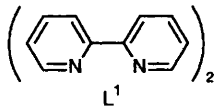
Mechanism of Alcohol Oxidation by *trans*-Dioxoruthenium(VI): The Effect of Driving Force on Reactivity†

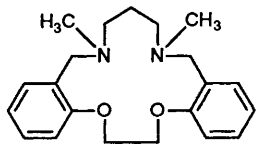
Chi-Ming Che,* Wai-Tong Tang, Wai-On Lee, Kwok-Yin Wong and Tai-Chu Lau
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

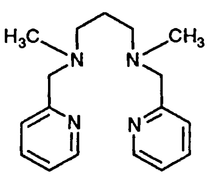
The effect of driving force on the rate of oxidation of alcohols by *trans*-$[Ru^{VI}LO_2]^{2+}$ {L^1 = (2,2'-bipyridine)$_2$; L^2 = *N,N'*-dimethyl-6,7,8,9,10,11,17,18-octahydro-5*H*-dibenzo[*en*][1,4,8,12]dioxadiazacyclopentadecine; L^3 = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)propylenediamine; L^4 = *meso*-2,3,7,11,12-pentamethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene; L^5 = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane} with $E^\circ(Ru^{VI}-Ru^{IV})$ ranging from 0.66 to 1.01 V *vs.* saturated calomel electrode has been investigated. In most cases the complexes behave as two-electron oxidants being reduced to *trans*-$[Ru^{IV}L(O)(H_2O)]^{2+}$. The rate constants (k_2) for alcohol oxidation increase with E° of the ruthenium oxidant. The slopes of the linear free-energy plots of log k_2 *vs.* E° for benzyl alcohol and propan-2-ol are −14.7 and −16.9 V^{-1} respectively. The oxidation is accompanied by large kinetic α-C–H bond isotope effects and negative $\Delta S^‡$ values, suggesting association of Ru=O and the α-C–H bond in the transition state. For *trans*-$[Ru^{VI}L^2O_2]^{2+}$ the existence of a linear free-energy relationship between log k_2 and the ionization energies of the alcohols and the large negative ρ values in Hammett plots for the oxidation of substituted benzyl alcohols indicate a charge-transfer mechanism. A common mechanism involving either a hydride or hydrogen atom abstraction is proposed.

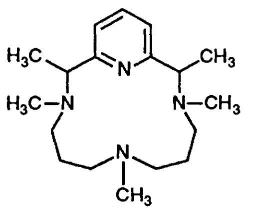
The chemistry of high-valent oxoruthenium complexes is currently under active investigation,[1,2] and a number of such complexes capable of oxidizing various organic functional groups have been reported. These oxidative reactions may proceed through either an oxygen-atom transfer or a hydrogen atom/hydride abstraction pathway. However, there has been little systematic study of the factors involved. Of particular importance is the relationship between driving force and reactivity.[3]

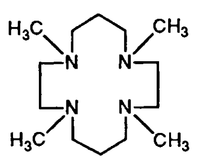
We report here results of a study on the oxidation of alcohols in aqueous and acetonitrile solutions by a series of cationic *trans*-dioxoruthenium(VI) complexes, *trans*-$[Ru^{VI}LO_2]^{2+}$ (L = L^1 to L^5).[4–8] This series of ruthenium(VI) complexes and the corresponding *trans*-$[Ru^{IV}L(O)(H_2O)]^{2+}$ are well characterized and stable in solutions. Furthermore they possess well defined $Ru^{VI}-Ru^{V}$ and $Ru^{VI}-Ru^{IV}$ couples with E° spanning over a wide range (Table 1), making them desirable for studying the reactivity dependence on driving force.


L^1


L^2


L^3


L^4


L^5

Experimental

Materials.—The complexes *trans*-$[Ru^{VI}LO_2]^{2+}$ (L = L^1 to L^5) were prepared as described previously.[4–8] Water and acetonitrile used in kinetic experiments were twice distilled over alkaline potassium permanganate. All alcohols were of analytical grade and purified by fractional distillation. [α,α'-$^2H_2$]Benzyl alcohol was prepared by the published method.[9] All other deuteriated alcohols were obtained from Aldrich. Deuterium oxide (Aldrich, 99.8 atom %), [$^2H_1$]trifluoroacetic acid and tetradeuterioacetic acid (Spectrophotometric grade, Merck) were used as received. Trifluoroacetic acid (Aldrich) was purified by fractional distillation under a nitrogen atmosphere. Tetra-*n*-butylammonium tetrafluoroborate (Electrometric grade, Southwestern Chemicals), sodium trifluoroacetate (Aldrich) and sodium acetate (Merck) were vacuum dried

---

† *Non-SI unit employed:* cal = 4.184 J.

Table 1 Formal potentials of Ru^{VI}–Ru^{IV} couples

Complex	E°/V *vs.* SCE
trans-$[Ru^{VI}L^1O_2]^{2+}$	1.01
trans-$[Ru^{VI}L^2O_2]^{2+}$	0.92
trans-$[Ru^{VI}L^3O_2]^{2+}$	0.89
trans-$[Ru^{VI}L^4O_2]^{2+}$	0.76
trans-$[Ru^{VI}L^5O_2]^{2+}$	0.66

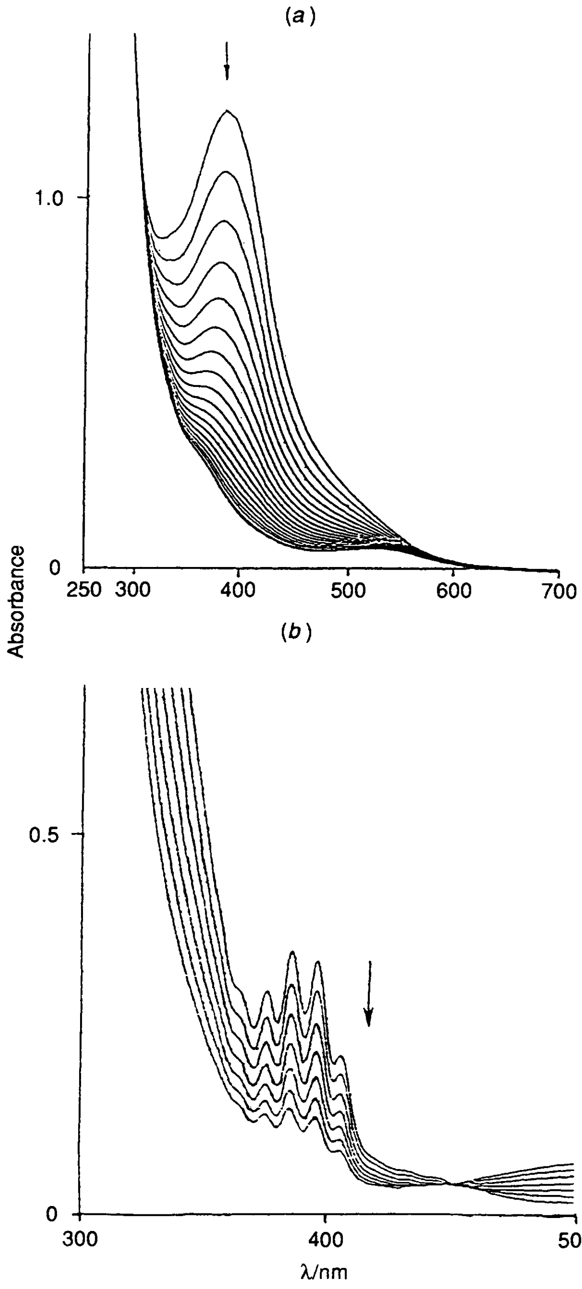


Fig. 1 The UV/VIS spectral changes for (*a*) *ca.* 1 mmol dm^{-3} *trans*-$[Ru^{VI}L^2O_2]^{2+}$ in the presence of *ca.* 0.5 mol dm^{-3} ethanol in 0.1 mol dm^{-3} $HClO_4$ and (*b*) *ca.* 1 mmol dm^{-3} *trans*-$[Ru^{VI}L^5O_2]^{2+}$ in the presence of *ca.* 0.7 mol dm^{-3} benzyl alcohol in acetonitrile

overnight at 65 °C before use. All other chemicals were analytical reagents used as received.

Instrumentation and Methods.—Stoichiometric oxidation was performed by stirring the ruthenium complex (20 mg) and alcohol (0.1 g) in acetonitrile (1 cm^3) for 1 h at room temperature. A control experiment in the absence of the ruthenium oxidant was performed for each reaction. The organic products were analysed on a Varian 2440 gas chromatograph equipped with a 10% Carbowax 20M on Chromosorb W column and a flame ionization detector. Component identification was established by gas chromatography–mass spectrometry. The individual gas chromatographic components were quantitated by the internal standard method employing a Shimadzu C-R3A electronic integrator.

Table 2 Stoichiometric oxidation of various alcohols by *trans*-dioxoruthenium(VI) complexes at 298 K

		Yield (%)[a]					
Substrate	Product	**1**	**2**	**3**	**4**	**5**	**6**
Ethanol	Acetaldehyde	96	98	96	—	—	0
Propan-2-ol	Acetone	90	95	95	—	—	0
Benzyl alcohol	Benzaldehyde[b]	89	95	90	96	95	90
Cyclohexanol	Cyclohexanone	98	86	98	—	—	0
Cyclobutanol	Cyclobutanone	—	90	85	—	—	0

[a] Yield based on amount of complex used. Complexes: *trans*-$[Ru^{VI}L^1O_2]^{2+}$ **1**, *trans*-$[Ru^{VI}L^2O_2]^{2+}$ **2**, *trans*-$[Ru^{VI}L^3O_2]^{2+}$ **3**, *trans*-$[Ru^{VI}L^4O_2]^{2+}$ **4**, *trans*-$[Ru^{VI}L^5O_2]^{2+}$ **5** and *trans*-$[Ru^{VI}L^2(O)(H_2O)]^{2+}$ **6**. [b] Reaction was done under a nitrogen atmosphere.

The UV/VIS spectra were recorded on a Shimadzu UV-240 spectrophotometer. For slow reactions, kinetic experiments were performed using a Unicam SP8000 spectrophotometer linked to an Apple II microcomputer *via* an AD/DA interface card (ADA lab, Interactive Microware). Stopped-flow kinetics was investigated using a Hi-Tech SF-51 stopped-flow module coupled with a Hi-Tech SU-40 spectrophotometer unit. The data-collection process was controlled by an Apple IIe microcomputer *via* an ADS-1 interface unit. The temperature was maintained to ±0.1 °C.

The kinetics of the oxidation reactions was followed by monitoring the decrease in absorbance of the ruthenium complex at 270–300 or 380–400 nm under the conditions that the alcohol was in at least 50-fold excess. Pseudo-first-order rate constants were obtained by non-linear least-squares fit (uniform weighting) of A_t *vs.* time t according to equation (1)

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

where A_∞ and A_0 are the final and initial absorbances respectively. Second-order rate constants, k_2, were obtained from linear least-squares fits of k_{obs} *vs.* $[Ru^{VI}]$. Each kinetic run was repeated three times and the mean value of k_{obs} was taken for calculation. Data for five half-lives were collected for each run. The correlation coefficient was 0.999 in each case. Activation parameters were calculated using the Eyring plot ($\ln k_2/T$ *vs.* $1/T$).

Results

Stoichiometry and Rate Law.—*trans*-Dioxoruthenium(VI) was reduced to *trans*-aquaoxoruthenium(IV) by alcohols in aqueous solution. Fig. 1(*a*) shows the UV/VIS spectral changes for the reduction of *trans*-$[Ru^{VI}L^2O_2]^{2+}$ by ethanol in 0.1 mol dm^{-3} $HClO_4$. Examination of the final spectrum of the solution revealed quantitative conversion into *trans*-$[Ru^{IV}L^2(O)(H_2O)]^{2+}$.[7] The observation of isosbestic points at 295 and 650 nm suggests no accumulation of any reaction intermediate throughout the reaction. Other alcohols were oxidized by *trans*-$[Ru^{VI}L^2O_2]^{2+}$ in a similar manner. With *trans*-$[Ru^{VI}L^4O_2]^{2+}$ or *trans*-$[Ru^{VI}L^5O_2]^{2+}$ as oxidant the oxidation has been found to be very slow even for benzyl alcohol. Fig. 1(*b*) shows the spectral changes accompanying the oxidation of benzyl alcohol by *trans*-$[Ru^{VI}L^5O_2]^{2+}$ in acetonitrile. The final

Table 3 Summary of the second-order rate constants (298 K) for the oxidation of alcohols by *trans*-dioxoruthenium(VI)

Substrate	Medium	k_2/dm^3 mol^{-1} s^{-1}	Oxidant *
Propan-2-ol	Water	2.0 ± 0.2	1
Benzyl alcohol	Water	$(2.08 \pm 0.2) \times 10$	1
Methanol	CH_3CN	$(5.50 \pm 0.5) \times 10^{-4}$	2
Ethanol	CH_3CN	$(1.16 \pm 0.1) \times 10^{-3}$	2
	Water	$(5.10 \pm 0.5) \times 10^{-3}$	2
Propan-1-ol	CH_3CN	$(1.50 \pm 0.2) \times 10^{-2}$	2
Propan-2-ol	Water	$(4.60 \pm 0.5) \times 10^{-2}$	2
Pentan-1-ol	CH_3CN	$(2.20 \pm 0.2) \times 10^{-2}$	2
Pentan-2-ol	CH_3CN	$(3.60 \pm 0.4) \times 10^{-2}$	2
Heptan-1-ol	CH_3CN	$(1.80 \pm 0.2) \times 10^{-2}$	2
Heptan-3-ol	CH_3CN	$(3.10 \pm 0.3) \times 10^{-2}$	2
Benzyl alcohol	CH_3CN	$(5.40 \pm 0.5) \times 10^{-1}$	2
	Water	$(6.85 \pm 0.7) \times 10^{-1}$	2
4-Chlorobenzyl alcohol	CH_3CN	$(3.30 \pm 0.3) \times 10^{-1}$	2
4-Methylbenzyl alcohol	CH_3CN	$(9.0 \pm 0.8) \times 10^{-1}$	2
4-Methoxybenzyl alcohol	CH_3CN	1.18 ± 0.1	2
4-Trifluoromethylbenzyl alcohol	CH_3CN	$(6.60 \pm 0.6) \times 10^{-2}$	2
Propan-2-ol	Water	$(1.90 \pm 0.2) \times 10^{-2}$	3
Benzyl alcohol	Water	$(9.30 \pm 0.8) \times 10^{-1}$	3
	Water	$(3.25 \pm 0.3) \times 10^{-3}$	4
	Water	$(1.98 \pm 0.2) \times 10^{-4}$	5
3-Chlorobenzyl alcohol	CH_3CN	$(4.9 \pm 0.5) \times 10^{-5}$	5
3-Methylbenzyl alcohol	CH_3CN	$(2.57 \pm 0.3) \times 10^{-4}$	5
3-Methoxybenzyl alcohol	CH_3CN	$(1.78 \pm 0.2) \times 10^{-4}$	5
4-Chlorobenzyl alcohol	CH_3CN	$(1.10 \pm 0.1) \times 10^{-3}$	5
4-Methylbenzyl alcohol	CH_3CN	$(4.8 \pm 0.4) \times 10^{-4}$	5
4-Methoxybenzyl alcohol	CH_3CN	$(1.18 \pm 0.1) \times 10^{-3}$	5

* As defined in Table 2.

ruthenium product is *trans*-[$Ru^{IV}L^5(O)(CH_3CN)]^{2+}$ as identified by its UV/VIS spectrum.[10] The complex *trans*-[$Ru^{VI}L^1O_2]^{2+}$, which has the highest $E°$, was instantaneously reduced to *trans*-[$Ru^{IV}L^1(O)(H_2O)]^{2+}$ by alcohols in aqueous solutions.

Table 2 summarizes the results on the stoichiometric oxidation of different alcohols by *trans*-dioxoruthenium(VI) complexes. Alcohol was oxidized to aldehyde or ketone quantitatively. Oxidation of primary alcohol stopped at the stage of aldehyde as no acid was detected by both UV/VIS and ^1H NMR spectroscopy. This finding is not unexpected because under the conditions employed alcohol was present in large excess. In most cases the stoichiometry (organic product to ruthenium oxidant) is 1:1. In some cases, for example, the oxidation of benzyl alcohol by *trans*-[$Ru^{VI}L^2O_2]^{2+}$ in acetonitrile, a 2:1 stoichiometry was found if sufficient time was allowed. In such cases the ruthenium complex was found to be reduced to *trans*-[$Ru^{II}L^2(CH_3CN)_2]^{2+}$. This finding is in accordance with the fact that *trans*-[$Ru^{IV}L^2(O)(H_2O)]^{2+}$ is also capable of oxidizing benzyl alcohol at an appreciable rate. However, it is much slower than that by *trans*-[$Ru^{VI}L^2O_2]^{2+}$ so that this secondary oxidation will not interfere with the kinetic experiments. It has also been found that the rates of oxidation of propan-1-ol and propan-1-al by *trans*-[$Ru^{VI}L^2O_2]^{2+}$ are comparable, the second-order rate constants being 0.015 and 0.045 dm^3 mol^{-1} s^{-1} respectively at 298 K.[11] Therefore subsequent oxidation of aldehyde will not introduce complications in the kinetic studies in view of the large excess of alcohol employed in these experiments.

The experimental rate law for the alcohol oxidation has been found to be as in equation (2) and the second-order rate

$$-d[Ru^{VI}]/dt = k_{obs}[Ru^{VI}] = k_2[\text{Alcohol}][Ru^{VI}] \quad (2)$$

constants (k_2) are listed in Table 3. In general, the rate constants are independent of the ionic strength of the solution and of the presence of oxygen. Change of the solvent from water to acetonitrile has only a slight effect on the reaction.

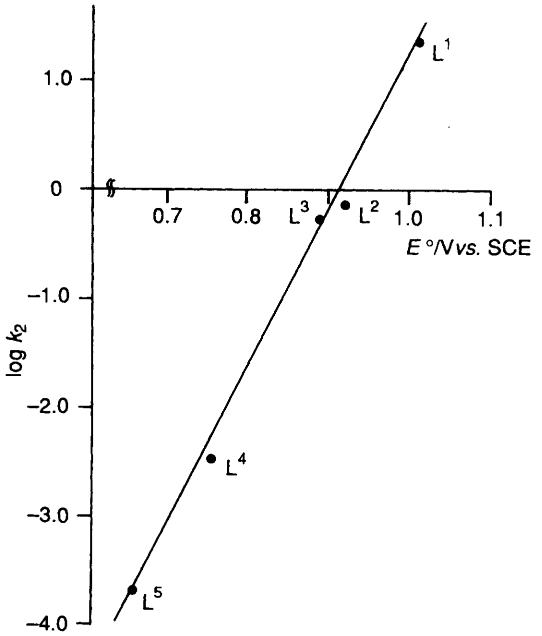


Fig. 2 Plot of log k_2 *vs.* $E°$ (Ru^{VI}–Ru^{IV}) for the oxidation of benzyl alcohol by *trans*-[$Ru^{VI}LO_2]^{2+}$

Linear Free-energy Relationship.—The rate constants (k_2) for the oxidation of benzyl alcohol and propan-2-ol increase with the $E°$ of the ruthenium oxidants. The linear free-energy relationship between log k_2 and $E°$ of the Ru^{VI}–Ru^{IV} couple is illustrated in Fig. 2. The slopes of the plots for the oxidation of benzyl alcohol and propan-2-ol are −14.7 and −16.9 V^{-1} respectively. In the oxidation of non-sterically hindered aliphatic alcohols by *trans*-[$Ru^{VI}L^2O_2]^{2+}$, log k_2 correlates linearly with the ionization potential of the alcohol (Fig. 3). The oxidation of *para*-substituted benzyl alcohols has also been investigated. Linear Hammett plots (Fig. 4) of ln k_2 against σ

Table 4 Kinetic isotope effect for the oxidation of alcohols by *trans*-$[Ru^{VI}L^2O_2]^{2+}$ at 298 K

Substrate	Medium	k_2/dm^3 mol^{-1} s^{-1}	
Methanol	CH_3CN	$(5.5 \pm 0.5) \times 10^{-4}$	$k_H/k_D = 8 \pm 1$
$[^2H_4]$Methanol	CH_3CN	$(6.8 \pm 0.6) \times 10^{-5}$	
Ethanol	H_2O	$(5.1 \pm 0.5) \times 10^{-3}$	$k_{C_2H_5OH}/k_{C_2H_5OD} = 1.0 \pm 0.1$
$[^2H_1]$Ethanol	D_2O	$(5.0 \pm 0.5) \times 10^{-3}$	
Ethanol	CH_3CN	$(1.16 \pm 0.1) \times 10^{-2}$	$k_{C_2H_5OH}/k_{C_2H_5OD} = 1.0 \pm 0.1$
$[^2H_1]$Ethanol	CH_3CN	$(1.10 \pm 0.1) \times 10^{-2}$	
Ethanol	CH_3CN	$(1.16 \pm 0.1) \times 10^{-2}$	$k_H/k_D = 8 \pm 1$
$[^2H_6]$Ethanol	CH_3CN	$(1.40 \pm 0.1) \times 10^{-3}$	
Propan-2-ol	CH_3CN	$(4.6 \pm 0.4) \times 10^{-2}$	$k_H/k_D = 11 \pm 1$
$[^2H_8]$Propan-2-ol	CH_3CN	$(4.2 \pm 0.4) \times 10^{-3}$	
Benzyl alcohol	CH_3CN	$(5.4 \pm 0.5) \times 10^{-1}$	$k_H/k_D = 19 \pm 2$
$[\alpha,\alpha'-^2H_2]$Benzyl alcohol	CH_3CN	$(2.9 \pm 0.3) \times 10^{-2}$	

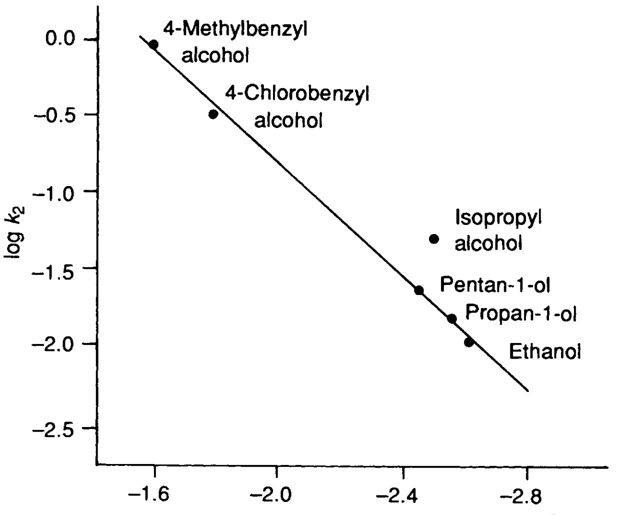


Fig. 3 Plot of log k_2 *vs.* the reduction potentials of alcohols with *trans*-$[Ru^{VI}L^2O_2]^{2+}$ as oxidant

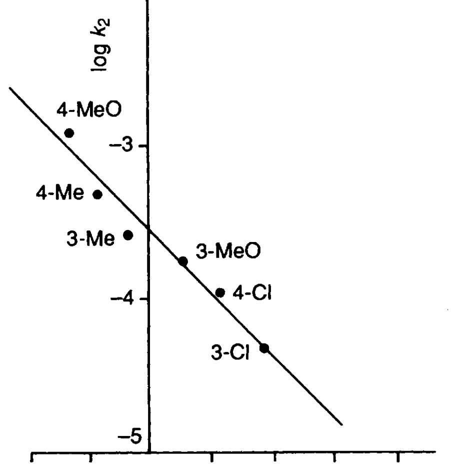


Fig. 4 Hammett plot for the oxidation of substituted benzyl alcohols by *trans*-$[Ru^{VI}L^5O_2]^{2+}$ in acetonitrile

of the *para* substituents with observed ρ values of −1.2 and −1.9 have been found for the oxidants *trans*-$[Ru^{VI}L^2O_2]^{2+}$ and *trans*-$[Ru^{VI}L^5O_2]^{2+}$ respectively.

Table 5 Kinetic isotope effect for the oxidation of benzyl alcohol by *trans*-$[Ru^{VI}LO_2]^{2+}$ in acetonitrile at 298 K

Complex	k_H/k_D
trans-$[Ru^{VI}L^1O_2]^{2+}$	17 ± 2
trans-$[Ru^{VI}L^2O_2]^{2+}$	19 ± 2
trans-$[Ru^{VI}L^3O_2]^{2+}$	15 ± 2
trans-$[Ru^{VI}L^4O_2]^{2+}$	18 ± 2

Kinetic Isotope Effect and Activation Parameters.—The substrate kinetic isotope effect (k_H/k_D) for the alcohol oxidation has been investigated and the results are summarized in Table 4. There was little solvent isotope effect (k_{H_2O}/k_{D_2O}) or OH deuterium effect (k_{ROH}/k_{ROD}) in the oxidation of ethanol by *trans*-$[Ru^{VI}L^2O_2]^{2+}$. At 25 °C, k_H/k_D for the alcohol oxidation by *trans*-$[Ru^{VI}L^2O_2]^{2+}$ decrease in the order: benzyl alcohol > propan-2-ol > ethanol > methanol. Changing L from L^1 to L^4, however, has only a slight effect on the k_H/k_D for the oxidation of benzyl alcohol (Table 5). Unlike in a previous report by Roecker and Meyer,[6] values of k_H/k_D for the oxidation of benzyl alcohol and propan-2-ol by *trans*-$[Ru^{VI}L^2O_2]^{2+}$ are temperature dependent (see Table 6).

The activation parameters for the oxidation of benzyl alcohol and propan-2-ol were investigated over the temperature range 277–323 K; the results are summarized in Table 6. In general, the $\Delta S^\ddagger$ values are large and negative and are insensitive to the structures of the alcohols and ruthenium oxidants.

Discussion

Previous studies revealed that *trans*-dioxoruthenium(VI) can act either as a two- or a one-electron oxidant.[4–8] In this work *trans*-$[Ru^{VI}LO_2]^{2+}$ acts as an overall two-electron oxidant since cyclobutanol was oxidized by *trans*-$[Ru^{VI}L^1O_2]^{2+}$ or *trans*-$[Ru^{VI}L^2O_2]^{2+}$ to cyclobutanone in high yield. Furthermore, the ruthenium product after alcohol oxidation was Ru^{IV} rather than Ru^V. Since *trans*-$[Ru^VLO_2]^+$ is known to be both kinetically and thermodynamically unstable with respect to disproportionation in aqueous solution,[12] it would be very short-lived even if it is present as a reactive intermediate. The disproportionation reaction (3) is favoured in the forward direction by a driving force ΔG° ranging from −41.4 to −57.4 kcal mol^{-1} at pH 1.1. This redox behaviour may also account for the clean spectral changes for the two-electron reduction of *trans*-$[Ru^{VI}LO_2]^{2+}$ to *trans*-$[Ru^{IV}L(O)(H_2O)]^{2+}$ or *trans*-$[Ru^{IV}L(O)(CH_3CN)]^{2+}$. The oxidation of alcohols by RuO_4 [13] and $[Ru^{IV}(bipy)_2(py)O]^{2+}$ (bipy = 2,2′-bipyridine, py = pyridine)[9] has been shown to occur by prior co-ordination of the alcohol substrate to the oxidant.

$$2\ \textit{trans}\text{-}[Ru^VLO_2]^+ + 2H^+ \longrightarrow \textit{trans}\text{-}[Ru^{VI}LO_2]^{2+} + \textit{trans}\text{-}[Ru^{IV}L(O)(H_2O)]^{2+} \quad (3)$$

In this work two mechanistic pathways are proposed for the

Table 6 Activation parameters for the oxidation of benzyl alcohol and propan-2-ol by *trans*-$[Ru^{VI}L^2O_2]^{2+}$

Substrate	T/K	k_2/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}
Benzyl alcohol	283.4	$(1.5 \pm 0.1) \times 10^{-1}$	10 ± 1	-26 ± 3
	290.7	$(2.8 \pm 0.2) \times 10^{-1}$		
	298.0	$(5.4 \pm 0.5) \times 10^{-1}$		
	307.2	$(7.6 \pm 0.7) \times 10^{-1}$		
	314.8	1.18 ± 0.1		
[α,α'-$^2H_2$]Benzyl alcohol	283.4	$(8.4 \pm 0.8) \times 10^{-3}$	12 ± 1	-22 ± 2
	291.2	$(1.9 \pm 0.2) \times 10^{-2}$		
	298.0	$(3.0 \pm 0.3) \times 10^{-2}$		
	307.2	$(6.0 \pm 0.5) \times 10^{-2}$		
	314.8	$(1.1 \pm 0.1) \times 10^{-1}$		
Propan-2-ol	283.4	$(1.6 \pm 0.1) \times 10^{-2}$	12 ± 1	-28 ± 3
	292.7	$(2.8 \pm 0.3) \times 10^{-2}$		
	298.0	$(4.5 \pm 0.4) \times 10^{-2}$		
	303.4	$(6.1 \pm 0.6) \times 10^{-2}$		
	310.6	$(8.9 \pm 0.9) \times 10^{-2}$		
[$^2H_8$]Propan-2-ol	283.4	$(1.2 \pm 0.1) \times 10^{-3}$	14 ± 2	-22 ± 3
	290.7	$(2.6 \pm 0.2) \times 10^{-3}$		
	298.0	$(3.9 \pm 0.4) \times 10^{-3}$		
	307.2	$(8.9 \pm 0.9) \times 10^{-3}$		
	314.8	$(1.5 \pm 0.1) \times 10^{-2}$		

oxidation of alcohols by *trans*-$[Ru^{VI}LO_2]^{2+}$. The first is a concerted two-electron hydride abstraction (Scheme 1). An alternative mechanism would be an initial one-electron H-atom abstraction by *trans*-$[Ru^{VI}LO_2]^{2+}$ giving rise to the caged R^1R^2COH radical and a ruthenium(V) intermediate (Scheme 2), which rapidly react to give Ru^{IV} and aldehyde or ketone. Kinetically it is difficult to distinguish these two pathways.

$$O{=}Ru^{VI}{=}O^{2+} + R^1R^2CHOH \longrightarrow O{=}Ru^{IV}{-}OH^{+} + R^1R^2COH^{+}$$

$$O{=}Ru^{IV}{-}OH^{+} + R^1R^2COH^{+} \longrightarrow O{=}Ru^{IV}{-}OH_2{}^{2+} + R^1R^2C{=}O$$

Scheme 1

$$O{=}Ru^{VI}{=}O^{2+} + R^1R^2CHOH \longrightarrow O{=}Ru^{V}{-}OH^{2+} + R^1R^2COH$$

$$O{=}Ru^{V}{-}OH^{2+} + R^1R^2COH \longrightarrow O{=}Ru^{IV}{-}OH_2{}^{2+} + R^1R^2C{=}O$$

Scheme 2

In this work, oxidation of alcohols by *trans*-$[Ru^{VI}LO_2]^{2+}$ was found to be accompanied by large kinetic C–H bond isotope effects and $\Delta S^‡$ values. This would mean that irrespective of Schemes 1 or 2, the transition state for the rate-determining step of oxidation involves a strong head-on coupling between the Ru=O moiety and the α-CH bond of the alcohol (Scheme 3). In this formulation the α-C–H bond acts as a donor whereas the Ru=O moiety, because of its electrophilic nature, behaves as an acceptor. The electrophilicity of a Ru=O unit arises from charge transfer from oxygen to ruthenium due to $p_\pi(O)$–$d_\pi(Ru)$ interaction. The nature of the bonding and valency for oxygen in highly oxidising oxometal complexes has previously been discussed by Sawyer.[14]

$$O{=}Ru^{VI}{=}O^{2+} + H{-}\overset{|}{\underset{|}{C}}{-}OH \longrightarrow [O{=}Ru{-}O\cdots H{-}\overset{|}{\underset{|}{C}}{-}OH]$$

Scheme 3

The rate of oxidation of alcohols by *trans*-$[Ru^{VI}L^2O_2]^{2+}$ is sensitive to the structure of the alcohols. The rate constants fall into the following sequence: methyl < primary < secondary < benzylic. The sensitivity of the reaction rates to the nature of the alcohols is best illustrated by the linear free-energy relationship between log k_2 and the ionization potential of the alcohols (Fig. 3). This indicates that the α-C–H bond cleavage is facilitated by charge transfer from the alcohol to the ruthenium oxidant. The Hammett plots for the oxidation of substituted benzyl alcohol by *trans*-$[Ru^{VI}L^2O_2]^{2+}$ and *trans*-$[Ru^{VI}L^5O_2]^{2+}$ with ρ values of −1.2 and −1.9 are also consistent with a build-up of positive charge at the alcohol by withdrawal of electron density to the oxoruthenium complexes in the transition state. This is also in accord with a charge-transfer mechanism.

Given the electron-transfer mechanism of oxidation, one would expect some correlation between the rate constants and driving force of the reaction. According to the Marcus equation for a reaction with small ΔG°, a theoretical slope equal to 8.4n (n = number of electrons transferred in the reaction) is expected for the plot of log (rate constant) *vs.* ΔG°. The observed slopes of -16.9 V^{-1} for the oxidation of propan-2-ol and -14.7 V^{-1} for the oxidation of benzyl alcohol by *trans*-$[Ru^{VI}LO_2]^{2+}$ are close to the value of -16.8 V^{-1} predicted by the Marcus equation for a two-electron hydride-transfer reaction. The application of Marcus theory to hydride-transfer reactions has previously been reported.[15]

It is interesting that the C–H kinetic isotope effect for the oxidation of benzyl alcohol is relatively insensitive to the E° of *trans*-$[Ru^{VI}LO_2]^{2+}$ (Table 5). According to Sawyer the reactivities of highly oxidising M=O complexes are due to the 'oxene' character of the oxygen atom. One would therefore expect that changing the E° of *trans*-$[Ru^{VI}LO_2]^{2+}$ by over 0.4 V would have some effect on the electrophilicity of the Ru=O moiety, which in turn would affect the extent of coupling between Ru=O and the α-C–H bond in the transition state. The results reported here clearly indicate that the electronic configuration of the Ru=O moiety rather than the E° of the ruthenium oxidant has a larger effect on the k_H/k_D values.

Although a common mechanism involving either a hydride or hydrogen atom abstraction exists in the oxidation of alcohols by *trans*-$[Ru^{VI}LO_2]^{2+}$, k_H/k_D at 25 °C varies from 8 for ethanol to 19 for benzyl alcohol. Furthermore, k_H/k_D for both propan-2-ol and benzyl alcohol are temperature dependent. For benzyl alcohol, $\Delta H^‡$ is 10 ± 1 kcal mol^{-1} which is smaller than the value of 12 ± 1 kcal mol^{-1} for $C_6H_5CD_2OH$. In the case of propan-2-ol similar findings were obtained [$\Delta H^‡$ = 12 ± 1 kcal mol^{-1} for $(CH_3)_2CHOH$ and 14 ± 2 kcal mol^{-1} for $(CD_3)_2CDOD$].

A large kinetic isotope effect has previously been reported for the oxidation of $(CD_3)_2CD_2OD$ by $[Ru^{IV}(bipy)_2(PPh_3)O]^{2+}$ (k_H/k_D = 36).[16] Roecker and Meyer[9] also reported a large

Table 7 Kinetic data for the oxidation of alcohols by oxoruthenium-(VI), -(V) and -(IV) complexes at 298 K

Complex	Substrate	k_2/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}
trans-$[Ru^{VI}L^2O_2]^{2+}$	Benzyl alcohol	$(5.4 \pm 0.5) \times 10^{-1}$	10 ± 1	-26 ± 3
	$[\alpha,\alpha'-^2H_2]$Benzyl alcohol	$(3.0 \pm 0.3) \times 10^{-2}$	12 ± 1	-22 ± 2
	Propan-2-ol	$(4.5 \pm 0.4) \times 10^{-2}$	12 ± 1	-28 ± 3
	$[^2H_8]$Propan-2-ol	$(3.9 \pm 0.4) \times 10^{-3}$	14 ± 2	-22 ± 3
$[Ru^{V}L(O)]^{2+}$	Benzyl alcohol	$(1.17 \pm 0.05) \times 10^2$	9.1 ± 1	-18 ± 2
	$[\alpha,\alpha'-^2H_2]$Benzyl alcohol	$(2.0 \pm 0.1) \times 10$	—	—
	Propan-2-ol	$(1.35 \pm 0.1) \times 10$	9.2 ± 1	-22 ± 2
	$[^2H_8]$Propan-2-ol	2.5 ± 0.1	—	—
$[Ru^{IV}(bipy)_2(py)O]^{2+}$	Benzyl alcohol	2.43 ± 0.03	5.7 ± 0.2	-38 ± 1
	$[\alpha,\alpha'-^2H_2]$Benzyl alcohol	4.8×10^{-2}	5.6 ± 0.6	-46 ± 2
	Methanol	$(3.5 \pm 0.1) \times 10^{-4}$	14 ± 2	-26 ± 6
	$[^2H_4]$Methanol	4.4×10^{-5}	17 ± 2	-21 ± 5

isotope effect with $[Ru^{IV}(bipy)_2(py)O]^{2+}$ (k_H/k_D = 9 and 50 for the oxidation of propan-2-ol and benzyl alcohol respectively). However, the reported k_H/k_D for the oxidation of benzyl alcohol by $[Ru^{IV}(bipy)_2(py)O]^{2+}$ was temperature independent, in contrast to the present results ($\Delta H^‡$ = 5.7 kcal mol^{-1} and $\Delta S^‡$ = −38 cal K^{-1} mol^{-1} for $C_6H_5CH_2OH$, $\Delta H^‡$ = 5.6 kcal mol^{-1} and $\Delta S^‡$ = −46 cal K^{-1} mol^{-1} for $C_6H_5CD_2OH$). In Meyer's work there is a drastic difference in $\Delta S^‡$ values for the oxidation of benzyl alcohol and aliphatic alcohols like methanol by Ru^{IV}=O. Roecker and Meyer[9] attributed their findings to a large orientational demand for the oxidation. In the present work the $\Delta S^‡$ values for the oxidation of propan-2-ol and benzyl alcohol by *trans*-$[Ru^{VI}LO_2]^{2+}$ are similar, implying that the orientational demand in alcohol oxidation is smaller.

In comparing the k_H/k_D values for the oxidation of various alcohols by *trans*-$[Ru^{VI}L^1O_2]^{2+}$ at 25 °C an increase from ethanol to propan-2-ol and benzyl alcohol was observed (even without accounting for the secondary kinetic isotope effect). The increase of k_H/k_D with decreasing α-C–H bond strength is not unexpected. If Scheme 3 is operating, the weaker the C–H bond strength the greater is the extent of C–H bond breakage in the activation step and a greater k_H/k_D value will then be observed.

It is interesting to compare the oxidation of alcohols by *trans*-$[Ru^{VI}LO_2]^{2+}$ with other oxoruthenium systems like $[Ru^{IV}(bipy)_2(py)O]^{2+}$(ref. 12) and $[Ru^{V}L(O)]^{2+}$ {HL = [2-hydroxy-2-(2-pyridyl)ethyl]bis[2-(2-pyridyl)ethyl]amine}.[17] The collective rate data are shown in Table 7. Some important differences appear to exist between the d^2-, d^3- and d^4-oxo systems in alcohol oxidation. For the oxidation of benzyl alcohol the measured kinetic isotope effects of 15–19 and 5.9 for Ru^{VI} and Ru^{V}, though substantial, are much smaller than the value of 50 obtained using $[Ru^{IV}(bipy)_2(py)O]^{2+}$ as oxidant.[9] Furthermore, in comparing the k_H/k_D values for the oxidation of benzyl alcohol and of aliphatic alcohols it was found that the difference decreased in the order $Ru^{IV} > Ru^{V}$, Ru^{VI}. Roecker and Meyer[9] attributed the large difference in k_H/k_D values for benzyl alcohol and methanol oxidation by $[Ru^{IV}(bipy)_2(py)O]^{2+}$ (50 and 9 respectively) to the coupling of the Ru=O moiety with a higher vibration level of the C–H bond of methanol. This postulation apparently explained the much lower $\Delta H^‡$ value for benzyl alcohol than for methanol in the ruthenium(IV) system. However, it was found that the $\Delta H^‡$ values for both benzyl and aliphatic alcohols in the ruthenium-(V) and -(VI) systems are similar. It appears that the kinetic isotope effect for the benzyl alcohol oxidation is sensitive to the electronic state of the Ru=O oxidant.

Acknowledgements

We acknowledge support from the University of Hong Kong and the Hong Kong Research Grant Council. W.-O. L. thanks the Croucher Foundation for a studentship.

References

1 W. P. Griffith, *Transition Met. Chem.*, 1990, **15**, 251.
2 W. P. Griffith, *Chem. Soc. Rev.*, in the press.
3 C. M. Che, W. T. Tang and C. K. Li, *J. Chem Soc., Dalton Trans.*, 1991, 3277.
4 C. M. Che, K. Y. Wong, W. H. Leung and C. K. Poon, *Inorg. Chem.*, 1986, **25**, 345.
5 C. M. Che, W. T. Tang, W. O. Lee, W. T. Wong and T. F. Lai, *J. Chem. Soc., Dalton Trans.*, 1989, 2011.
6 C. M. Che, W. T. Tang and C. K. Li, *J. Chem. Soc., Dalton Trans.*, 1990, 3735.
7 C. M. Che, W. T. Tang, W. T. Wong and T. F. Lai, *J. Am. Chem. Soc.*, 1989, **111**, 9048.
8 C. M. Che, K. Y. Wong and C. K. Poon, *Inorg. Chem.*, 1985, **24**, 1797.
9 L. Roecker and T. J. Meyer, *J. Am. Chem. Soc.*, 1987, **109**, 746.
10 C. M. Che, T. F. Lai and K. Y. Wong, *Inorg. Chem.*, 1987, **26**, 2289.
11 W. T. Tang, Ph.D. Thesis, University of Hong Kong, 1989.
12 C. M. Che, K. Lau and C. K. Poon, *J. Am. Chem. Soc.*, 1990, **112**, 5176.
13 D. G. Lee, U. A. Spitzer, J. Cleland and M. E. Olson, *Can. J. Chem.*, 1976, **54**, 2124.
14 D. T. Sawyer, *Comments Inorg. Chem.*, 1987, **6**, 103.
15 R. M. G. Roberts, D. Ostovic and M. M. Kreevoy, *Faraday Discuss. Chem. Soc.*, 1982, **74**, 257.
16 M. E. Marmion and K. J. Takeuchi, *J. Chem. Soc., Dalton Trans.*, 1988, 2385.
17 C. M. Che, C. Ho and T. C. Lau, *J. Chem. Soc., Dalton Trans.*, 1991, 1259.

Received 6*th January* 1992; *Paper* 2/00050D