*-substituted styrenes, benzaldehydes and arylacetaldehydes were found as side products. The epoxide yields are in the range of 31–71%. Unlike the stoichiometric reactions the yields are higher in CH_2Cl_2 than in benzene. The absolute configuration of styrene and chlorostyrene oxides were determined to be (*R*). The epoxidation of *cis*-β-methylstyrene was highly stereospecific with up to 91% stereoretention in dichloromethane. The absolute configuration of *cis*-β-methylstyrene oxide was determined to be (1*R*,2*S*). In the cases of *trans*-β-methylstyrene and 1-phenylcyclohexene, low e.e. values, 17 and 8% respectively, were obtained. Unlike the results obtained with the ruthenium(II) D_2-porphyrin catalyst,[17] there is only a little difference in e.e. of the organic epoxides when changing the solvent from CH_2Cl_2 to benzene.

Comparison between stoichiometric and catalytic epoxidation by [Ru^{VI}(por*)O$_2$]

The comparison of the e.e. values of organic epoxides obtained in stoichiometric and in catalytic alkene epoxidations is an objective of this work. In the catalytic styrene epoxidation, arylacetaldehyde and benzaldehyde were obtained as side products. This is similar to the stoichiometric reaction. Of the five alkenes (styrene, 4-chlorostyrene, 4-methylstyrene, *cis*-β-methylstyrene and 1,2-dihydronaphthalene) studied in this work similar e.e. values for both the catalytic and stoichiometric reactions were obtained. This strongly argues that the [Ru^{VI}(por*)O$_2$] complex is the major oxidizing active intermediate in the catalytic epoxidation.

Conclusion

In this work the first detailed study of a well defined chiral *trans*-dioxoruthenium(VI) porphyrin complex as a stoichiometric oxidant for epoxidation of alkenes is presented. Its use as a catalyst for alkene epoxidation by PhIO has also been examined. The linearity of Hammett plots (log k_{rel} *vs.* TE) observed for the oxidation of *para*-substituted styrenes by the [Ru^{VI}(por*)O$_2$] complex supports a carbon center radical intermediate formed during the course of oxygen atom transfer reactions. The parallel enantioselectivity between the catalytic and stoichiometric epoxidations suggests that [Ru^{VI}(por*)O$_2$] is the major oxidizing intermediate in the catalytic alkene epoxidation by PhIO.

Acknowledgements

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