Kinetics of Oxidation of Aromatic Hydrocarbons and Tetrahydrofuran by *trans*-Dioxoruthenium(VI) Complexes

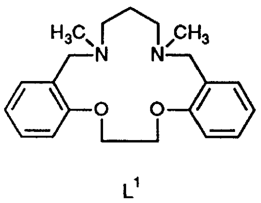
Chi-Ming Che,* Wai-Tong Tang, Kwok-Yin Wong and Chi-Keung Li
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

The kinetics of oxidation of aromatic hydrocarbons and tetrahydrofuran by *trans*-$[Ru^{VI}LO_2]^{2+}$ {L = 2 bipy(bipy = 2,2′-bipyridine), L^1 = 6,7,14,15,16,17,18,19-octahydro-14,18-dimethyl-13*H*-dibenzo[*e*,*n*]-[1,4,8,12]dioxadiazacyclopentadecine, L^2 = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)propylenediamine and L^3 = *meso*-2,3,7,11,12-pentamethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene} has been studied. In acetonitrile the second-order rate constants follow the order: toluene < ethylbenzene < cumene. The kinetic isotope effects for the oxidation of ethylbenzene by *trans*-$[RuLO_2]^{2+}$ (L = L^1 or L^2) are 16 and 12 : 1 respectively. In the oxidation of tetrahydrofuran by *trans*-$[RuL^1O_2]^{2+}$, k_2 was found to be 0.170 mol^{-1} dm^3 s^{-1} at 298 K with a measured kinetic isotope effect of 20 : 1. A linear correlation between log(rate constant) and $E°(Ru^{VI}–Ru^{IV})$ for the oxidation of tetrahydrofuran has been observed. The activation parameters for the oxidation reactions have also been determined. A hydrogen-atom abstraction mechanism is suggested for the oxidation of C–H bonds by *trans*-dioxoruthenium(VI) complexes.

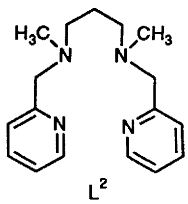
The selective functionalization of C–H bonds under mild conditions is an important area of research.[1] Recent work by various groups has shown that oxoruthenium complexes are capable of oxidizing a wide variety of organic substrates.[2] Mechanistic studies on the oxidation of hydrocarbons by some oxoruthenium-(IV)[3] and -(V)[4] systems suggested a hydrogen-atom or hydride-transfer mechanism. Herein are described kinetic studies on the oxidation of C–H bonds in aromatic hydrocarbons and tetrahydrofuran by some *trans*-dioxoruthenium(VI) complexes.

Experimental

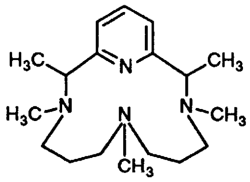
Materials.—Deionized water used in kinetic studies was doubly distilled over alkaline $KMnO_4$. Trifluoroacetic acid (Aldrich) was purified by distillation under nitrogen. Acetonitrile (Mallinkrodt AR) was first treated with $KMnO_4$ overnight and then distilled over CaH_2 under nitrogen. $[^2H_{10}]$Ethylbenzene and $[^2H_8]$tetrahydrofuran (Aldrich) were used as received. Tetrabutylammonium tetrafluoroborate (Electrometric grade, Southwestern Chemical) was vacuum dried overnight at 65 °C. The organic substrates were of analytical grade and purified by repeated recrystallization or fractional distillation. The compounds *trans*-$[Ru^{VI}L^1O_2][ClO_4]_2$ (L^1 = 6,7,14,15,16,17,18,19-octahydro-14,18-dimethyl-13*H*-dibenzo[*e*,*n*][1,4,8,12]dioxadiazacyclopentadecine),[5] *trans*-$[Ru^{VI}L^2O_2][ClO_4]_2$ [L^2 = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)propylenediamine],[6] *trans*-$[Ru^{VI}(bipy)_2O_2][ClO_4]_2$ (bipy = 2,2′-bipyridine)[7] and *trans*-$[Ru^{VI}L^3O_2][ClO_4]_2$ {L^3 = *meso*-2,3,7,11,12- pentamethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}[8] were prepared as described previously.



L^1



L^2



L^3

Instrumentation and Techniques.—Kinetic experiments employed either a Unicam SP8000 spectrophotometer linked to an Apple IIe microcomputer or a HI-TECH SF-51 stopped-flow spectrophotometer. Temperature was maintained to ±0.1 °C with a thermostatted water-bath. The rate of reaction was followed by monitoring the decrease in absorbance of the ruthenium complex at 350–400 nm. Pseudo-first-order rate constants were calculated on the basis of a least-squares fit by the relation $\ln|A_\infty - A_t| = -k_{obs}t + \ln|A_\infty - A_0|$ where A_∞ is the final absorbance upon completion of reaction, A_0 the initial absorbance and A_t the absorbance at time t and k_{obs} is the first-order rate constant. Runs were initiated by mixing equal volumes of a 1 mmol dm^{-3} solution of the ruthenium complex and a known concentration of organic substrate in at least ten-fold excess. Each run was repeated three times and the mean value of k_{obs} taken. Kinetic data over five half-lives were used for the calculation of k_{obs}. The second-order rate constants (k_2) were obtained from plots of k_{obs} *vs.* [organic substrate]. Activation parameters $\Delta H^‡$ and $\Delta S^‡$ were obtained from the slope and intercept of plots of $\ln(k_2/T)$ *vs.* $1/T$.

Results and Discussion

Oxidation of Aromatic Hydrocarbons.—The stoichiometric oxidation of toluene, ethylbenzene and cumene by *trans*-$[Ru^{VI}LO_2]^{2+}$ (L = L^1 or L^2) has been studied and reported.[5,6] Toluene was oxidized to benzaldehyde. With ethylbenzene, the secondary C–H bond was oxidized to give acetophenone and *sec*-phenylethyl alcohol. In the case of cumene only 2-phenyl isopropyl alcohol was obtained. Thus, *trans*-$[Ru^{VI}LO_2]^{2+}$ selectively oxidise tertiary C–H bonds in the presence of primary and secondary ones.

Spectral changes with clean isosbestic points (Fig. 1) were

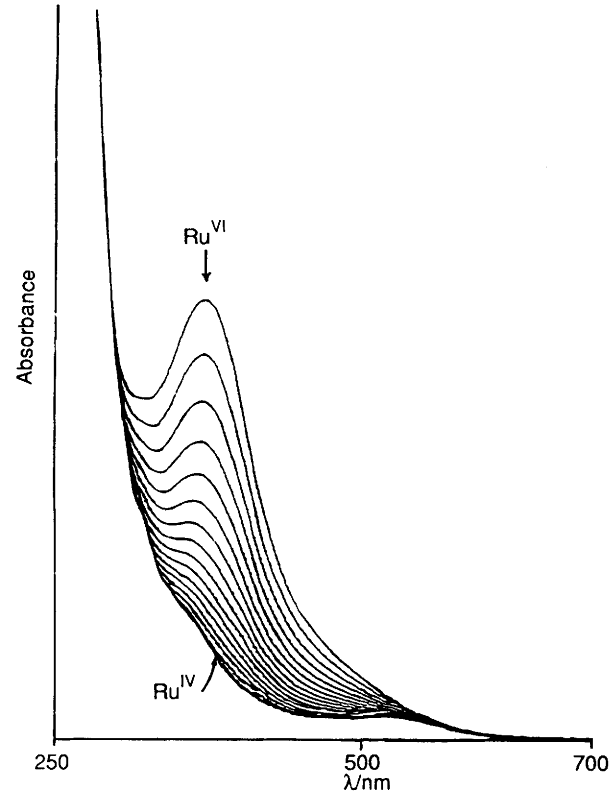


Fig. 1 UV/VIS spectral changes for the reaction between *trans*-$[RuL^1O_2]^{2+}$ (10^{-3} mol dm^{-3}) and cumene (1 mol dm^{-3}) at room temperature in acetonitrile. Scan interval 2 min

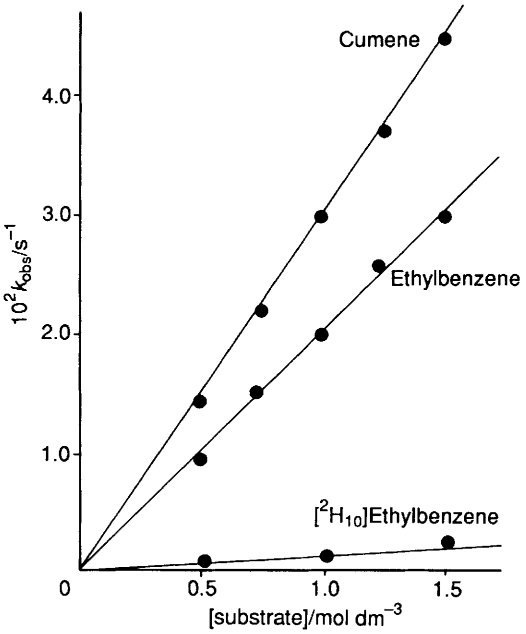


Fig. 2 Plots of k_{obs} *vs.* [aromatic hydrocarbon] for the oxidation of aromatic hydrocarbons by *trans*-$[RuL^1O_2]^{2+}$ in acetonitrile at 298 K

obtained for the oxidation of the above aromatic hydrocarbons by *trans*-$[RuL^1O_2]^{2+}$. The UV/VIS spectrum of the final ruthenium product is identical to that of *trans*-$[Ru^{IV}L^1(O)(OH_2)]^{2+}$ in acetonitrile[5] indicating that the reaction involved the reduction of Ru^{VI} to Ru^{IV}.

Under the condition that [aromatic hydrocarbon] $\gg$ [Ru^{VI}], the experimental rate law was found to be as in equation (1)

$$\text{rate} = k_{obs}[Ru^{VI}] \quad (1)$$

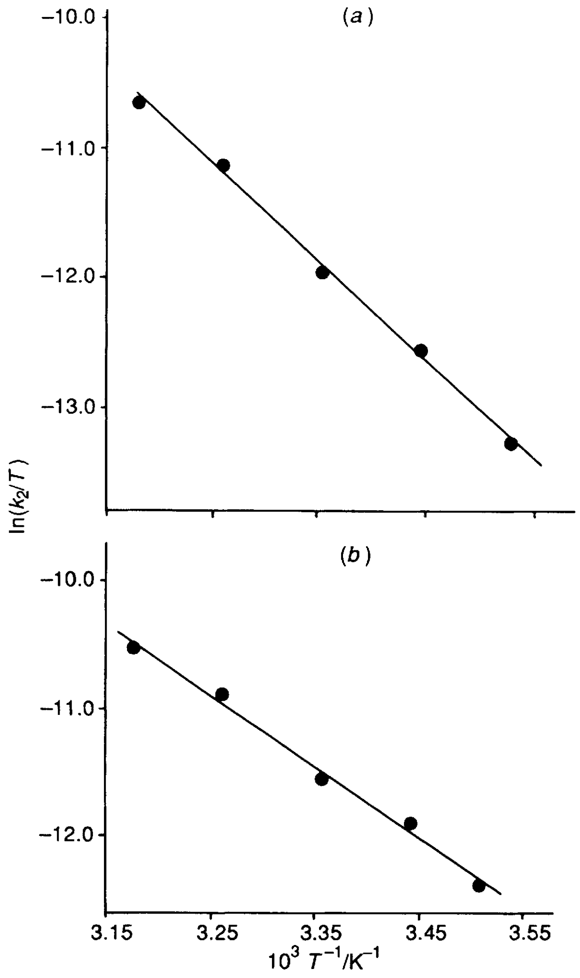


Fig. 3 Eyring plots for the oxidation of (*a*) ethylbenzene and (*b*) cumene by *trans*-$[RuL^1O_2]^{2+}$ in acetonitrile

where $k_{obs} = k_2$[aromatic hydrocarbon]. Fig. 2 shows plots of k_{obs} *vs.* [aromatic hydrocarbon] for the oxidation by *trans*-$[RuL^1O_2]^{2+}$. The rate constants k_2 (Table 1) follow the order toluene < ethylbenzene < cumene. The fact that toluene was oxidized to benzaldehyde suggests a two-step reaction [equations (2) and (3)].

$$Ru^{VI} + PhCH_3 \longrightarrow Ru^{IV} + PhCH_2OH \quad (2)$$

$$Ru^{VI} + PhCH_2OH \longrightarrow Ru^{IV} + PhCHO \quad (3)$$

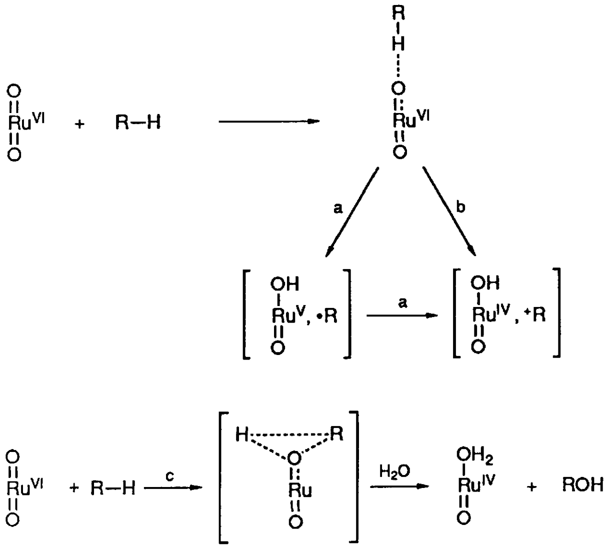
At 298 K, k_2 for the oxidation of benzyl alcohol and toluene by *trans*-$[RuL^1O_2]^{2+}$ is 0.54 and 1.8 × 10^{-5} dm^3 mol^{-1} s^{-1} respectively.[9] This suggests that benzyl alcohol is 10^4 times more reactive than toluene. In order to avoid the secondary reduction of Ru^{VI} by benzyl alcohol, a large excess (× 1000) of toluene was used in the kinetic studies. In the stoichiometric oxidation of ethylbenzene, acetophenone was formed. It is likely that this came from the oxidation of *sec*-phenylethyl alcohol by *trans*-$[Ru^{VI}LO_2]^{2+}$. In order to determine the extent of α-C–H bond cleavage in the activation step, the oxidation of [^{2}H$_{10}$]ethylbenzene by *trans*-$[Ru^{VI}LO_2]^{2+}$ has also been studied. The measured k_H/k_D of 16 ± 2 and 12 ± 2:1 (Table 1) for L = L^1 and L^2 respectively strongly suggests an important role for such bond cleavage.

Activation parameters for the oxidation of cumene and ethylbenzene were determined over the temperature range 283–315 K and the results are summarized in Table 1. Two representative Eyring plots are given in Fig. 3. The negative $\Delta S^{\ddagger}$ values and large kinetic isotope effect on the rate constants

Table 1 Summary of kinetic data for the oxidation of aromatic hydrocarbons in acetonitrile and tetrahydrofuran in 0.1 mol dm^{-3} CF_3SO_3H by *trans*-dioxoruthenium(VI) complexes. Second-order rate constants are reported at 298 K; cal = 4.184 J

Substrate	10^3 k/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}	k_H/k_D
Cumene[a]	1.90 ± 0.22	11 ± 2	−31 ± 3	
Cumene[a] (+0.05 mol dm^{-3} Bu^{t}OH)	2.90 ± 0.25			
Cumene[a] (+0.05 mol dm^{-3} water)	3.00 ± 0.28			
Ethylbenzene[a]	1.98 ± 0.12	14 ± 1	−22 ± 2	16
[$^2H_{10}$]Ethylbenzene[b]	0.12 ± 0.01			
Toluene[a]	0.018 ± 0.002			
Cumene[b]	1.96 ± 0.14	14 ± 1	−25 ± 2	
Ethylbenzene[b]	1.32 ± 0.09	13 ± 2	−24 ± 3	12
[$^2H_{10}$]Ethylbenzene[b]	0.11 ± 0.02			
Tetrahydrofuran[c]	3500 ± 270			
Tetrahydrofuran[a]	170 ± 10	10 ± 1	−28 ± 2	20
[$^2H_8$]Tetrahydrofuran[a]	8.42 ± 0.73			
Tetrahydrofuran[b]	12.0 ± 1.0			
Tetrahydrofuran[d]	4.21 ± 0.16	14 ± 1	−28 ± 3	

[a] *trans*-$[RuL^1O_2]^{2+}$. [b] *trans*-$[RuL^2O_2]^{2+}$. [c] *trans*-$[Ru(bipy)_2O_2]^{2+}$. [d] *trans*-$[RuL^3O_2]^{2+}$.



Scheme 1

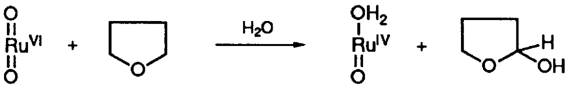
indicate a transition state having strong lead-in interaction between the α-C–H bond of the aromatic hydrocarbons and the Ru=O moiety of *trans*-$[Ru^{VI}LO_2]^{2+}$.

Either a hydrogen-atom or hydride-abstraction mechanism is possible. There is no evidence for the formation of products arising from coupling of $PhC(CH_3)_2^•$ radicals in the oxidation of cumene. This, together with the fact that the yields of organic products and rate constants for oxidation are independent of the addition of radical scavengers, strongly argues against a mechanism involving the formation of out-cage radical intermediates. Scheme 1 outlines a possible mechanism for the oxidation. Pathway a involves an initial hydrogen-atom abstraction followed by a rapid in-cage one-electron transfer before the radical intermediates R$^•$ and O=Ru^V–OH diffuse out to the solution. Such a pathway would be very difficult to distinguish from pathway b which involves a two-electron hydride abstraction. Pathway c involves a concerted transition state.

Thompson and Meyer[3a] have shown that both solvent and added nucleophile play an important role in the oxidation of aromatic hydrocarbons by $[Ru(bipy)_2(py)O]^{2+}$ (py = pyridine). Presumably, the added nucleophile assists the loss of hydride ion by charge neutralization at the metal atom with electron-pair donation as hydride transfer occurs to Ru=O. In this work, however, water or Bu^{t}OH was found to have no effect on the rate of oxidation of cumene by *trans*-$[RuL^1O_2]^{2+}$ (Table 1).

From Table 1, there is only a small difference in the rates of oxidation of cumene and ethylbenzene in contrast to the difference in the secondary and tertiary C–H bond energy. This may be attributed to the presence of methyl groups in cumene that hinder the approach of the ruthenium oxidant.

Oxidation of Tetrahydrofuran.—In stoichiometric oxidation, tetrahydrofuran (thf) was oxidized by *trans*-dioxoruthenium(VI) to γ-butyrolactone.[5–7] The kinetics of oxidation by *trans*-$[Ru^{VI}LO_2]^{2+}$ was studied in 0.1 mol dm^{-3} CF_3CO_2H. For L = L^1 well defined isosbestic points at 295 and 650 nm were observed throughout the reaction, the spectral changes being the same as those shown in Fig. 1. The UV/VIS spectrum of the final product is identical to that of Ru^{IV}. Thus the reaction can be described as a two step process [equations (4) and (5)].



(4)

(5)

The experimental rate law found is as in equation (6) where

$$\text{rate} = k_{obs}[Ru^{VI}] \qquad (6)$$

$k_{obs} = k_2$[thf]. The kinetic data are summarized in Table 1. Fig. 4 shows a representative plot of k_{obs} *versus* [thf]. For the oxidation by *trans*-$[Ru^{VI}L^1O_2]^{2+}$ the kinetic isotope effect k_H/k_D was found to be 20 ± 2:1, substantially larger than that reported by Lee and Engl[10] for the oxidation of tetrahydrofuran by RuO_4 (k_H/k_D = 1.5:1). The activation parameters for the oxidation by *trans*-$[Ru^{VI}LO_2]^{2+}$ (L = L^1 or L^3) are summarized in Table 1. Fig. 5 shows a plot of log k_2 *versus* $E°$ (Ru^{VI}–Ru^{IV}) for *trans*-$[Ru^{VI}LO_2]^{2+}$. The best straight line drawn has a slope of 19.6 V^{-1}.

General.—Previous electrochemical studies revealed that *trans*-$[Ru^{VI}LO_2]^{2+}$ functions either as a two- or a one-electron

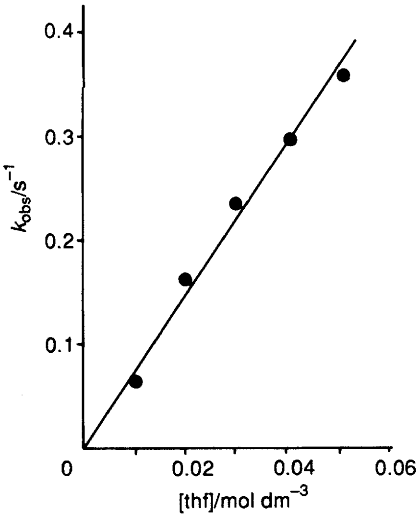


Fig. 4 Plot of k_{obs} *vs.* [tetrahydrofuran] for the oxidation by *trans*-$[\mathrm{Ru(bipy)_2O_2}]^{2+}$ in 0.1 mol dm^{-3} CF_3CO_2H at 298 K

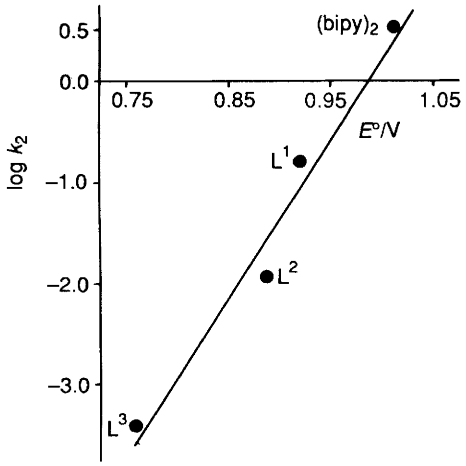


Fig. 5 Plot of log k_2 *vs.* E° of the $\mathrm{Ru^{VI}}$–$\mathrm{Ru^{IV}}$ couple for the oxidation of tetrahydrofuran by *trans*-$[\mathrm{Ru^{VI}LO_2}]^{2+}$ in 0.1 mol dm^{-3} CF_3CO_2H at 298 K

oxidant, depending on the pH of the medium. At pH 1 the E° ($\mathrm{Ru^{VI}}$–$\mathrm{Ru^{IV}}$) values are 1.01, 0.92, 0.89 and 0.76 V *vs.* saturated calomel electrode for L = (bipy)$_2$, L^1, L^2 and L^3 respectively,[5–8] suggesting that these oxoruthenium(VI) complexes are strong oxidants.

In this work the kinetic isotope effects (k_H/k_D) for the oxidation of ethylbenzene and tetrahydrofuran by *trans*-$[\mathrm{RuL^1O_2}]^{2+}$ are 16 ± 2 and 20 ± 2:1 respectively, comparable to those of 14 ± 2:1 for the oxidation of cyclohexane by *trans*-$[\mathrm{Ru(5,5'\text{-}dmbipy)_2O_2}]^{2+}$ (5,5′-dmbipy = 5,5′-dimethyl-2,2′-bipyridine)[11] and 12 ± 2:1 for the oxidation of ethylbenzene by *trans*-$[\mathrm{RuL^2O_2}]^{2+}$. This suggests a common linear $[\mathrm{O{=}Ru^{VI}{=}O\cdots H{-}\overset{|}{\underset{|}{C}}{-}}]$ transition state. Such an associative mechanism is also supported by the large negative $\Delta S^\ddagger$ values for the oxidation reactions. Several pathways are feasible for the oxidation of C–H bonds by *trans*-$[\mathrm{Ru^{VI}LO_2}]^{2+}$ (Scheme 1).

Pathways a and b are the two-electron hydride and one-electron hydrogen-atom abstraction respectively. It is difficult to distinguish between them, especially in the case where the hydrogen-atom abstraction is followed by a rapid in-cage oxygen rebound or electron transfer from $\mathrm{O{=}Ru^{V}{-}OH}$ to the $R^\bullet$ radical. However, in view of previous results on the oxidation of cyclohexane by *trans*-$[\mathrm{Ru^{VI}(5,5\text{-}dmbipy)_2O_2}]^{2+}$,[11] a H-atom abstraction is favoured for the oxidation of aromatic hydrocarbons by *trans*-dioxoruthenium(VI). Pathway c is a concerted insertion process but in view of the large kinetic isotope effects for the oxidation we favour a linear transition state.

The C–H bond oxidation by *trans*-$[\mathrm{Ru^{VI}LO_2}]^{2+}$ is likely to be facilitated by charge transfer from the C–H bond to the $\mathrm{Ru^{VI}{=}O}$ oxidant. This is at least true for tetrahydrofuran where a linear free-energy relationship between the rate constants and E° of *trans*-$[\mathrm{Ru^{VI}LO_2}]^{2+}$ has been observed (Fig. 5). For the oxidation of cumene and ethylbenzene, *trans*-$[\mathrm{RuL^1O_2}]^{2+}$ has higher rate constants than those of *trans*-$[\mathrm{RuL^2O_2}]^{2+}$ because the former oxidant has a higher E°. *trans*-Dioxo(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)ruthenium(VI) with a E° value ≈ 200 mV lower than that of *trans*-$[\mathrm{RuL^2O_2}]^{2+}$ has been reported to be inactive towards oxidation of aromatic hydrocarbons at room temperature.[12]

Acknowledgements

We acknowledge support from the University of Hong Kong, Croucher Foundation and the University and Polytechnic Granting Committee.

References

1 *Activation and Functionalization of Alkanes*, ed. C. L. Hill, Wiley, New York and Chichester, 1989.
2 W. P. Griffith, *Transition Met. Chem.*, 1990, **15**, 251.
3 (*a*) M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 5070; (*b*) L. Roecker and T. J. Meyer, *J. Am. Chem. Soc.*, 1987, **109**, 746.
4 C. M. Che, C. Ho and T. C. Lau, *J. Chem. Soc., Dalton Trans.*, 1991, 1259.
5 C. M. Che, W. T. Tang, W. T. Wong and T. F. Lai, *J. Am. Chem. Soc.*, 1989, **111**, 9048.
6 C. M. Che, W. T. Tang and C. K. Li, *J. Chem. Soc., Dalton Trans.*, 1990, 3735.
7 C. M. Che, K. Y. Wong, W. H. Leung and C. K. Poon, *Inorg. Chem.*, 1986, **25**, 345.
8 C. M. Che, W. T. Tang, W. O. Lee, W. T. Wong and T. F. Lai, *J. Chem. Soc., Dalton Trans.*, 1989, 2011.
9 W. T. Tang, Ph.D. Thesis, University of Hong Kong, 1989.
10 D. G. Lee and M. Vander Engl, *Can. J. Chem.*, 1972, **50**, 3129.
11 C. M. Che, W. T. Tang and C. K. Li, *J. Chem. Soc., Dalton Trans.*, 1991, 379.
12 C. M. Che, T. F. Lai and K. Y. Wong, *Inorg. Chem.*, 1987, **26**, 2289.

Received 9*th April* 1991; *Paper* 1/01640G