Synthesis, Reactivities and Electrochemistry of *trans*-Dioxoruthenium(VI) Complexes of π-Aromatic Diimines

Chi-Ming Che,* Wai-Ho Leung, Chi-Keung Li and Chung-Kwong Poon
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

The synthesis and electrochemistry of *trans*-$[Ru^{III}(L)_2(OH)(H_2O)][ClO_4]_2$ [L = 1,10-phenanthroline (phen) or 5,5′-dimethyl-2,2′-bipyridine(dmbipy)] are described. Oxidation of *trans*-$[Ru^{III}(L)_2(OH)(H_2O)]^{2+}$ by Ce^{IV} in water gave *trans*-$[Ru^{VI}(L)_2O_2]^{2+}$ which were isolated as the yellow perchlorate salts. The complex *trans*-$[Ru^{VI}(dmbipy)_2O_2][ClO_4]_2$ is a powerful oxidant with $E^\circ(Ru^{VI}-Ru^{IV}) = 1.0$ V *vs.* saturated calomel electrode at pH 1.0. In acetonitrile or acetone, it oxidizes alcohols to ketones/aldehydes, tetrahydrofuran to γ-butyrolactone, alkenes to epoxides and saturated or aromatic hydrocarbons to alcohols/ketones. Oxidation of saturated alkanes occurs preferentially at the tertiary C–H bond. In the presence of CCl_4, cyclohexane is oxidized to cyclohexyl chloride instead of cyclohexanone. The mechanisms of alcohol and cyclohexane oxidation were investigated by kinetic experiments and by isotope labelling studies.

The design of inorganic oxidants for the stoichiometric and catalytic oxidation of saturated hydrocarbons is an area of general interest.[1] Our interest in this area stems from the oxidation chemistry of cytochrome P-450, which is known to catalyse the hydroxylation of unactivated C–H bonds under mild conditions.[2] Despite extensive studies in this area however, there are only a few examples of inorganic systems which can oxidize alkanes selectively under mild conditions. The oxidation of organic substrates by the classical oxidant MnO_4^- is difficult to control and is usually accompanied by cleavage of a C–C bond.

Recent studies from various groups of workers have shown the rich oxidation chemistry of high-valent ruthenium oxo complexes.[3] Griffith and co-workers[4] demonstrated that it is possible to carry out the catalytic and selective oxidation of organic substrates with ruthenium(VI) and ruthenium(VII) oxo complexes as catalysts. However, their studies were confined mostly to the oxidation of alcohols. The *trans*-dioxoruthenium(VI) complexes of neutral nitrogen-donor ligands usually have high redox potentials but exhibit a much simpler redox chemistry than RuO_4.[5a,f,h] Recently we have prepared the *trans*-dioxoruthenium(VI) complex *trans*-$[Ru^{VI}(bipy)_2O_2]^{2+}$ (bipy = 2,2′-bipyridine), which has an Ru^{VI}–Ru^{IV} couple as high as 1.02 V *vs.* saturated calomel electrode (SCE) at pH 1.0.[5a] However, the application of *trans*-$[Ru^{VI}(bipy)_2O_2][ClO_4]_2$ for organic oxidation is limited because of its low solubility in most common organic solvents. We anticipated that this problem could be overcome by introducing substituent groups on the 2,2′-bipyridine ring, which can alter both the physical and chemical properties of the ruthenium oxidant.

Herein we describe the synthesis, electrochemistry and reactivity of *trans*-$[Ru^{VI}(dmbipy)_2O_2]^{2+}$ (dmbipy = 5,5′-dimethyl-2,2′-bipyridine). This complex differs from other *trans*-dioxoruthenium(VI) species reported[5] as it is capable of oxidizing saturated C–H bonds under mild conditions.

Experimental

Materials.—The compound $RuCl_3 \cdot xH_2O$ was obtained from Aldrich and 5,5-dimethyl-2,2-bipyridine (dmbipy)[6] and *trans*-$[Ru^{III}(phen)_2(OH)(H_2O)][ClO_4]_2$ (phen = 1,10-phenanthroline)[7] were prepared by literature methods. Organic chemicals used in the stoichiometric oxidation and kinetic studies were purified by standard procedures[8] and their purities were checked by gas chromatography.

cis-$[Ru^{II}(dmbipy)_2Cl_2]$.—A mixture of $RuCl_3 \cdot xH_2O$ (0.52 g) and dmbipy (0.73 g) in ethylene glycol (10 cm^3) was heated at 160 °C under nitrogen for 4 h. The solution was cooled to room temperature and water (10 cm^3) added to precipitate the product which was filtered off and washed with water and acetone. The crude product was recrystallized from chloroform–diethyl ether, yield 60–70% (Found: C, 51.4; H, 4.8; N, 10.1. $C_{24}H_{24}Cl_2N_4Ru$ requires C, 51.6; H, 4.7; N, 10.0%).

trans-$[Ru^{III}(dmbipy)_2(OH)(H_2O)][ClO_4]_2$ **1**.—In a procedure similar to that for *trans*-$[Ru^{III}(bipy)_2(OH)(H_2O)][ClO_4]_2$, a mixture of *cis*-$[Ru^{II}(dmbipy)_2Cl_2]$ (0.5 g) and sodium carbonate (2 g) in degassed water (40 cm^3) was heated at reflux for 3 h under a nitrogen atmosphere to give a deep red solution. Upon cooling to room temperature, the complex *cis*-$[Ru^{II}(dmbipy)_2(CO_3)]$ was deposited. This was filtered off and washed with water. A solution of *cis*-$[Ru^{II}(dmbipy)_2(H_2O)_2]^{2+}$ was prepared by dissolving *cis*-$[Ru^{II}(dmbipy)_2(CO_3)]$ in 0.1 mol dm^{-3} $HClO_4$, and filtering to remove any undissolved material. The deep red solution was irradiated with a high-pressure mercury lamp (400 W, Applied Photophysics) for 3 h under aerobic conditions. The product precipitated from the solution as a golden-yellow solid, overall yield 40–50% (Found: C, 40.7; H, 3.6; Cl, 10.3; N, 8.0. $C_{24}H_{27}Cl_2N_4O_{19}Ru$ requires C, 41.0; H, 3.8; Cl, 10.1; N, 8.0%); UV–visible spectrum (0.1 mol dm^{-3} CF_3SO_3H) λ_{max} 263 (ε_{max} 40 530), 316 (35 200) and 397 (sh) nm (5360 dm^3 mol^{-1} cm^{-1}); μ_{eff}(Guoy method) 1.9 at room temperature.

trans-$[Ru^{VI}(dmbipy)_2O_2][ClO_4]_2$ **2**.—To a well stirred suspension of *trans*-$[Ru^{III}(dmbipy)_2(OH)(H_2O)][ClO_4]_2$ in water (0.3 g in 50 cm^3) was added $[NH_4]_2[Ce(NO_3)_6]$ (1 g). After stirring for 20 min, the yellow product was collected by filtration and washed with water (yield, 80%). This compound must be stored in a refrigerator and protected from UV light (Found: C, 41.2; H, 3.4; N, 8.1. $C_{24}H_{24}Cl_2N_4O_{10}Ru$ requires C, 41.2; H, 3.4; N, 8.0%); $\mu_{eff} = 0$ (solid sample, Guoy method); IR $\nu(RuO_2)$ at 845 cm^{-1}.

trans-$[Ru^{VI}(phen)_2O_2][ClO_4]_2$ **3**.—This compound was

---

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

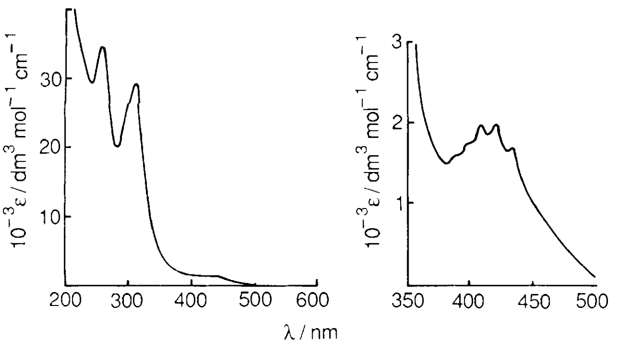


Fig. 1 UV-visible absorption spectrum of **2** in purified acetonitrile

prepared similarly from *trans*-[Ru^{III}(phen)$_2$(OH)(H$_2$O)][ClO$_4$]$_2$, yield *ca.* 75% (Found: C, 41.4; H, 2.5; N, 8.3. $C_{24}H_{20}Cl_2O_{10}Ru$ requires C, 41.6; H, 2.3; N, 8.9%); IR ν(RuO$_2$) at 850 cm^{-1}.

trans-[Ru^{II}(dmbipy)$_2$(CH$_3$CN)$_2$][ClO$_4$]$_2$.—A mixture of *trans*-[Ru^{VI}(dmbipy)$_2$O$_2$][ClO$_4$]$_2$ (0.2 g) and norborn-2-ene (1 g) or benzyl alcohol (1 cm^3) in acetonitrile (20 cm^3) was stirred at room temperature for 0.5 h and, if necessary, the solution filtered. Upon addition of diethyl ether, a bright yellow solid was precipitated which was collected by filtration and air dried. Yield > 80% (Found: C, 44.9; H, 3.9; N, 11.1. $C_{28}H_{30}Cl_2N_6O_8Ru$ requires C, 44.8; H, 4.0; N, 11.2%); IR ν(CH$_3$CN) at 2320 cm^{-1}.

Physical Measurements.—UV–visible spectra were obtained on a Shimadzu UV-240 spectrophotometer and NMR spectra on a JEOL model FX 90Q (90 MHz) spectrometer. Magnetic susceptibilities were determined using the Guoy method using Hg[Co(SCN)$_4$] as calibrant. The pK_a values were determined spectrophotometrically at two independent wavelengths.

Cyclic voltammetry and constant-potential coulometry were performed using a Princeton Applied Research (PAR) model 175 universal programmer, model 173 potentiostat and model 179 digital coulometer. The working electrode was pyrolytic graphite (basal-plane or edge-plane, Union Carbide), which was pretreated by procedures described previously.[5l]

Stoichiometric Oxidation of Organic Substrates.—Stoichiometric oxidation was performed by suspending the ruthenium-oxo oxidant (25 mg) in acetone or acetonitrile (1 cm^3) containing the organic substrate (solid, 100 mg; liquid, 1 cm^3) under a nitrogen atmosphere. The reaction mixture was stirred magnetically for 4 h at room temperature. A control experiment in the absence of ruthenium complex was performed for each reaction under similar conditions. The organic products were analysed by gas chromatography, ^{1}H NMR and UV–visible spectroscopy. Gas chromatographic analyses were conducted using a Varian model 940 gas chromatograph equipped with a flame ionization detector. The components were identified by comparing the retention times with authentic samples and by mass spectral analysis. The *cis*- and *trans*-stilbene oxides were identified by ^{1}H NMR spectroscopy using deoxybenzoin as internal standard.

Competitive Oxidation of Cyclohexane and [^{2}H$_2$]*Cyclohexane with Cyclopentane.*—Complex **2** (30 mg) was added to a stirred acetonitrile solution (2 cm^3) of cyclohexane (0.1 cm^3) and cyclopentane (0.1 cm^3) under degassed conditions and the reaction mixture stirred for 4 h. Chromatographic analysis revealed two products only: cyclohexanone and cyclopentanone. The same competitive experiment was performed using cyclopentane (0.1 cm^3) and [^{2}H$_2$]cyclohexane (0.1 cm^3). The ratio of the yield of cyclohexanone (relative to cyclopentanone) to that of [^{2}H$_2$]-cyclohexanone (relative to cyclopentanone) gave the kinetic isotope effect, which had a value of 14 ± 2.

Kinetic Measurements.—The reactions between alcohols and complex **2** in 0.1 mol dm^{-3} CF$_3$SO$_3$H were studied by stopped-flow spectrophotometry. A Hi-Tech SF-51 stopped-flow module coupled with a Hi-Tech SU-40 spectrophotometer unit was used for the kinetic experiments. The data collection process was controlled by an Apple IIe microcomputer *via* an ADS-1 interface unit, also from Hi-Tech. The concentration of the alcohol was at least 100 fold in excess over the ruthenium oxidant. Each reaction was followed by monitoring the decrease in absorbance of complex **2** at 300 nm. Pseudo-first-order rate constants, k_{obs}, were obtained by the non-linear least-squares fit of A_t to time t according to equation (1) where A_0 and A_∞ are

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

the initial and final absorbances respectively. Second-order rate constants were obtained from the linear plots of k_{obs} *vs.* concentration of the alcohol.

Results and Discussion

In a manner similar to the preparation of *trans*-[Ru^{III}(bipy)$_2$(OH)(H$_2$O)]$^{2+}$,[7] *trans*-[Ru^{III}(dmbipy)$_2$(OH)(H$_2$O)][ClO$_4$]$_2$ **1** was obtained by broad-band irradiation of *cis*-[Ru^{II}(dmbipy)$_2$(H$_2$O)]$^{2+}$ under aerobic conditions. Its optical spectrum is virtually the same as that of *trans*-[Ru^{III}(bipy)$_2$(OH)(H$_2$O)]$^{2+}$, showing the complete absence of the metal-to-ligand charge transfer bands present in the starting ruthenium(II) species. The measured μ_{eff} value of 1.9 is in accordance with the Ru^{III} formulation $t_{2g}{}^5$. The assignment of a *trans* configuration is based on its electrochemistry, which is the same as that of *trans*-[Ru^{VI}(dmbipy)$_2$O$_2$]$^{2+}$. Reversible Ru^{VI}–Ru^{IV}, Ru^{IV}–Ru^{III} and Ru^{III}–Ru^{II} couples in acidic solutions are typically observed for *trans*-tetraamine(dioxo)ruthenium(VI) complexes.[5a,f,h] The pK_a of **1** has been determined spectrophotometrically and has a value 5.8, which is lower than the value of 10.2 found for [Ru^{II}(bipy)$_2$(py)(H$_2$O)]$^{2+}$ (py = pyridine).[9]

It has been reported that the oxidation of *trans*-[Ru^{III}(bipy)$_2$(OH)(H$_2$O)]$^{2+}$ by Ce^{IV} in water gave *trans*-[Ru^{VI}(bipy)$_2$O$_2$]$^{2+}$.[5a] In this work, *trans*-[Ru^{VI}(dmbipy)$_2$O$_2$][ClO$_4$]$_2$ **2** and *trans*-[Ru^{VI}(phen)$_2$O$_2$][ClO$_4$]$_2$ **3** were prepared similarly. Both complexes are diamagnetic and show one intense IR band at 845–850 cm^{-1}, assignable to the ν_{asym}(RuO$_2$) stretch. Complex **3** is very insoluble both in water and organic solvents, and, for this reason, no further study on this compound has been undertaken. Complex **2** has a higher solubility than its bipy or phen analogue in both acetonitrile and acetone. Its UV–visible spectrum (Fig. 1) displays a vibronic structured absorption band at 420 nm, which is due to the spin-allowed $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{\pi^*})^1$ ($d_{\pi^*} = d_{xz}, d_{yz}$) transition characteristic of *trans*-tetraamine(dioxo)ruthenium(VI) species. Complex **2** is an air-stable yellow solid and can be stored at 0 °C in the dark. In solution however, even in highly purified acetonitrile, it is reduced slowly to *trans*-[Ru^{II}(dmbipy)$_2$(CH$_3$CN)$_2$]$^{2+}$ by the solvent.

Electrochemistry.—The electrochemistry of *trans*-dioxoruthenium(VI) complexes such as *trans*-[Ru^{VI}(bipy)$_2$O$_2$]$^{2+}$ [5a] and *trans*-[Ru^{VI}(tmc)O$_2$]$^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)[5f] in aqueous solution has been investigated previously. At low pH, reversible Ru^{VI}–Ru^{IV}, Ru^{IV}–Ru^{III} and Ru^{III}–Ru^{II} redox couples have been observed whereas at high pH the two-electron Ru^{VI}–Ru^{IV} couple splits into two reversible one-electron couples Ru^{VI}–Ru^{V} and Ru^{V}–Ru^{IV}. Scheme 1 summarises the electrochemistry of *trans*-dioxoruthenium(VI) N-donor complexes.

The reversibility of the [Ru^{IV}(O)(OH$_2$)]–[Ru^{III}(OH)(OH$_2$)] couple is strongly affected by the nature of the electrode surface. Quasi-reversible–reversible couples ($\Delta E_p \approx$ 60–80 mV) are observed at slow scan rates and with edge-plane pyrolytic graphite as the working electrode.

At low pH,

$$[Ru^{VI}O_2]^{2+} + 2e^- + 2H^+ \longrightarrow [Ru^{IV}O(H_2O)]^{2+}$$

$$[Ru^{IV}O(H_2O)]^{2+} + e^- + H^+ \longrightarrow [Ru^{III}(OH)(H_2O)]^{2+}$$

$$[Ru^{III}(OH)(H_2O)]^{2+} + e^- + H^+ \longrightarrow [Ru^{II}(H_2O)_2]^{2+}$$

At high pH,

$$[Ru^{VI}O_2]^{2+} + e^- \longrightarrow [Ru^{V}O_2]^+$$

$$[Ru^{V}O_2]^+ + e^- + H^+ \longrightarrow [Ru^{IV}O(OH)]^+$$

$$[Ru^{IV}O(OH)]^+ + e^- + H^+ \longrightarrow [Ru^{III}(OH)_2]^+$$

$$[Ru^{III}(OH)_2]^+ + e^- + 2H^+ \longrightarrow [Ru^{II}(OH_2)_2]^{2+}$$

Scheme 1 Equatorial ligands (4N) omitted

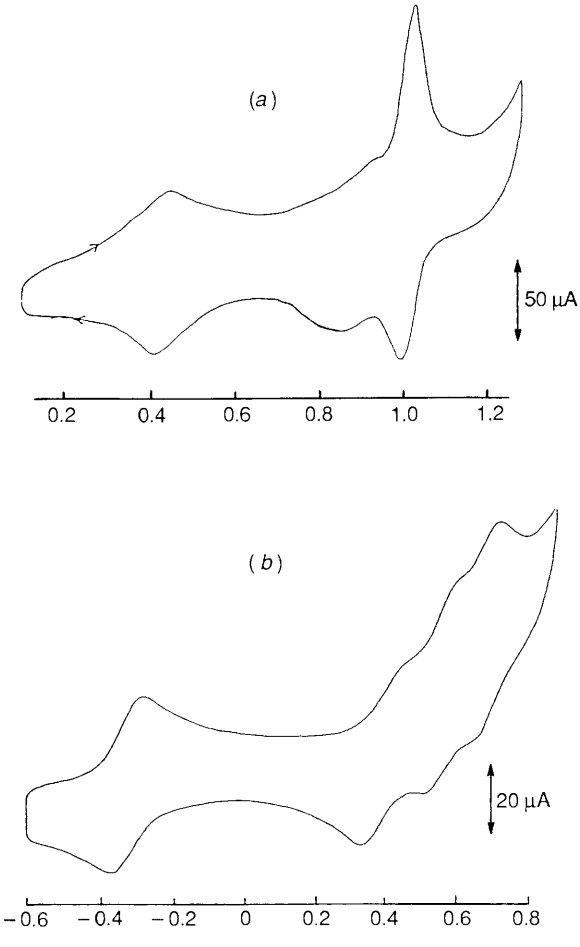


Fig. 2 Cyclic voltammograms of **1** (or **2**) (10^{-3} mol dm^{-3}) at pH 1.0 (*a*) and 9.2 (*b*). Working electrode, edge-plane pyrolytic graphite; scan rate, 50 mV s^{-1}

Fig. 2 shows the cyclic voltammograms of complex **1** at pH 1.0 and 9.2. The same result was obtained for **2**. The electrochemical data showing the dependence of E° *versus* pH for all the redox couples are given in Table 1. Except for the Ru^{VI}–Ru^{V} couple, the E° values for all the redox couples shift cathodically with increase in pH; Fig. 3 shows the plots of E° *versus* pH. The observed slopes of *ca.* −60 mV per pH unit for the Ru^{VI}–Ru^{IV} and Ru^{IV}–Ru^{III} couples are in accordance with their formulations as $2H^+$–2e and $1H^+$–1e couples respectively. For Ru^{III}–Ru^{II}, there are two straight line segments with slopes of *ca.* −60 and −117 mV per pH unit. The break point occurs at pH 5.9, which should be the pK_a of **1**. This value is in good agreement with the pK_a value of 5.8 determined spectrophotometrically.

Table 1 E° *versus* pH for various couples of complex **1** in aqueous solution (ionic strength = 0.2 mol dm^{-3})

	E°/V *vs.* SCE				
pH	III–II	IV–III	V–IV	VI–IV	VI–V
1.10	0.42	0.89		1.00	
2.63	0.31	0.79		0.93	
3.43	0.28	0.74		0.88	
4.63	0.20	0.68		0.81	
5.10	0.16	0.65		0.78	
6.07	0.07	0.60		0.73	
6.99	−0.05	0.55		*	
7.69	−0.14	0.40	*		*
8.50	−0.24	0.42	0.58		0.67
9.20	−0.35	0.38	0.55		0.67
10.23	−0.39	0.33	0.49		0.67
11.06	−0.44	0.26	0.43		0.67

* Couple is ill defined.

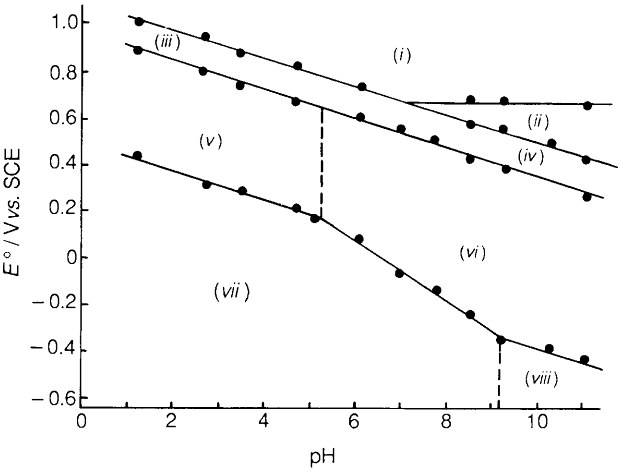


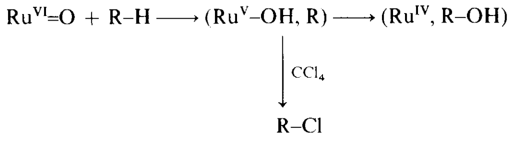
Fig. 3 Plots of E° *vs.* pH for various redox couples of **2**. Major species in solution: (*i*) $[Ru^{VI}(dmbipy)O_2]^{2+}$, (*ii*) $[Ru^{V}(dmbipy)O_2]^+$, (*iii*) $[Ru^{IV}(dmbipy)O(H_2O)]^{2+}$, (*iv*) $[Ru^{IV}(dmbipy)O(OH)]^+$, (*v*) $[Ru^{III}(dmbipy)(OH)(H_2O)]^{2+}$, (*vi*) $[Ru^{III}(dmbipy)(OH)_2]^+$, (*vii*) $[Ru^{II}(dmbipy)(H_2O)_2]^{2+}$ and (*viii*) $[Ru^{II}(dmbipy)(OH)(H_2O)]^+$

The electrochemistry of *trans*-$[Ru^{VI}(phen)_2O_2]^{2+}$ is similar to that of its bipy or dmbipy analogue. However, this complex strongly adsorbs on the surface of the pyrolytic graphite electrode.[10] For this reason, no detailed electrochemical study has been performed.

Oxidation of Organic Substrates.—Complex **2** has been found to be a powerful oxidant. Table 2 summarises the results on the stoichiometric oxidation of organic substrates by **2** in acetonitrile. In each reaction investigated, the major ruthenium product isolated was *trans*-$[Ru^{II}(dmbipy)_2(CH_3CN)_2]^{2+}$. Complex **2** rapidly oxidizes secondary alcohols to ketones and primary alcohols to aldehydes. Tetrahydrofuran and ethylbenzene were also oxidized to give γ-butyrolactone and acetophenone respectively in high yields under mild conditions. In the reactions of **2** with aromatic hydrocarbons, only the benzylic C–H bonds were oxidized. Since the oxidation of cumene and ethylbenzene occurred preferentially at the tertiary and secondary carbon atoms respectively, the reactivities of the benzylic C–H bonds follow the expected order: tertiary > secondary > primary.

Complex **2** is also an active oxo-transfer reagent reacting with alkenes such as cyclooctene and norborn-2-ene to give the respective epoxides in high yields. With styrene and *cis*- and *trans*-stilbenes, both epoxidation and oxidative cleavage of the C=C bonds were found. The reaction with *cis*-stilbene gave a mixture of *cis*- and *trans*-stilbene oxides and benzaldehyde, indicating a redox mechanism for the epoxidation.[11]

An important finding about **2** is that it can oxidize saturated alkanes under mild conditions. Cyclohexane, 2,3-dimethylbutane and adamantane (tricyclo[3.3.1.1^{3,7}]decane) were oxidized to the cyclohexanone, 2,3-dimethylbutan-2-ol and adamantan-1-ol respectively. However, the rates of oxidation at room temperature were too slow to compete with the reduction of the Ru^{VI} complex by the solvent. Since only one organic product was found in the oxidation of 2,3-dimethylbutane and adamantane, the Ru^{VI} oxidant selectively oxidizes tertiary C–H bonds in preference to primary or secondary C–H bonds. When the oxidation of cyclohexane was carried out in the presence of CCl_4, the organic product was cyclohexyl chloride instead of cyclohexanone. This indicates that a H-atom abstraction pathway occurs with the formation of an intermediate cyclohexyl radical (Scheme 2).



$$\begin{tikzcd} \mathrm{Ru^{VI}{=}O} + \mathrm{R{-}H} \arrow[r] & (\mathrm{Ru^{V}{-}OH, R}) \arrow[r] \arrow[d, "\mathrm{CCl_4}"] & (\mathrm{Ru^{IV}, R{-}OH}) \\ & \mathrm{R{-}Cl} & \end{tikzcd}$$

Scheme 2 R–H = alkane, such as cyclohexane

The measured kinetic isotope effect for the oxidation of cyclohexane has been determined to be 14 ± 2, a value which is not unreasonable for a H-atom abstraction mechanism. Nevertheless the result clearly indicates that there is a substantial interaction between the Ru=O moiety and the C–H bond in the transition state during alkane oxidation by **2**. Large kinetic isotope effects have also been reported previously in the H-atom abstraction from alkanes mediated by metalloporphyrin oxo complexes.[1,2]

Kinetic studies have been performed on the oxidation of alcohols. Fig. 4 shows the UV–visible spectral changes when an excess of propan-2-ol or cyclohexanol was added to a solution of complex **2** in 0.1 mol dm^{-3} CF_3SO_3H. The Ru^{VI} oxidant was reduced immediately to a species having virtually the same UV–visible spectrum as that of *trans*-$[Ru^{IV}(bipy)_2O(H_2O)]^{2+}$ and so is assigned tentatively as *trans*-$[Ru^{IV}(dmbipy)_2O(H_2O)]^{2+}$. Thus the stoichiometry of the reaction is as given in equation (2).

$$[Ru^{VI}O_2]^{2+} + RR'CHOH \longrightarrow [Ru^{IV}O(H_2O)]^{2+} + RR'C{=}O \quad (2)$$

When oxidation of an alcohol was monitored at 300 nm, the rate law was found to be $d[Ru^{VI}]/dt = k[Ru^{VI}][\text{alcohol}]$. In each kinetic run, a plot of k_{obs} *vs.* [alcohol] (Fig. 5) was linear and with zero intercept, indicating that the Ru^{VI} complex had not decomposed during the kinetic measurements. From the plots of the kinetic data, the second-order rate constants obtained at 298 K were 3.60, 0.19, 0.17 and 0.11 dm^3 mol^{-1} s^{-1} for benzyl alcohol, $[^2H_2]$benzyl alcohol, propan-2-ol and cyclohexanol respectively. These values are higher than those determined by Roecker and Meyer[12] using $[Ru^{IV}(bipy)_2(py)O]^{2+}$ as oxidant. This suggests that **2** is a stronger oxidant than $[Ru^{IV}(bipy)_2(py)O]^{2+}$ despite the fact that their E° values are similar. The measured kinetic isotope effect for the oxidation of benzyl alcohol is 19, a value slightly higher than that found in the cyclohexane oxidation. Activation parameters for the oxidation of benzyl alcohol have also been determined over the temperature range 286–306 K and the results are listed in Table 3. The plot of $\ln(k_2/T)$ *vs.* $1/T$ is linear and the calculated activation enthalpy and entropy are 8.3 ± 1 kcal mol^{-1} and −23 ± 3 cal K^{-1} mol^{-1} respectively. The large and negative activation entropy together with the observed large kinetic isotope effect of 19 suggest an associative mechanism, either a hydride abstraction or a hydrogen-atom abstraction for the oxidation of alcohol by **2** (Scheme 3).

Table 2 Results of the stoichiometric oxidation of organic substrates by complex **2** in acetonitrile under degassed conditions and at room temperature for 4 h

Substrate	Product[a]	% mol product/ mol **2**
Cyclohexene	Cyclohexenone	200
Benzyl alcohol	Benzaldehyde	200
Cyclohexanol	Cyclohexanone	90
Propan-2-ol	Acetone	90
Pentan-2-ol	Pentan-2-one	100
Toluene	Benzaldehyde	40
	Benzoic acid	30
Ethylbenzene	Acetophenone	90
Cumene	2-Phenylpropan-2-ol	80
Tetrahydrofuran	γ-Butyrolactone	70
Norborn-2-ene	*exo*-Norborn-2-ene oxide	70
Cyclooctene	Cyclooctene oxide	70
Styrene	Benzaldehyde	43
	Styrene oxide	54
cis-Stilbene	Benzaldehyde	23
	cis-Stilbene oxide	62
	trans-Stilbene oxide	15
trans-Stilbene	*trans*-Stilbene oxide	55
	Benzaldehyde	33
2,3-Dimethylbutane	2,3-Dimethylbutan-2-ol	55
Adamantane	Adamantan-1-ol	61
Cyclohexane	Cyclohexanone[b]	20

[a] Percentage yield with respect to mol of organic starting material: cyclohexenone, 100; cyclohexanone, 95; acetophenone, 90; γ-butyrolactone, 85; norborn-2-ene oxide, 80; cyclooctene oxide, 70%. Reaction conditions are the same as described in the Experimental section except that 50 mg of the ruthenium oxo oxidant were used in each determination. [b] k_H/k_D = 14 ± 2.

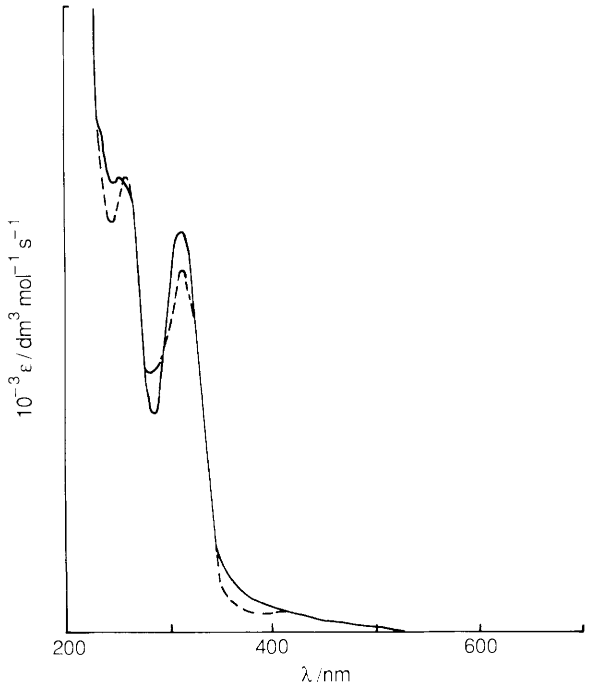
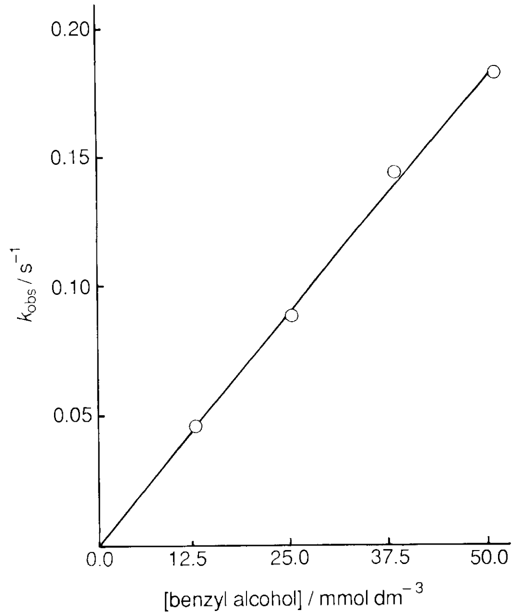


Fig. 4 UV–visible spectral changes for the oxidation of cyclohexanol by **2** in 0.1 mol dm^{-3} CF_3SO_3H. Initial spectrum (····), final spectrum (—)

Both pathways are feasible and it is very difficult to differentiate between them. However, in view of the large kinetic isotope effect of 19 and previous studies by Roecker and Meyer,[12] a hydride mechanism is preferred.



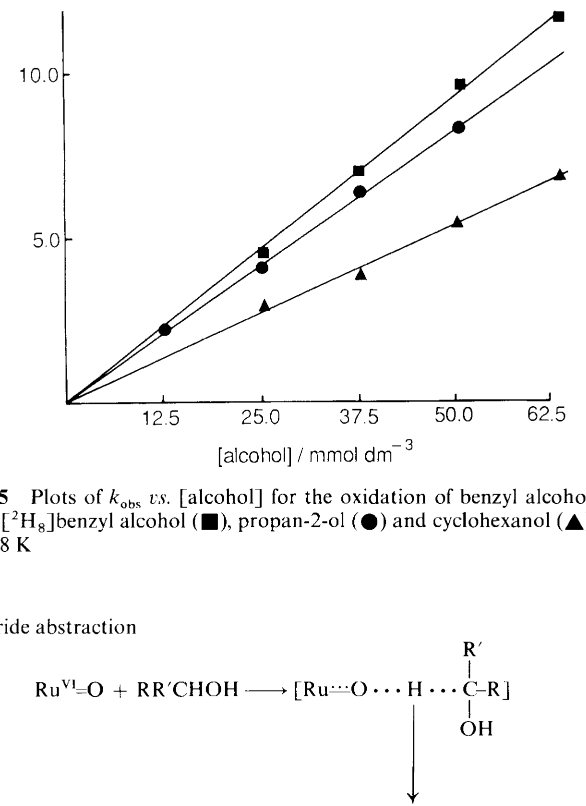
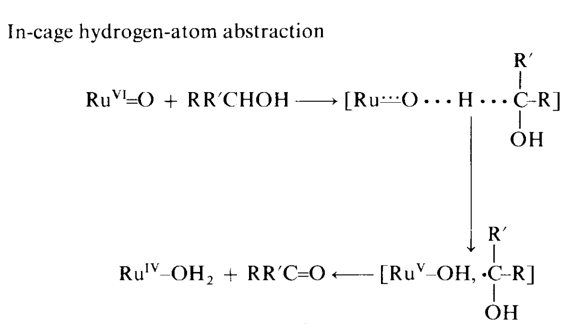


Fig. 5 Plots of k_{obs} *vs.* [alcohol] for the oxidation of benzyl alcohol (○), [$^2H_8$]benzyl alcohol (■), propan-2-ol (●) and cyclohexanol (▲) at 298 K



Scheme 3

Table 3 Pseudo-first-order (k_{obs}) and second-order (k) rate constants for the reaction between complex **2** and benzyl alcohol in ~0.1 mol dm^{-3} CF_3SO_3H at different temperatures

T/K	[benzyl alcohol]/ mmol dm^{-3}	k_{obs}/s^{-1}	k*/dm^3 mol^{-1} s^{-1}
286.5	12.5	0.023	1.98
	25.0	0.051	
	37.5	0.075	
	50.0	0.099	
290.5	12.5	0.034	2.44
	25.0	0.060	
	37.5	0.094	
	50.0	0.120	
298.0	12.5	0.045	3.60
	25.0	0.086	
	37.5	0.139	
	50.0	0.177	
306.0	12.5	0.069	5.48
	25.0	0.133	
	37.5	0.209	
	50.0	0.269	

* Second-order rate constants were obtained from the slopes of the plots of k_{obs} *vs.* [benzyl alcohol].

Comparison with Other trans-*Dioxoruthenium*(VI) *Complexes.*—A number of *trans*-dioxoruthenium(VI) complexes have recently been reported in the literature. These include (*i*) *trans*-$[RuO_2(HIO_6)_2]^{6-}$,[5b] (*ii*) *trans*-$[RuO_2(X)_2(py)_2]$ (X = Cl or O_2CMe),[5b–d] *trans*-dioxo(porphyrinato)ruthenium(VI)[5h–j] and (*iii*) *trans*-$[Ru(L)_2O_2]^{2+}$ (L = tetraamine).[5a,f–h] Although the electrochemistry of the anionic (*i*) and neutral [(*ii*) and (*iii*)] ruthenium(VI) oxo complexes has not been studied, these species are expected to have a lower E° value than the dicationic *trans*-$[Ru^{VI}(L)O_2]^{2+}$ because of a charge effect. Among the *trans*-$[Ru^{VI}(L)O_2]^{2+}$ complexes, **2** has an E° value as high as that of *trans*-$[Ru^{VI}(bipy)_2O_2]^{2+}$ and hence it should be the strongest oxidant. This is reflected by the ability of **2** to oxidize the unactivated C–H bonds of cyclohexane under mild conditions, a previously unreported property for *trans*-dioxoruthenium(VI) complexes.

Oxidation of C–H bonds by cytochrome P-450 and its biomimetic models has been studied previously.[1,2] Groves and Nemo[13] reported that the 'Fe(tpp)Cl + PhIO' system (H_2tpp = 5,10,15,20-tetraphenylporphyrin) selectively oxidizes tertiary C–H bonds in the presence of secondary and primary ones. Oxidation of cyclohexane by this system was also found to have a kinetic isotope effect of 12.9. In our work, the reactivity of **2** in alkane hydroxylation is surprisingly similar to the systems studied by Groves and Nemo.[13] This provides indirect evidence for the metal–oxo intermediate, as has been suggested in the biomimetic oxidation by PhIO mediated by metalloporphyrins.

Conclusion

Complex **2** has been found to be a powerful oxidant with a high redox potential. It is capable of oxidizing a wide variety of organic substrates, including the C–H bonds of saturated alkanes. In the hydroxylation of both aliphatic and aromatic hydrocarbons, the reactivity of C–H bonds follows the usual sequence: tertiary > secondary > primary. It is anticipated that the suitable design of *trans*-dioxoruthenium(VI) complexes may lead to new inorganic oxidants for selective alkane functionalization.

Acknowledgements

Financial support from the University of Hong Kong and the University and Polytechnic Granting Committee are gratefully acknowledged. W.-H. L. thanks the Croucher Foundation of Hong Kong for a Croucher Foundation Studentship.

References

1 *Activation and Functionalization of Alkanes*, ed. C. L. Hill, Wiley, New York, 1989.

2 F. P. Guengerich and T. L. Macdonald, *Acc. Chem. Res.*, 1984, **17**, 9; D. Mansuy, *Pure, Appl. Chem.*, 1987, **59**, 579; J. H. Dawson and M. Sono, *Chem. Rev.*, 1987, **87**, 1255.

3 W. P. Griffith, *Transition Met. Chem.*, 1990, **15**, 251.

4 G. Green, W. P. Griffith, D. M. Hollinshead, S. V. Ley and M. Schroder, *J. Chem. Soc., Perkin Trans. 1*, 1984, 681; W. P. Griffith, S. V. Ley, G. P. Whitcombe and A. D. White, *J. Chem. Soc., Chem. Commun.*, 1987, 1625; A. C. Dengel, A. M. El-Hendawy, W. P. Griffith, C. A. O'Mahoney and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1990, 737.

5 (*a*) C. M. Che, K. Y. Wong, W. H. Leung and C. K. Poon, *Inorg. Chem.*, 1986, **25**, 345; (*b*) A. M. El-Hendawy, W. P. Griffith, B. Piggott and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1988, 1983; (*c*) A. M. El-Hendawy, W. P. Griffith, F. I. Taha and M. N. Moussa, *J. Chem. Soc., Dalton Trans.*, 1989, 901; (*d*) T. C. Lau and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 1987, 798; (*e*) S. Perrier and J. K. Kochi, *Inorg. Chem.*, 1988, **27**, 4165; (*f*) C. M. Che, K. Y. Wong and C. K. Poon, *Inorg. Chem.*, 1985, **24**, 1797; (*g*) C. M. Che, W. T. Tang, W. T. Wong and T. F. Lai, *J. Am. Chem. Soc.*, 1989, **111**, 9048; (*h*) C. M. Che, W. T. Tang, W. O. Lee, W. T. Wong and T. F. Lai, *J. Chem. Soc., Dalton Trans.*, 1989, 2011; C. M. Che, W. T. Tang, C. K. Li, *J. Chem. Soc., Dalton Trans.*, 1990, 3735; (*i*) W. H. Leung and C. M. Che, *J. Am. Chem. Soc.*, 1989, **111**, 8812; (*j*) J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, 1985, **107**, 5790; (*k*) J. T. Groves and R. Quinn, *Inorg. Chem.*, 1984, **23**, 3844; (*l*) C. M. Che, K. Y. Wong and F. C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.*, 1987, **226**, 211.

6 G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 4947; P. E. Rosevear and W. H. F. Sasse, *J. Heterocycl. Chem.*, 1971, **8**, 483.

7 B. Durham, S. R. Wilson, D. J. Hodgson and T. J. Meyer, *J. Am. Chem. Soc.*, 1980, **102**, 600.

8 D. O. Perrin, W. L. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, New York, 1980.

9 B. A. Moyer and T. J. Meyer, *Inorg. Chem.*, 1981, **20**, 436.

10 C. M. Che, W. H. Leung and C. K. Poon, *J. Chem. Soc., Chem. Commun.*, 1987, 173.

11 A. J. Castellino and T. C. Bruice, *J. Am. Chem. Soc.*, 1988, **110**, 158.

12 L. Roecker and T. J. Meyer, *J. Am. Chem. Soc.*, 1987, **109**, 746.

13 J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, 1983, **105**, 6243.

Received 27*th July* 1990; *Paper* 0/03425H