Kinetics of Alkene Oxidation by Cationic *trans*-Dioxoruthenium(VI) Complexes. Effect of Driving Force on Rate Constants†

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The kinetics of alkene oxidation by a series of isostructural *trans*-dioxoruthenium(VI) complexes with $E°(Ru^{VI}-Ru^{V})$ ranging from 0.23 to 0.7 V *vs.* saturated calomel electrode has been investigated in acetonitrile. The experimental rate law is rate = $k_2[Ru^{VI}][alkene]$. A linear free-energy relationship between log k_2 and $E°(Ru^{VI}-Ru^{V})$ for the oxidation of styrene and norbornene has been observed. Both steric and electronic effects of alkenes as well as the $E°$ of the dioxoruthenium(VI) complexes affect the rate constants. For the oxidation of *para*-substituted styrenes, a linear Hammett plot of log k_2 *versus* σ^+ for the *para* substituents with a ρ value of −2.1 was found. A charge-transfer mechanism alone is insufficient to explain the experimental findings.

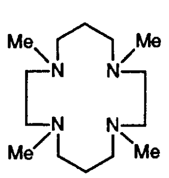
The study of oxidation of alkenes by oxo metal complexes has received much attention in the past decades.[1,2] Despite the various efforts in this area, the mechanism by which an oxygen atom is transferred from a M=O unit to a C=C bond is still a matter of controversy and various mechanisms have been proposed.[2]

Although oxo metal complexes are not uncommon, there are not many examples of this kind which are capable of oxidizing alkenes and alkanes under mild conditions. Recent works by various groups have shown that high-valent oxo ruthenium complexes are powerful stoichiometric oxidants for organic oxidation.[3] Importantly, it has been demonstrated that the physical properties and reduction potentials of *trans*-dioxoruthenium(VI) complexes are easily tuned through varying the structure of auxiliary ligands.[4,5] Thus a series of isoelectronic and isostructural complexes *trans*-$[Ru^{VI}LO_2]^{2+}$ ($L = L^1-L^4$) having $E°(Ru^{VI}-Ru^{V})$ spanning a range of 0.47 V have been prepared.[4] These complexes are well suited for the study of rate dependence on driving force. Herein is described a kinetic study of alkene oxidation by these *trans*-$[Ru^{VI}LO_2]^{2+}$ complexes.

Experimental

Materials.—The complexes *trans*-$[Ru^{VI}LO_2][ClO_4]_2$ were prepared by literature methods.[4a,e–g] Acetonitrile (A.R., Mall) for the kinetic study was first treated with $KMnO_4$ overnight and then distilled over CaH_2 under N_2. The organic substrates were of analytical grade and purified by repeated recrystallization or fractional distillation under vacuum.[6]

Stoichiometric Oxidation.—Stoichiometric oxidation was performed by dissolving the ruthenium complex (20 mg) in degassed acetonitrile (2 cm^3) containing alkene (0.1 g). The reaction mixture was stirred with a magnetic stirrer at room temperature and under a nitrogen atmosphere. A control experiment in the absence of the metal oxidant was performed for each reaction. The time for completion of oxidation depends on the nature of the ruthenium oxidant. The organic products were analysed by gas chromatography, ^{1}H NMR and mass spectrometry.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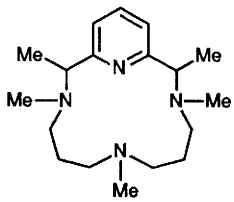
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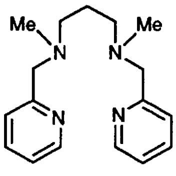
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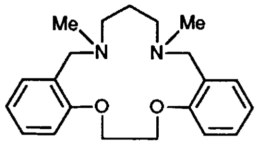
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Gas chromatographic analyses were conducted using a Varian model 940 gas chromatograph equipped with a flame ionization detector. The chromatographic columns were a 10% (w/w) Carbowax 20M on Chromosorb W (80–100 mesh size, 1/8 in × 6 ft stainless-steel column) and a 10% (w/w) SE-30 on Chromosorb W (80–100 mesh size, 1/8 in × 6 ft stainless-steel column) with nitrogen as carrier gas. Components were identified by comparing their retention times with those of authentic samples and by gas chromatographic–mass spectral analysis. Individual components were quantitated by the internal standard method employing a Shimadzu C-43A electronic integrator.

cis-Stilbene oxide and *trans*-stilbene oxide were analysed by ^{1}H NMR spectroscopy. At the end of the oxidation the solution was evaporated to dryness. After addition of 1,1-diphenylethylene, the mixture was extracted with n hexane at least five times. The combined extracts were rotary evaporated to dryness and redissolved in $CDCl_3$ for ^{1}H NMR analysis. The chemical shifts are reported relative to tetramethylsilane, the epoxide protons of *trans*- and *cis*-stilbene oxide and methylene protons of 1,1-diphenylethylene appearing as singlets at δ 3.85, 4.34 and 5.45 respectively. The singlet at δ 4.26 and doublets at δ 4.86 (J = 2.4) and 9.92 (J = 2.4 Hz) are assigned to the protons of deoxybenzoin and diphenylacetaldehyde. The amounts of the different products were determined by integration.

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† *Non-SI units employed*: in = 2.54×10^{-2} m, ft = 0.3048 m, cal = 4.184 J, eV ≈ 1.6×10^{-19} J.

Table 1 Results of stoichiometric oxidation of alkenes by *trans*-$[Ru^{VI}L^3O_2]^{2+}$ and *trans*-$[Ru^{VI}L^4O_2]^{2+}$ in degassed acetonitrile

		Yield (%)	
Substrate	Product	*trans*-$[Ru^{VI}L^3O_2]^{2+}$	*trans*-$[Ru^{VI}L^4O_2]^{2+}$
Styrene	Styrene oxide	56	20
	Benzaldehyde	39	60
cis-Stilbene	*cis*-Stilbene oxide	2	—
	trans-Stilbene oxide	18	—
	Benzaldehyde	20	50
trans-Stilbene	*trans*-Stilbene oxide	27	—
	Benzaldehyde	20	53
Cyclohexene	Cyclohex-2-enone	93	70
	Cyclohex-2-enol	0	20
Norbornene	*exo*-2,3-Epoxynorbornane	85	70
Cyclooctene	Cyclooctene oxide	60	75

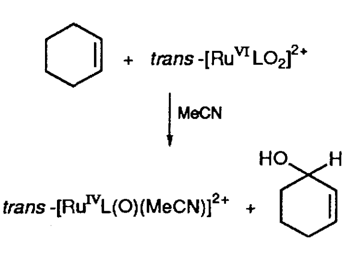
Kinetic Studies.—The UV/VIS spectra were recorded on a Shimadzu UV-240 spectrophotometer. The kinetics was studied by use of a Unicam SP-8000 spectrophotometer linked to an Apple II microcomputer *via* an AD/DA interface. The temperature of the solution was maintained to ± 0.1 C with a water-bath (bath and circulator model 2800, Masterline, Fourma Scientific). The rate of alkene oxidation was followed by monitoring the decrease in absorbance of the ruthenium oxidant at 380–400 nm under the condition that the alkene was in at least a 100-fold excess. Pseudo-first order rate constants were calculated on the basis of a least-squares fit (uniform weighting) using the relation (1) where A_∞ = final absorbance

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

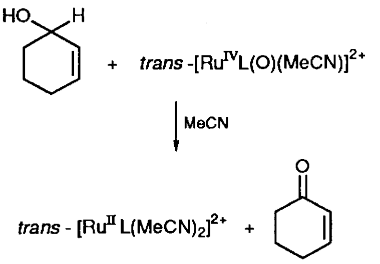
at completion of reaction, A_0 = initial absorbance, A_t = absorbance measured at time t and k_{obs} = first-order rate constant. The second-order rate constants were obtained by plotting k_{obs} *versus* alkene concentration. In each case studied a linear plot was obtained the slope of the best straight line being equal to the value of k_2.

Results

In previous works, *trans*-$[Ru^{VI}LO_2]^{2+}$ complexes have been found to be active oxidants for alkene oxidation.[4b,e–g,i] Depending on the structure of the alkene, both oxidative C=C bond cleavage and allylic oxidation were observed. The results of stoichiometric oxidation in this work are summarized in Table 1. Here product yield is defined as the moles of organic product formed as a percentage of the moles of ruthenium oxidant used, and hence it reflects the stoichiometry of oxidation. For cyclohexene, allylic oxidation is the prevailing pathway giving cyclohex-2-enone together with minor amount of cyclohex-2-enol. Since the yield of cyclohexenone is greater than 70% in each case a two-step reaction is suggested [equations (2) and (3)]. We have found that *trans*-$[Ru^{IV}L^4(O)(MeCN)]^{2+}$ is capable of oxidizing cyclohex-2-enol to cyclohex-2-enone under similar conditions.[7] Similar reaction with $[Ru^{IV}(bipy)(py)O]^{2+}$ (bipy = 2,2′-bipyridine, py = pyridine) as oxidant has also been reported.[8]

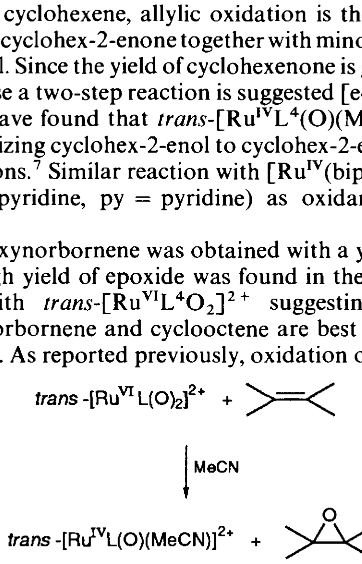


(2)



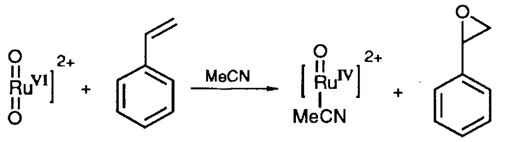
(3)

Exo-2,3-Epoxynorbornene was obtained with a yield >70%. Similarly, a high yield of epoxide was found in the reaction of cyclooctene with *trans*-$[Ru^{VI}L^4O_2]^{2+}$ suggesting that the oxidation of norbornene and cyclooctene are best represented by equation (4). As reported previously, oxidation of styrene by



(4)

trans-dioxoruthenium(VI) gave a mixture of styrene oxide and benzaldehyde with the latter being the dominant product.[4g–i] In this work we found that both styrene oxide and benzaldehyde were formed at the early stage of oxidation. The results in Table 1 indicate that the oxidation is represented by equations (5) and (6). Similarly, we found that *cis*- and *trans*-stilbenes reacted with *trans*-$[Ru^{VI}L^4O_2]^{2+}$ to give a mixture of epoxides (minor) and benzaldehyde (major). The reaction is not stereoretentive as both *cis*- and *trans*-stilbene oxides were obtained in the oxidation of *cis*-stilbene by *trans*-$[Ru^{VI}L^3O_2]^{2+}$.



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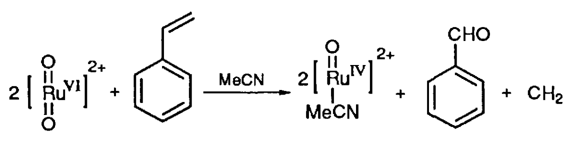

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Rate Law, Activation Parameters and Substituent Effects.—Kinetic studies on the oxidation of alkenes by *trans*-$[Ru^{VI}LO_2]^{2+}$ (L = L^1–L^4) were performed in acetonitrile. Typical UV/VIS spectral changes illustrated by using styrene as substrate and *trans*-$[Ru^{VI}L^2O_2]^{2+}$ and *trans*-$[Ru^{VI}L^4O_2]^{2+}$ as oxidants are shown in Figs. 1(*a*) and 1(*b*) respectively.

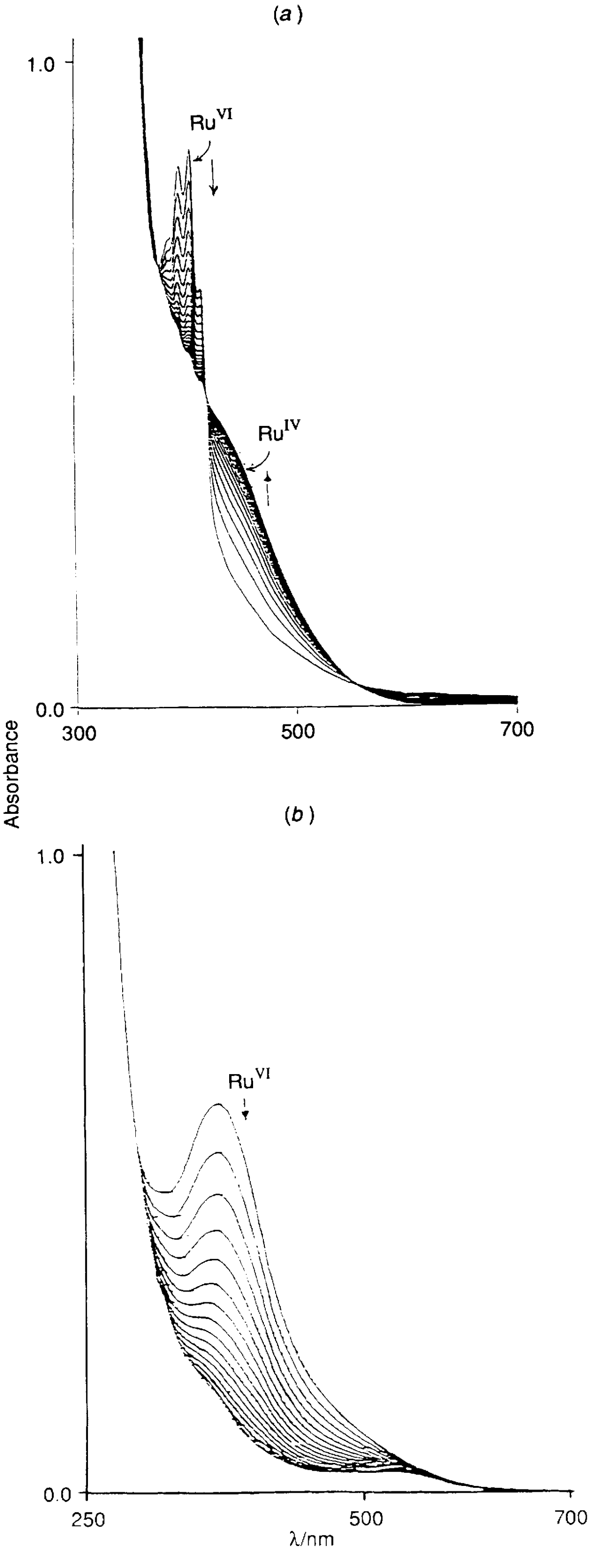


Fig. 1 The UV/VIS spectral changes in the oxidation of styrene by (*a*) *trans*-$[Ru^{VI}L^2O_2]^{2+}$ (scan interval 12 mins [styrene] 0.5 mol dm^{-3}), (*b*) *trans*-$[Ru^{VI}L^4O_2]^{2+}$ (scan interval 2 min, [styrene] 0.1 mol dm^{-3}), in acetonitrile at 298 K

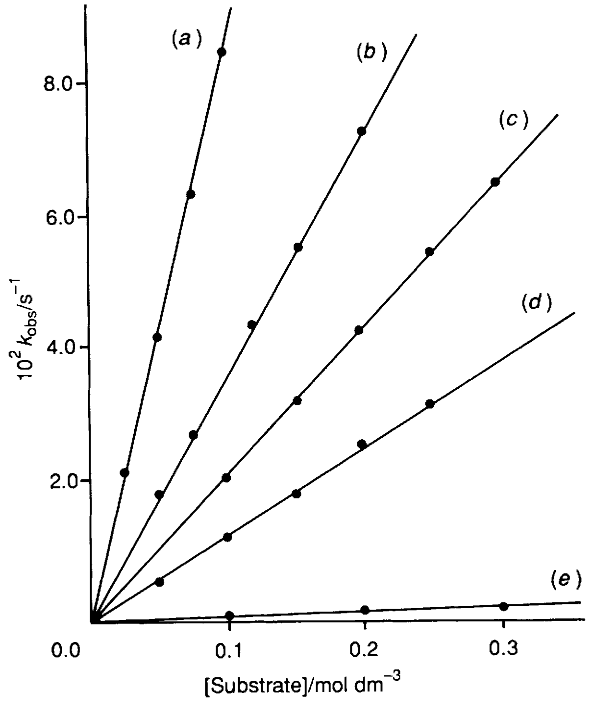


Fig. 2 Plot of k_{obs} *versus* concentration of alkenes for the oxidation of some alkenes by *trans*-$[Ru^{VI}L^4O_2]^{2+}$ in acetonitrile at 298 K. Alkenes: (*a*) norbornene, (*b*) cyclohexene, (*c*) styrene, (*d*) cyclooctene and (*e*) *trans*-stilbene

Table 2 Second-order rate constants for the oxidation of alkenes by *trans*-$[Ru^{VI}L^4O_2]^{2+}$ in acetonitrile at 25 °C

Substrate	k_2/dm^3 mol^{-1} s^{-1}	Ionization potential/eV
cis-Stilbene	$(1.69 \pm 0.11) \times 10^{-3}$	8.20
trans-Stilbene	$(7.80 \pm 0.57) \times 10^{-3}$	8.00
Cyclooctene	$(1.37 \pm 0.08) \times 10^{-1}$	8.98
Cyclohexene	$(3.50 \pm 0.24) \times 10^{-1}$	9.00
Norbornene	$(8.40 \pm 0.55) \times 10^{-1}$	8.81
2-3-Dimethylbut-2-ene	$(2.62 \pm 0.19) \times 10^{-1}$	8.30
4-Chlorostyrene	$(1.21 \pm 0.07) \times 10^{-1}$	
Styrene	$(2.09 \pm 0.13) \times 10^{-1}$	8.47
Styrene[a]	$(2.20 \pm 0.14) \times 10^{-1}$	
Styrene[b]	$(2.15 \pm 0.14) \times 10^{-1}$	
4-Fluorostyrene	$(3.20 \pm 0.23) \times 10^{-1}$	
4-Methylstyrene	1.27 ± 0.08	8.20
α-Methylstyrene	$(4.00 \pm 0.28) \times 10^{-1}$	
trans-β-Methylstyrene	$(8.82 \pm 0.53) \times 10^{-2}$	8.37

[a] The reaction was carried out in the presence of 0.1 mol dm^{-3} tetra-*n*-butylammonium fluoroborate as supporting electrolyte. [b] The reaction was carried out under degassed conditions.

The ruthenium product obtained in each case has a very similar optical spectrum to that of *trans*-$[Ru^{VI}L(O)(H_2O)]^{2+}$ in acetonitrile[4e–g,9] indicating that the oxidation is accompanied by a reduction of Ru^{VI} to Ru^{IV}. With a 100-fold excess of alkene, pseudo-first-order kinetics was found over three or more half-lives. The observed first-order rate constants, k_{obs}, vary linearly with the alkene concentration as illustrated by the plots in Fig. 2. For every reaction studied the plot of k_{obs} *versus* [alkene] passes through the origin indicating that the reduction of *trans*-$[Ru^{VI}LO_2]^{2+}$ by solvent or its self-decomposition occur at a very much slower rate. No rate saturation kinetics was found and the experimental rate law is as in equation (7).

$$-d[Ru^{VI}]/dt = k_2[Ru^{VI}][\text{alkene}] \qquad (7)$$

The rate constants are in Tables 2 and 3. In the oxidation of styrene by *trans*-$[Ru^{VI}L^4O_2]^{2+}$ removing air or adding supporting electrolyte has no effect on the rate constant. The $\Delta S^\ddagger$ values for the oxidation of styrene by *trans*-$[Ru^{VI}L^4O_2]^{2+}$, *trans*-$[Ru^{VI}L^3O_2]^{2+}$ and *trans*-$[Ru^{VI}L^2O_2]^{2+}$ are similar. The Hammett plot for the oxidation of *para*-substituted styrenes by

Table 3 Second-order rate constants for the oxidation of alkenes by *trans*-$[Ru^{VI}L^2O_2]^{2+}$ **2**, *trans*-$[Ru^{VI}L^3O_2]^{2+}$ **3** and *trans*-$[Ru^{VI}L^4O_2]^{2+}$ **4** in acetonitrile at different temperature

Alkene	Oxidant	T/K	k_2/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}
Norbornene	**4**	283.4	3.7×10^{-1}	10 ± 1	−23 ± 3
		290.7	5.8×10^{-1}		
		298.0	8.4×10^{-1}		
		307.2	1.7		
Cyclohexene	**4**	286.5	1.5×10^{-1}	10 ± 1	−25 ± 3
		292.9	2.4×10^{-1}		
		298.0	3.5×10^{-1}		
		304.9	4.4×10^{-1}		
cis-Stilbene	**4**	289.1	8.0×10^{-4}	15 ± 2	−21 ± 3
		298.0	1.7×10^{-3}		
		304.9	3.3×10^{-3}		
		314.9	7.7×10^{-3}		
trans-β-Methylstyrene	**4**	289.1	4.4×10^{-2}	13 ± 1	−20 ± 2
		298.0	8.8×10^{-2}		
		304.9	1.5×10^{-1}		
		315.1	3.2×10^{-1}		
Styrene	**4**	286.5	8.8×10^{-2}	11 ± 1	−22 ± 3
		292.9	1.3×10^{-1}		
		298.0	2.1×10^{-1}		
		304.9	3.1×10^{-1}		
trans-β-Methylstyrene	**3**	289.1	1.4×10^{-2}	13 ± 1	−23 ± 3
		298.0	2.9×10^{-2}		
		304.9	4.5×10^{-2}		
		315.1	9.9×10^{-2}		
Styrene	**3**	292.2	6.7×10^{-2}	12 ± 1	−24 ± 3
		298.0	9.2×10^{-2}		
		304.7	1.5×10^{-1}		
		313.5	2.6×10^{-1}		
Styrene	**2**	313.5	1.5×10^{-3}	15 ± 2	−24 ± 4
		321.3	3.0×10^{-3}		
		326.5	4.7×10^{-3}		
		338.5	9.9×10^{-3}		

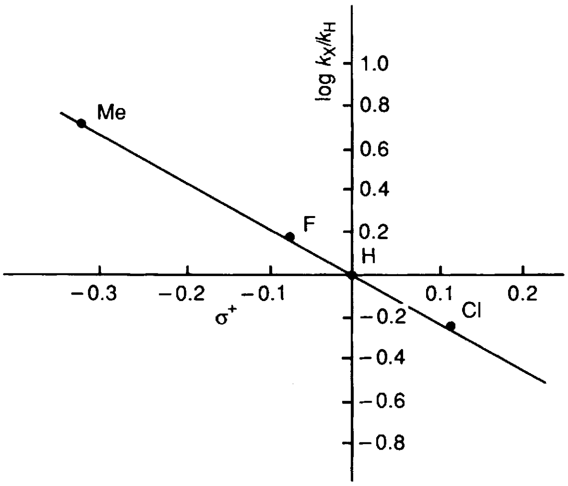


Fig. 3 Hammett plot for the oxidation of *para*-substituted styrenes by *trans*-$[Ru^{VI}L^4O_2]^{2+}$ in acetonitrile at 298 K

trans-$[Ru^{VI}L^4O_2]^{2+}$ in acetonitrile is shown in Fig. 3. The linear correlation of $\log(k_X/k_H)$ *versus* σ^+ of the *para* substituents with an observed slope of −2.1 is an indication of the development of a positive charge at the α-carbon of styrene in the transition state. Table 4 lists the reduction potentials of *trans*-$[Ru^{VI}LO_2]^{2+}$ and the rate constants for oxidation of styrene and norbornene. The plots of k_2 *versus* $E^\circ(Ru^{VI}–Ru^V)$ are shown in Fig. 4. The best straight line drawn has a slope of 12 ± 3 V^{-1} for styrene and 14 ± 3 V^{-1} for norbornene.

Discussion

The generally accepted mechanisms for the oxidation of alkenes by oxo metal complexes are depicted in Scheme 1. The interaction of the Ru=O moiety and C=C bond could be best described as concerted in nature as in pathways **B** and **C** or charge transfer in nature as in pathways **A** and **D**.

Table 4 Second-order rate constants for the oxidation of styrene and norbornene by *trans*-dioxoruthenium(VI) in acetonitrile at 25 °C and the reduction potentials of the $Ru^{VI}–Ru^V$ couple

Substrate	Complex	E° ($Ru^{VI}–Ru^V$)/ V *vs.* SCE	k_2/dm^3 mol^{-1} s^{-1}
Styrene	*trans*-$[RuL^1O_2]^{2+}$	0.23	1.00×10^{-6}
	trans-$[RuL^2O_2]^{2+}$	0.40	1.50×10^{-5}
	trans-$[RuL^3O_2]^{2+}$	0.53	9.20×10^{-2}
	trans-$[RuL^4O_2]^{2+}$	0.70	2.10×10^{-1}
Norbornene	*trans*-$[RuL^1O_2]^{2+}$	0.23	$< 1.0 \times 10^{-6}$
	trans-$[RuL^2O_2]^{2+}$	0.40	9.31×10^{-6}
	trans-$[RuL^3O_2]^{2+}$	0.53	2.70×10^{-1}
	trans-$[RuL^4O_2]^{2+}$	0.70	8.40×10^{-1}

Pathway **A** involves the formation of a very high-energy alkene-derived carbocation radical **I** and dioxoruthenium(V). Such a pathway would play a significant role only in the case where the reduction potential of the ruthenium oxidant and the oxidation potential of the alkene are comparable. In this work the E° values of *trans*-$[Ru^{VI}LO_2]^{2+}$ lie in the range 0.23–0.7 V *vs.* saturated calomel electrode (SCE),[4a,e–g,9] which are at least 0.8 V less than the oxidation potentials of styrene and norbornene. Hence, on thermodynamic grounds, pathway **A** is unlikely to play any significant role in oxidation. Such a pathway has also been excluded by Bruice and co-workers[10] in the oxidation of alkenes by oxo[5,10,15,20-tetrakis(2,6-dibromophenyl)porphyrinato]chromium(V) where the Cr^V=O oxidant has an even higher E° value (0.865 V *vs.* SCE) than that of *trans*-$[Ru^{VI}L^4O_2]^{2+}$.

Pathway **B** is a concerted addition, giving the epoxide directly. This pathway was suggested by Sawyer and co-

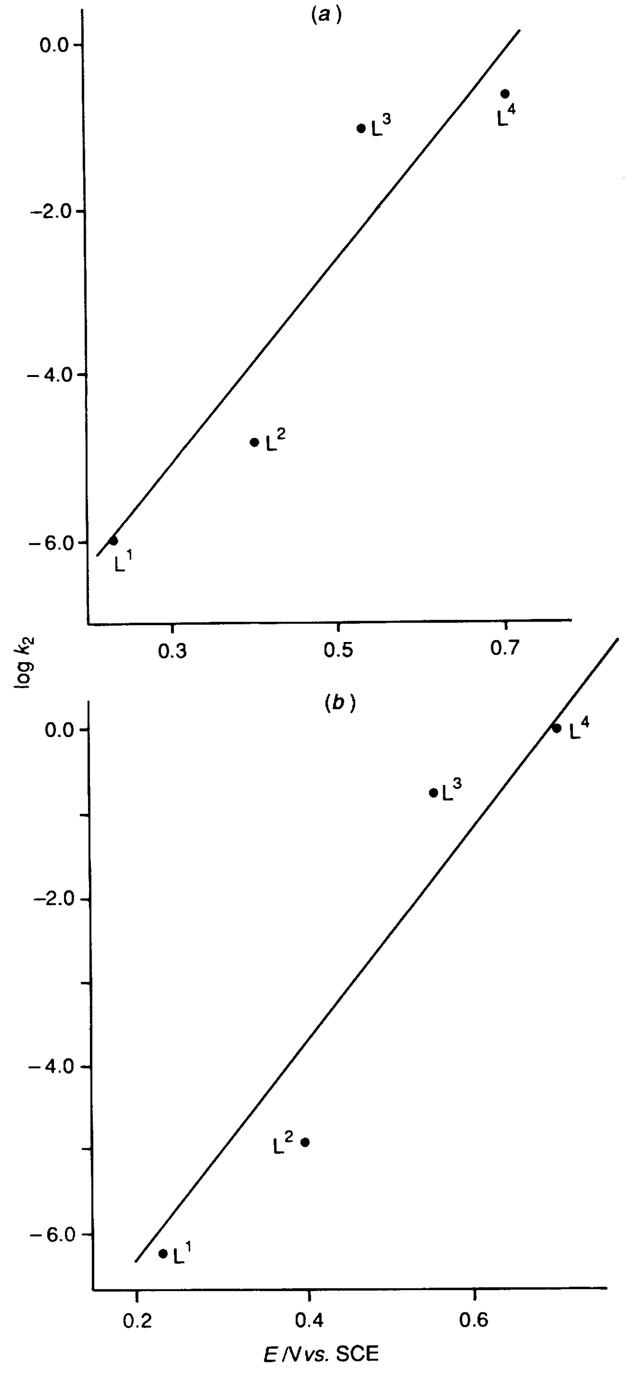
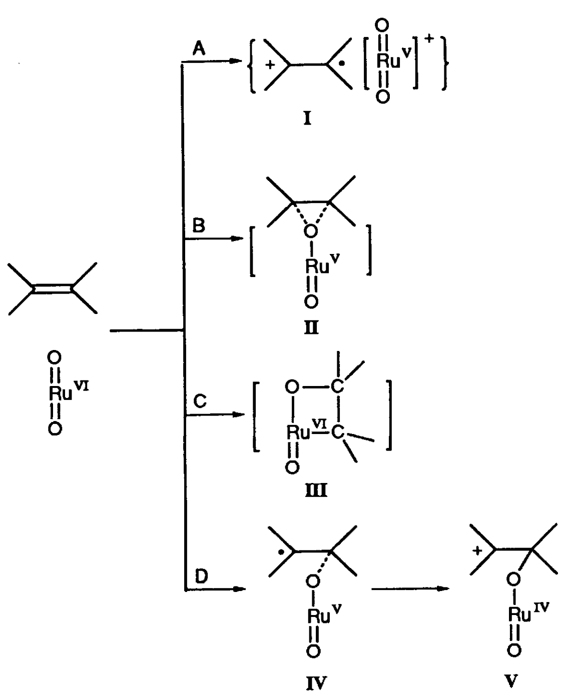


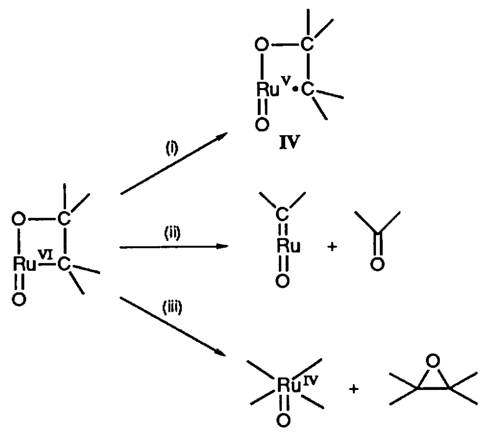
Fig. 4 Plot of log k_2 *versus* $E°(Ru^{VI}–Ru^{V})$ for the oxidation of (*a*) styrene and (*b*) norbornene by *trans*-$[Ru^{VI}LO_2]^{2+}$ in acetonitrile at 298 K

workers[11] to account for the stereospecific epoxidation of alkenes catalysed by iron(III) porphyrin. In this work, non-stereospecific epoxidation and oxidative cleavage of alkenes by *trans*-$[Ru^{VI}LO_2]^{2+}$ have been found. Oxidation of *cis*-stilbene by *trans*-$[Ru^{VI}L^3O_2]^{2+}$ and *trans*-$[Ru^{VI}L^4O_2]^{2+}$ gave a mixture of *cis*- and *trans*-stilbene oxides (minor) and benzaldehyde (major).[4e,f] These organic products cannot be accounted for by this pathway. Furthermore, as discussed later, charge transfer from the alkene to the ruthenium oxidant is likely to play a significant role in the rate-determining step of oxidation. For these reasons, pathway B is not favoured.

Pathway C is also a concerted reaction involving the formation of a metallaoxetane as intermediate. Breakdown of the metallaoxetane could lead to the events in Scheme 2. Formation of product(s) resulting from oxidative C=C bond cleavage has in fact been observed in the reactions of *trans*-$[Ru^{VI}LO_2]^{2+}$ and other *trans*-dioxoruthenium(VI) complexes[4h] with styrene and *cis*- and *trans*-stilbenes. Reaction (ii) in Scheme 2 could account for such findings. One would expect the rate constants for metallaoxetane formation to be more sensitive to the steric rather than electronic effects of the alkenes. While a linear free-energy relationship has been observed for the oxidation of styrene and substituted styrenes by *trans*-dioxoruthenium(VI) (Figs. 3 and 4), no linear correlation has been found between log(rate constants) and ionization potentials of alkenes as illustrated by the data in Fig. 5. In this figure the data points are very scattered. For example, the rate constants for the oxidation of *cis*- and *trans*-stilbenes and *trans*-β-methylstyrene are smaller than that of norbornene despite norbornene having the highest oxidation potential (Table 2). This suggests that a charge-transfer mechanism alone is insufficient to account for the experimental finding. The dependence of the rate constants on the structure of the alkenes would imply a close association of the reactants in the transition state. Of course, the stability of the intermediate **IV** in pathway D of Scheme 1 is also subjected to the steric effect of the alkene.



Scheme 1



Scheme 2

Pathway D involves the formation of a short-lived intermediate **IV**, which may collapse to give an epoxide or

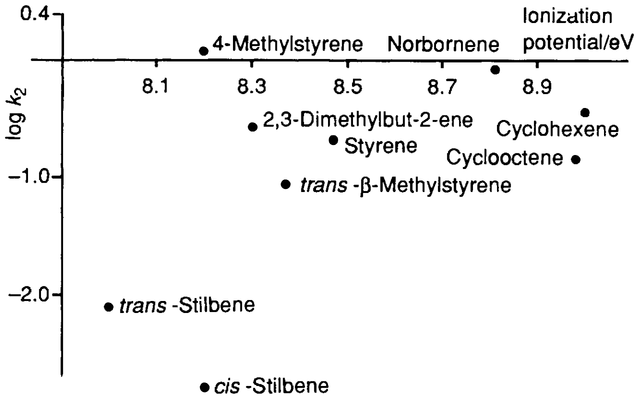


Fig. 5 Plot of log k_2 *versus* ionization potential of alkenes for the oxidation of alkenes by *trans*-$[Ru^{VI}L^4O_2]^{2+}$

metallaoxetane intermediate or undergo further electron transfer to give a carbocation species **V**. Rotation of the C–C bond in **IV** would lead to non-stereospecific epoxidation. The ESR experiments yielded no conclusive results as to whether a radical intermediate was formed or not during the oxidation. Since the formation of intermediate **IV** would involve charge transfer from the alkene to *trans*-dioxoruthenium(VI), it would not be surprising to find that a linear free-energy relationship exists between log(rate constants) and E° (ruthenium oxidant) for the oxidation of styrene and norbornene. The slopes of the two best straight lines drawn in Figs. 4(*a*) and 4(*b*) are 12 ± 3 and 14 ± 3 V^{-1} respectively. Although these values are not very reliable due to insufficient data points, they are, however, greater than the value of 9 V^{-1} reported by Bruice and co-workers[10,12] for the epoxidation of norbornene by a series of oxochromium(V) porphyrins and the theoretical value of 8.4 V^{-1} for a truly one-electron-transfer process. This may suggest a greater extent of charge transfer in the oxidation of alkenes by *trans*-$[Ru^{VI}LO_2]^{2+}$ than by $Cr^V{=}O$ porphyrin. The much larger slopes than 8.4 V^{-1} could be accounted if the structure of the reaction intermediate lies in between **IV** and **V** in Scheme 1. Further evidence supporting the importance of charge transfer in the oxidation comes from the observed linear Hammett plot of log(rate constants) *versus* σ^+ of *para* substituents X for the oxidation of *para*-substituted styrenes by *trans*-$[Ru^{VI}L^4O_2]^{2+}$. A ρ value of −2.1 is obtained which is in accordance with the attacking species being electrophilic and the development of positive charge on the α-carbon of the styrene in the transition state. Such a ρ value is more negative than the ones reported by Traylor and Mikszta1[13] (ρ = −0.84), Lindsay-Smith and Sleath[14] (ρ = −0.93) and Groves and Watanable[15] (ρ = −1.9) on the PhIO oxidation of substituted styrenes catalysed by chloro[5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]iron(III), chloro(5,10,15,20-tetraphenylporphyrinato)iron(III) and chloro(5,10,15,20-tetramesitylporphyrinato)iron(III) respectively. From the experimental findings, we suggest that pathways A and B are unlikely to play any significant role in the oxidation of alkenes by *trans*-$[Ru^{VI}LO_2]^{2+}$. It is, however, impossible to decide the relative contribution of pathways C and D in the oxidation. In fact, none of these two pathways can explain the entire experimental findings. The similar $\Delta S^\ddagger$ values (Table 3) irrespective of the structure of the ruthenium oxidant and alkenes suggests a similar structure for the transition state in the oxidation. If the metallaoxetane intermediate plays a dominant role, the $\Delta S^\ddagger$ values are expected to be sensitive to the alkene structure, and this is not observed in this work. We suggest that the structure of the transition state shuttles between **IV** and **III** in Scheme 1. Unless the breakage of the metallaoxetane intermediate *via* pathway (ii) in Scheme 2 occurs at a much faster rate than the transformation of **IV** to **III**, it remains to be explained why the oxidation of styrene and *cis*-and *trans*-stilbenes by *trans*-$[Ru^{VI}LO_2]^{2+}$ in degassed acetonitrile leads to the formation of benzaldehyde as the major product.

Acknowledgements

We acknowledge supports from the Hong Kong Research Grants Council and the University of Hong Kong. C. K. L. and W. Y. Y. are grateful for a scholarship administered by the Sir Edward Youde Foundation of Hong Kong.

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Received 15*th May* 1992; *Paper* 2/02530B