

Tuning the Reactivities of Ruthenium–Oxo Complexes with Robust Ligands. A Ruthenium(IV)–Oxo Complex of 6,6'-Dichloro-2,2'-bipyridine as an Active Oxidant for Stoichiometric and Catalytic Organic Oxidation †

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The synthesis and characterization of $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})(\text{H}_2\text{O})]^{2+}$ (terpy = 2,2':6',2''-terpyridine; dcbipy = 6,6'-dichloro-2,2'-bipyridine) are described. Oxidation of this complex with Ce^{IV} gave $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}]^{2+}$, isolated as a greenish yellow perchlorate salt. The $\text{Ru}^{\text{IV}}=\text{O}$ complex is paramagnetic ($\mu_{\text{eff}} = 2.83$) and exhibits a $\text{Ru}=\text{O}$ stretch at 780 cm^{-1} . It is a powerful oxidant with $E^\circ(\text{Ru}^{\text{IV}}-\text{Ru}^{\text{III}}) = 1.13\text{ V}$ vs. saturated calomel electrode at pH 1.0 and can selectively oxidize the tertiary C–H bond of adamantane. The mechanism of alkene oxidation by $\text{Ru}^{\text{IV}}=\text{O}$ has been investigated and discussed. The complex $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})(\text{H}_2\text{O})]^{2+}$ is a robust catalyst for the oxidation of saturated alkanes by *tert*-butyl hydroperoxide.

During the past decade an extensive co-ordination chemistry of six-co-ordinate polypyridyl complexes of Ru^{II} and Ru^{III} based on the ligands pyridine(py), 2,2'-bipyridine(bipy), 2,2':6',2''-terpyridine(terpy) and 1,10-phenanthroline(phen) has been developed. An equally versatile chemistry also exists for complexes of Ru^{IV} , Ru^{V} and Ru^{VI} whenever they are accessible by the formation of a metal–oxo bond.¹

Meyer and co-workers have reported that the ruthenium(IV)–oxo complexes $[\text{Ru}(\text{terpy})(\text{bipy})\text{O}]^{2+}$ and $[\text{Ru}(\text{bipy})_2(\text{py})\text{O}]^{2+}$ are active oxidants for a variety of organic substrates.¹ Their work has stimulated our interest in developing more reactive but robust metal–oxo oxidants by suitable variation of the structure of the auxiliary α -diimine ligand. Previous work in metalloporphyrin chemistry² showed that introduction of electron-withdrawing substituents on the ligand(s) would increase the oxidative stability and reactivity of the metal catalysts. Furthermore, a decrease in the σ -donor strength of the co-ordinated ligands would be expected to increase the E° of the $\text{Ru}=\text{O}$ oxidant. In this regard, the ligand 6,6'-dichloro-2,2'-bipyridine (dcbipy) was chosen to replace bipy in the system $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{bipy})\text{O}]^{2+}$.³ Herein is described the synthesis, characterization, and reactivities of $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}]^{2+}$, which has been found to be an active and robust oxidant. Oxidation of hydrocarbons with *tert*-butyl hydroperoxide and the mechanism of alkene oxidation by oxoruthenium(IV) are also described.

Experimental

Materials.—The ligand dcbipy and the complex $[\text{Ru}^{\text{III}}(\text{terpy})\text{Cl}_3]$ were synthesised by published methods.⁴ Deionized water and acetonitrile used in the kinetic experiments were distilled from alkaline potassium permanganate. *tert*-Butyl hydroperoxide (18%) in di-*tert*-butyl peroxide was purchased from Merck. All substrates were obtained from Aldrich Chemical Co. and purified by vacuum distillation or sublimation. Their purity was checked by gas chromatography.

$[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})(\text{H}_2\text{O})][\text{CF}_3\text{SO}_3]_2 \cdot \text{H}_2\text{O}$. A mixture of $[\text{Ru}(\text{terpy})\text{Cl}_3]$ (0.4 g) and dcbipy (0.35 g) in ethylene glycol (3 cm^3) was refluxed for 4 h. After cooling, ethanol (5 cm^3) was

added and the mixture was filtered to remove the excess of ligand and starting metal complex. Concentrated HCl (1 cm^3) was added dropwise to the filtrate. Upon cooling in a refrigerator the dark purple solid $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{Cl}]\text{Cl}$ was obtained. This was used *in situ* without further purification. A mixture of $\text{Ag}(\text{CF}_3\text{SO}_3)$ (0.15 g) and $[\text{Ru}(\text{terpy})(\text{dcbipy})\text{Cl}]\text{Cl}$ (0.3 g) in acetone–water (3:1, 20 cm^3) was heated at reflux for 30 min. The AgCl formed was filtered off and the volume reduced to *ca.* 5 cm^3 . On standing a red microcrystalline product appeared, which was filtered off, washed with ice-cold water, diethyl ether and dried *in vacuo*. Yield: 0.45 g (63%) (Found: C, 36.2; H, 2.30; Cl, 8.05; N, 8.25. Calc. for $\text{C}_{27}\text{H}_{21}\text{Cl}_2\text{F}_6\text{N}_5\text{RuS}_2$: C, 36.3; H, 2.35; Cl, 7.95; N, 7.85%).

The salt $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})(\text{H}_2\text{O})][\text{ClO}_4]_2$ was prepared by metathesis of $[\text{Ru}(\text{terpy})(\text{dcbipy})(\text{H}_2\text{O})][\text{CF}_3\text{SO}_3]_2$ with an aqueous solution of NaClO_4 . Ultraviolet–visible [in water, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$): 272 (16 200), 310 (35 300), 486 (5440) and 582 (790).

$[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}][\text{ClO}_4]_2 \cdot 1.5\text{H}_2\text{O}$. The complex $[\text{Ru}(\text{terpy})(\text{dcbipy})(\text{H}_2\text{O})][\text{ClO}_4]_2$ (0.1 g) in water (15 cm^3 , $\approx 70^\circ\text{C}$) was added to an aqueous solution (20 cm^3) containing $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$ (2 g) and NaClO_4 (2 g) at room temperature. A greenish yellow solid was precipitated which was filtered off, washed with a little ice-cold water and air dried. Yield: 0.06 g (60%) (Found: C, 37.0; H, 2.4; Cl, 17.7; N, 9.05. Calc. for $\text{C}_{25}\text{H}_{21}\text{Cl}_4\text{N}_5\text{O}_{10.5}\text{Ru}$: C, 37.4; H, 2.50; Cl, 17.7; N, 8.75%). Ultraviolet–visible [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$): (in water) 283(sh) (10 500), 322 (13 600) and 352(sh) (5080); (in MeCN) 262 (18 400), 317 (19 100) and 452(sh) (1390).

Instrumentation.—Ultraviolet–visible spectra were recorded on a Shimadzu UV-240 spectrophotometer, infrared spectra as Nujol mulls on a Nicolet model 20 FXC FT-IR spectrophotometer. Cyclic voltammetry was conducted with a Princeton Applied Research Instruments model 175 Universal Programmer and model 173 potentiostat–galvanostat. The working electrode was edge-plane pyrolytic graphite. Magnetic susceptibility was determined by the Evans method.

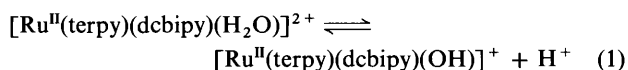
Organic Oxidation.—For both stoichiometric and catalytic oxidations, the organic products were analysed on a Varian 2440 gas chromatograph equipped with a flame ionization detector. The reactions were carried out under a nitrogen

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

atmosphere and at room temperature with continuous stirring; the conditions are given in Tables 2 and 3. The kinetics of oxidation of alkenes and alcohols by $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcby})\text{O}]^{2+}$ in MeCN or HClO_4 (0.1 mol dm^{-3}) was followed by monitoring the changes in the absorbance of Ru^{IV} or Ru^{II} at 350 or 310 nm and under conditions that the organic substrate was in excess of the $\text{Ru}^{\text{IV}}=\text{O}$ complex. Plots of $\ln(A_\infty - A_t)$ versus time were linear, and the first-order rate constants were calculated from $\ln(A_\infty - A_t) = -k_{\text{obs}}t + \ln(A_\infty - A_0)$, where A_∞ = absorbance at completion of reaction, A_0 = initial absorbance, A_t = absorbance measured at time t and k_{obs} = first-order rate constant. Data for the first three half-lives were used to calculate k_{obs} .

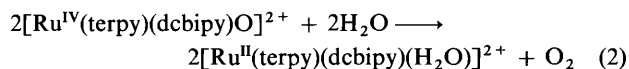
Results and Discussion

The ultraviolet-visible spectrum of $[\text{Ru}^{\text{II}}(\text{terpy})(\text{dcby})(\text{H}_2\text{O})]^{2+}$ in water displays an intense absorption band at 486 nm, which is red-shifted from that of its bpy analogue ($\lambda_{\text{max}} = 477 \text{ nm}$). The decrease in the metal-to-ligand charge-transfer (m.l.c.t.) transition energy is in accordance with the electronic effects of the Cl substituent, which would lower the energy of the π^* orbital of the bpy ligand. As determined by spectrophotometry, the $\text{p}K_a$ value of $[\text{Ru}(\text{terpy})(\text{dcby})(\text{H}_2\text{O})]^{2+}$ was found to be 10.9 ± 0.2 . Fig. 1 shows the spectral changes for reaction (1). The corresponding value of $[\text{Ru}^{\text{II}}(\text{terpy})(\text{bipy})-$



$(\text{H}_2\text{O})]^{2+}$ is 9.7.⁵ The higher $\text{p}K_a$ value of $[\text{Ru}(\text{terpy})(\text{dcby})(\text{H}_2\text{O})]^{2+}$ can be rationalized by the weaker σ -donor strength of the dcby ligand. Oxidation of $[\text{Ru}^{\text{II}}(\text{terpy})(\text{dcby})(\text{H}_2\text{O})]^{2+}$ by Ce^{IV} gave $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcby})\text{O}]^{2+}$, isolated as a greenish yellow ClO_4^- salt. As expected for a d^4 metal-oxo system,¹ $[\text{Ru}(\text{terpy})(\text{dcby})\text{O}]^{2+}$ is paramagnetic with a measured μ_{eff} of 2.83 close to the spin-only value for two unpaired electrons. Its IR spectrum exhibits an absorption peak at 780 cm^{-1} , assignable to the $\nu(\text{Ru}=\text{O})$ stretch. Similar $\nu(\text{Ru}=\text{O})$ stretching frequencies have been found for other $\text{Ru}^{\text{IV}}=\text{O}$ complexes.¹

At room temperature, $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcby})\text{O}]^{2+}$ is stable in highly purified acetonitrile and in $0.1 \text{ mol dm}^{-3} \text{ CF}_3\text{SO}_3\text{H}$ within 0.5–1 h. It is, however, unstable in acidic solutions (pH 1) upon heating to 60°C . The complex was found to be converted into $[\text{Ru}^{\text{II}}(\text{terpy})(\text{dcby})(\text{H}_2\text{O})]^{2+}$ within 3 h with a yield ranging from 70 to 80% as determined by spectrophotometry. The conversion of $\text{Ru}^{\text{IV}}=\text{O}$ into Ru^{II} was accelerated by broadband irradiation of the solution with ultraviolet-visible light (350 W high-pressure mercury short-arc lamp, $\lambda > 350 \text{ nm}$). After completion of the photolysis, usually 0.5 h, 0.8 mol equivalent of O_2 was produced per mol of $\text{Ru}^{\text{IV}}=\text{O}$ consumed. Thus reaction (2) is established. Given that the E° of the



$[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcby})\text{O}]^{2+}-[\text{Ru}^{\text{II}}(\text{terpy})(\text{dcby})(\text{H}_2\text{O})]^{2+}$ couple is 1.06 V at pH 1.0 (see later), reaction (2) is thermodynamically feasible although it is kinetically slow.

Electrochemistry.—The electrochemistry of $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcby})\text{O}]^{2+}$ is very similar to that of its bpy analogue, which has been subjected to detailed studies.⁵ At pH 1–7 its cyclic voltammogram (Fig. 2) consists of two waves: a reversible wave corresponding to the $\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$ couple and a second, quasi-reversible/irreversible wave with a much smaller peak current, which is due to the $\text{Ru}^{\text{IV}}-\text{Ru}^{\text{III}}$ couple. The reversibility of the latter couple is highly dependent on the nature of the electrode. A quasi-reversible wave was observed only with an edge-plane pyrolytic graphite electrode and at $\text{pH} > 3$. The E° values of

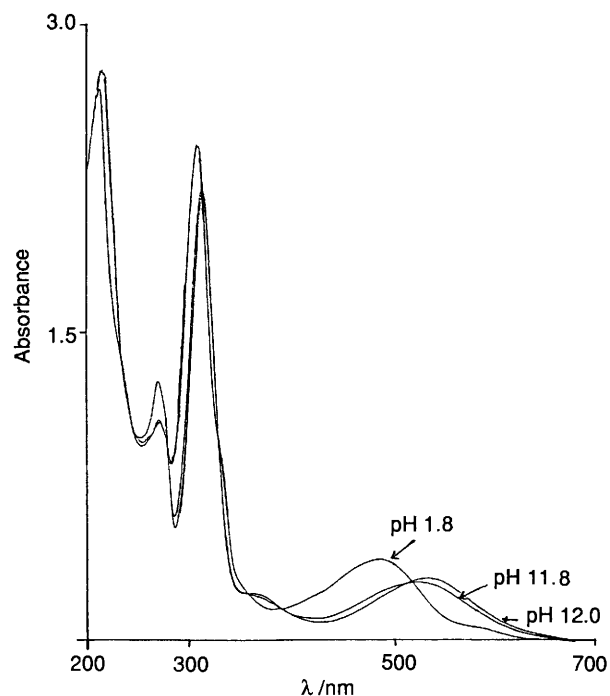


Fig. 1 Ultraviolet-visible spectra of $[\text{Ru}^{\text{II}}(\text{terpy})(\text{dcby})(\text{H}_2\text{O})]^{2+}$ at different pH

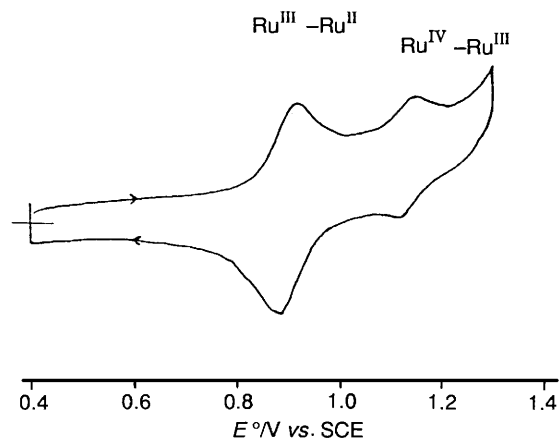


Fig. 2 Cyclic voltammogram of $[\text{Ru}^{\text{II}}(\text{terpy})(\text{dcby})(\text{H}_2\text{O})]^{2+}$ at pH 1.0

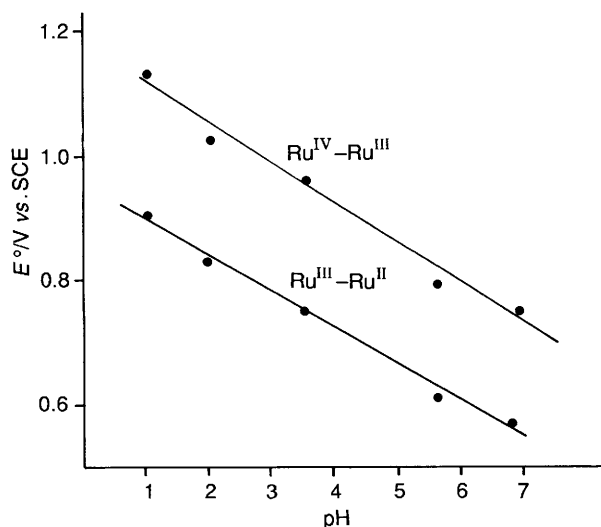


Fig. 3 Plot of the E° values vs. pH

Table 1 A comparison of electrochemical data and pK_a values of some $[\text{Ru}^{\text{II}}(\text{terpy})\text{L}(\text{H}_2\text{O})]^{2+}$ complexes

L*	$E^\circ/\text{V vs. SCE, pH 7.0}$		pK_a
	$\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$	$\text{Ru}^{\text{IV}}-\text{Ru}^{\text{III}}$	
dmobipy	0.42	0.55	
bipy	0.49	0.62	9.7
dcbipy	0.55	0.74	10.9
tmen	0.35	0.54	11.2

* dmobipy = 4,4'-Dimethoxy-2,2'-bipyridine; tmen = *N,N,N',N'*-tetramethylethane-1,2-diamine.

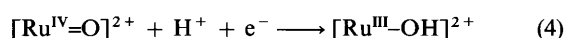
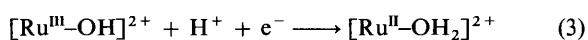
Table 2 Stoichiometric oxidation of organic substrates (100 mg) by $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}][\text{ClO}_4]_2$ (30 mg) in acetonitrile (2 cm³) at room temperature under a nitrogen atmosphere; reaction time 4 h

Substrate	Product	Yield (%)
Norbornene	<i>exo</i> -2,3-Epoxynorbornane	93
Styrene	Styrene oxide	85
	Benzaldehyde	24
Cyclooctene	Cyclooctene oxide	16
<i>cis</i> -Stilbene	Benzaldehyde	24
<i>trans</i> -Stilbene	Benzaldehyde	32
Ethylbenzene	Acetophenone	70
	1-Phenylethanol	31
Adamantane	Adamantan-1-ol	28
Cyclohexane	Cyclohexanone	Trace
Benzyl alcohol	Benzaldehyde	100
Propan-2-ol	Acetone	95
Cyclohexene	Cyclohexenone	100

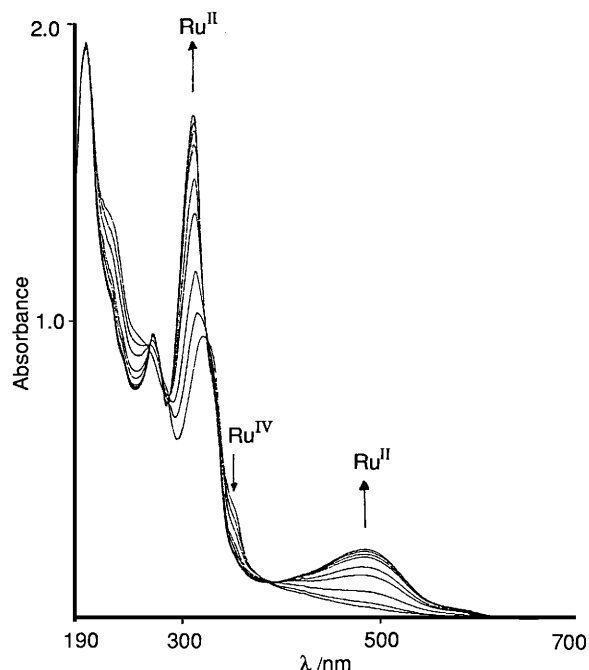
Table 3 Kinetic data for the oxidation of organic substrates by $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}][\text{ClO}_4]_2$ at 298 K

Substrate (concentration/mol dm ⁻³)	$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Medium
Norbornene (0.05–0.16)	$(1.1 \pm 0.1) \times 10^{-2}$	MeCN
Cyclooctene (0.02–0.06)	$(3.4 \pm 0.3) \times 10^{-2}$	MeCN
Styrene (0.04–0.13)	$(2.8 \pm 0.2) \times 10^{-2}$	MeCN
4-Chlorostyrene (0.05–0.2)	$(3.4 \pm 0.2) \times 10^{-2}$	MeCN
4-Fluorostyrene (0.05–0.3)	$(3.0 \pm 0.2) \times 10^{-2}$	MeCN
4-Methylstyrene (0.05–0.2)	$(6.3 \pm 0.4) \times 10^{-2}$	MeCN
4-Methoxystyrene (9×10^{-4} – 3×10^{-3})	8.65 ± 0.4	MeCN
Propan-2-ol (0.16–0.8)	$(7.71 \pm 0.4) \times 10^{-3}$	MeCN
Benzyl alcohol (0.01–0.05)	2.23 ± 0.2	0.1 mol dm ⁻³ HClO ₄
$[\alpha,\alpha'\text{-}^2\text{H}_2]$ Benzyl alcohol (0.02–0.08)	$(5.7 \pm 0.3) \times 10^{-2}$ $k_H/k_D = 39 \pm 4$	0.1 mol dm ⁻³ HClO ₄

both couples shift by about 60 mV per pH unit over the above mentioned pH range. Fig. 3 shows a plot of the electrochemical data. Thus the electrode reactions should involve one proton and one electron transfer as described by equations (3) and (4).



The cyclic voltammogram of $[\text{Ru}^{\text{II}}(\text{terpy})(\text{dcbipy})(\text{H}_2\text{O})]^{2+}$ is identical to that of the corresponding ruthenium(IV) oxo species. A comparison between the electrochemical data for various

**Fig. 4** Ultraviolet-visible spectral changes in the oxidation of norbornene (0.1 mol dm⁻³) by $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}]^{2+}$ in acetonitrile. Scan interval, 3 min

$[\text{Ru}^{\text{II}}(\text{terpy})\text{L}(\text{H}_2\text{O})]^{2+}$ species where L is a chelating bidentate nitrogen donor is shown in Table 1. As expected the E° values for the $\text{Ru}^{\text{IV}}-\text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$ couples decrease in the order: $\text{dcbipy} > \text{bipy}^5 > \text{dmobipy}^5 \approx \text{tmen}^6$ which is also the order of decreasing σ -donor strength of L. The range of E° values for the $\text{Ru}^{\text{IV}}-\text{Ru}^{\text{III}}$ couple is about 200 mV, indicating that systematic fine tuning of the redox potential of the $\text{Ru}^{\text{IV}}=\text{O}$ oxidant can be achieved by modifying the structure of the chelating ligand L.

Reactivities and Kinetic Studies.—Stoichiometric oxidation. The complex $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}]^{2+}$ has been found to be an active oxidant capable of oxidizing a wide variety of organic substrates. Table 2 summarizes the results of stoichiometric oxidation in acetonitrile. For each reaction, the ruthenium product was $[\text{Ru}^{\text{II}}(\text{terpy})(\text{dcbipy})(\text{MeCN})]^{2+}$, identified by its m.l.c.t. band at 452 nm. Even in the absence of organic substrate, $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}]^{2+}$ would also be reduced by the solvent to $[\text{Ru}^{\text{II}}(\text{terpy})(\text{dcbipy})(\text{MeCN})]^{2+}$ after several hours. This may explain the relatively low percentage yields found for some inert substrates such as adamantane and cyclohexane. As shown in Table 2, alcohols were efficiently oxidized to the corresponding aldehyde/ketone. Reactions with norbornene and styrene gave the corresponding epoxides in nearly quantitative yields. For cyclooctene the yield of epoxide is low. Since the rate constants for the reduction of $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}]^{2+}$ by norbornene and cyclooctene are comparable (see Table 3), the low yield of cyclooctene oxide means the operation of a competing pathway, likely to be allylic oxidation by the $\text{Ru}^{\text{IV}}=\text{O}$. In accord with this suggestion, oxidation of cyclohexene gave cyclohexenone as the only product. With *cis*- and *trans*-stilbenes, oxidative cleavage of the C=C with the production of benzaldehyde seems to be the dominant reaction pathway. No epoxide was detected by ¹H NMR spectroscopy. The complex $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}]^{2+}$ is also capable of oxidizing aromatic hydrocarbons and saturated hydrocarbons. Ethylbenzene and adamantane were selectively oxidized at the respective secondary C-H and tertiary C-H position. No reaction with cyclohexane was found under the reaction conditions employed.

Organic oxidation. The kinetic data for the oxidation of alkenes and alcohols are summarized in Table 3. The reactions

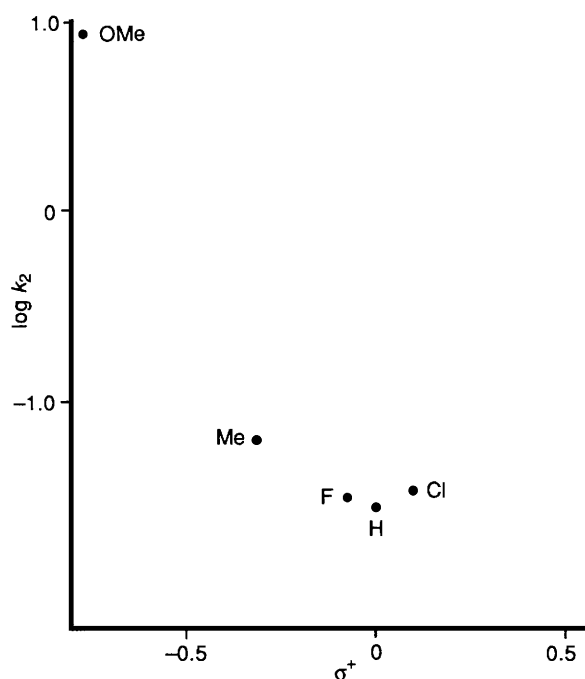
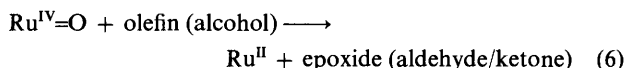


Fig. 5 Plot of $\log(\text{rate constant})$ vs. the substituent constants (σ^+) for the oxidation of *para*-substituted styrenes ($p\text{-XC}_6\text{H}_4\text{CH}=\text{CH}_2$)

are first order with respect to $[A]$ ($A = \text{alkene or alcohols}$) but independent of $[\text{Ru}^{\text{IV}}]$. No rate saturation has been observed. The experimental rate law is (5). Fig. 4 shows the spectral

$$\begin{aligned} -d[\text{Ru}^{\text{IV}}]/dt &= k_2[A][\text{Ru}^{\text{IV}}] + k_0 \\ &= k_{\text{obs}}[\text{Ru}^{\text{IV}}] \end{aligned} \quad (5)$$

changes corresponding to the oxidation of norbornene. Similar changes have been observed with other substrates. Thus the stoichiometry of the oxidation reactions is as in equation (6). In



most of the oxidation reactions investigated linear functions obtained from the plots of k_{obs} vs. $[A]$ have small non-zero intercepts (k_0). This may be due to the reduction of the $\text{Ru}^{\text{IV}}=\text{O}$ complex by the solvent. No attempt has been made to investigate k_0 which was very small compared with the actual rates of oxidation.

Alcohols. The mechanism of alcohol oxidation by $\text{Ru}^{\text{IV}}=\text{O}$ complexes of π -aromatic diimines has been investigated in depth by Meyer and co-workers.⁷ In this work, the oxidation of benzyl alcohol and propan-2-ol by $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}]^{2+}$ was investigated for comparison. The kinetic isotope effect ($k_{\text{H}}/k_{\text{D}}$) for the oxidation of benzyl alcohol is 39 (Table 3). This value is consistent with findings by Meyer⁷ and Takeuchi⁸ and their co-workers where the respective $k_{\text{H}}/k_{\text{D}}$ values for $[\text{Ru}^{\text{IV}}(\text{bipy})_2(\text{py})\text{O}]^{2+}$ and $[\text{Ru}^{\text{IV}}(\text{bipy})_2(\text{PR}_3)\text{O}]^{2+}$ ($\text{PR}_3 = \text{tertiary phosphine}$) are 50 and 36. The large kinetic isotope effect has been suggested as an indication of a concerted hydride-abstraction pathway.⁷ Interestingly, a comparison of the oxidation of propan-2-ol by the three systems $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}]^{2+}$, $[\text{Ru}^{\text{IV}}(\text{bipy})_2(\text{py})\text{O}]^{2+}$ and $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{tmen})\text{O}]_2^{2+}$ reveals that the rate constants differ by a factor of about 2 despite the $E^\circ[\text{Ru}^{\text{IV}}-\text{Ru}^{\text{III}}]$ values ranging over 200 mV. This suggests that the redox potential of the $\text{Ru}^{\text{IV}}=\text{O}$ oxidant is not the sole factor in affecting the rate of reaction. As suggested by Cundari and Drago⁹ and Meyer and co-workers,⁷ formation

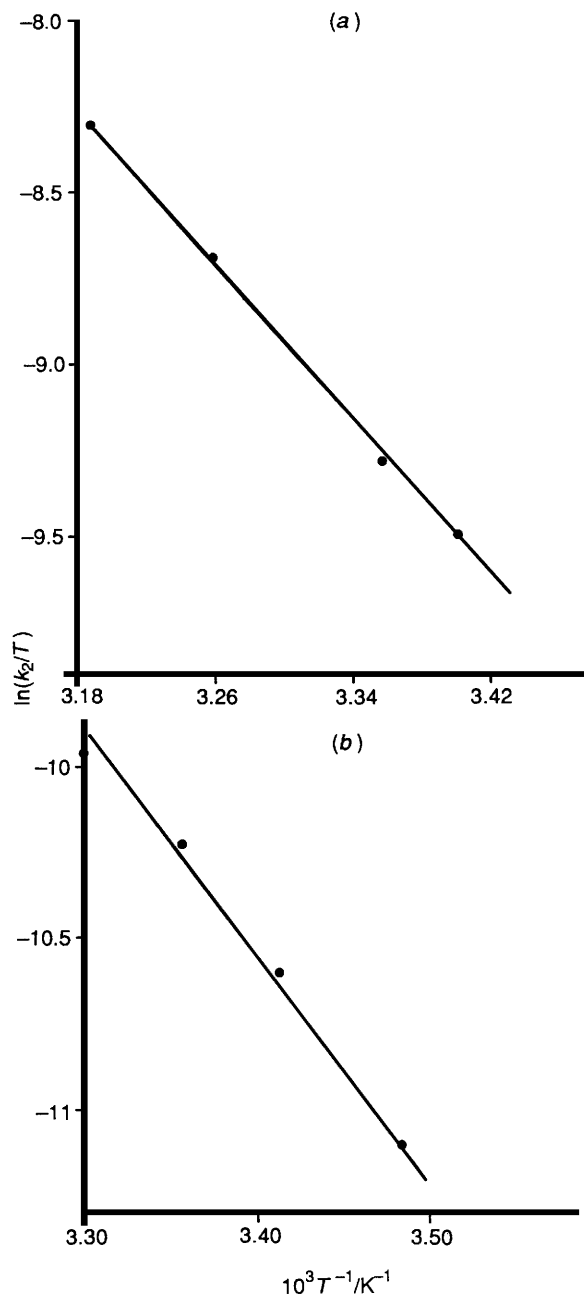


Fig. 6 Plot of $\ln(k_2/T)$ vs. $1/T$ for the oxidation of styrene (a) and norbornene (b)

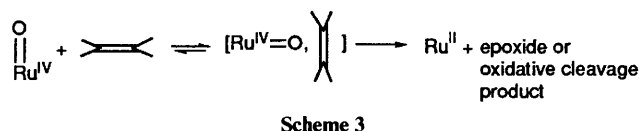
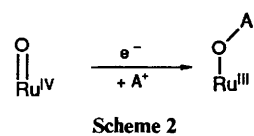
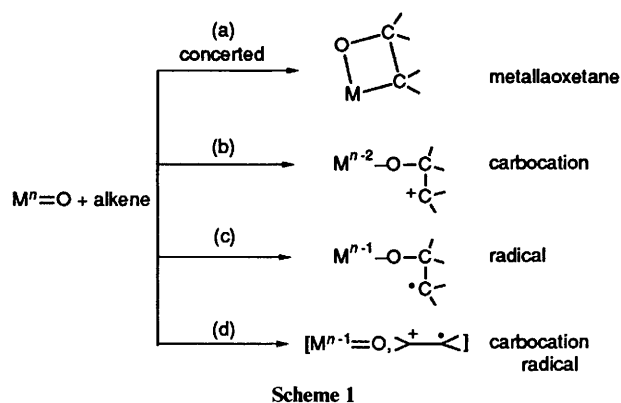
of an associated complex ($\text{Ru}^{\text{IV}}=\text{O}$, alcohol) prior to oxidation could be an important step in determining the overall rate of oxidation.

Alkenes. We have attempted to correlate the rate constants with the E° values of the $\text{Ru}^{\text{IV}}=\text{O}$ oxidant. At pH 1 the $\text{Ru}^{\text{IV}}-\text{Ru}^{\text{III}}$ couple has a value of 0.93, 0.99 and 1.13 V vs. SCE for $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{tmen})\text{O}]^{2+}$,⁶ $[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})\text{O}]^{2+}$ and $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}]^{2+}$ respectively. However, the rate constants for the oxidation of styrene, norbornene and cyclooctene by $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{dcbipy})\text{O}]^{2+}$ (ref. 6) are only 1.5–6-fold larger than that by $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{tmen})\text{O}]^{2+}$. With styrene as an example, the rate constants for the three systems are within a fraction of 2 but there is a 200 mV difference in their E° values. This is in contrast to the *trans*-dioxoruthenium(vi) system where the values of $\log k_2$ ($k_2 = \text{rate constant}$) correlate linearly with the E° values of the *trans*- $[\text{Ru}^{\text{VI}}\text{LO}_2]^{2+/+}$ couples ($L = \text{macrocyclic tertiary amine ligand}$).¹⁰ Thus for the dioxoruthenium(vi) system an increase in ≈ 150 mV will usually correspond to a 10-fold increase in the rate of oxidation.¹⁰

Table 4 Comparison of kinetic data for the oxidation of alkenes and alcohols by three different Ru^{IV}=O complexes^a

Substrate	10 ² k ₂ /dm ³ mol ⁻¹ s ⁻¹			ΔH [‡] /kcal mol ⁻¹		ΔS [‡] /cal K ⁻¹ mol ⁻¹	
	1	2	3	1	2	1	2
<i>(a)</i> Oxidation of alkenes in MeCN							
Styrene	1.48	2.80	2.00	7.2	11.1 ± 1.1	-43	-28.2 ± 3.0
<i>cis</i> -Stilbene	0.143						
<i>trans</i> -Stilbene	0.19						
Norbornene		1.08	0.33		12.3 ± 1.2		-26 ± 3
Cyclooctene		3.42	0.53				
4-Chlorostyrene		3.37					
4-Fluorostyrene		2.99					
4-Methylstyrene		6.30					
4-Methoxystyrene		865					
<i>(b)</i> Oxidation of alcohols							
	k ₂ /dm ³ mol ⁻¹ s ⁻¹			k _H /k _D			
	1	2	3	1	2		
Benzyl alcohol ^b	2.43	2.23		50	39		
[α,α'- ² H ₂]Benzyl alcohol ^b	0.048	0.057					
Propan-2-ol ^c	8.7 × 10 ⁻³	7.71 × 10 ⁻³	4.3 × 10 ⁻³				

^a Complexes: [Ru^{IV}(bipy)₂(py)O]²⁺ **1**, [Ru^{IV}(terpy)(dcbipy)O]²⁺ **2** and [Ru^{IV}(terpy)(tmen)O]²⁺ **3**. In 0.1 mol dm⁻³ HClO₄. ^b In MeCN.



The dependence of log *k*₂ on the substituent constants (σ^+) of *para*-substituted styrenes is shown in Fig. 5. The correlation is non-linear and with the exception of *p*-methoxystyrene the rate constants all fall within a narrow range, showing very little dependence on σ^+ . This non-linear relationship contrasts with the findings for other reactive metal-oxo systems like those of iron,¹¹ chromium¹² and manganese¹³ where a linear free-energy relationship for the oxidation is usually observed.

The temperature dependence of the rate constants for norbornene and styrene oxidation was studied and the results are in Table 4. The kinetic data are plotted in Fig. 6. The ΔH^\ddagger and ΔS^\ddagger values are 12.3 ± 1.2 kcal mol⁻¹ and -26.3 ± 3 cal K⁻¹ mol⁻¹ for norbornene and 11.1 ± 1.1 kcal mol⁻¹ and -28.2 ± 3 cal K⁻¹ mol⁻¹ for styrene. The large and negative ΔS^\ddagger values indicate that the reactions involve pre-association of the reactants. However, no rate saturation kinetics has been

observed. Large and negative ΔS^\ddagger values have also been reported for the oxidation of styrene by the related [Ru^{IV}-(bipy)₂(py)O]²⁺ (ref. 14) and [Ru^{IV}(bipy)₂(PPh₃)O]²⁺.¹⁵

According to previous mechanistic studies,¹¹⁻¹³ several possible intermediates have been proposed in the epoxidation of alkenes by metal-oxo complexes (Scheme 1). Bruice and Kochi and co-workers¹² proposed the intermediacy of an acyclic metal-oxo carbocation [pathway (b)] to account for the linear correlation of log(rate constant) with E° (metal-oxo oxidant or alkene) and the formation of rearranged products for oxochromium systems. Alternatively Traylor and Mikszal^{13c} suggested a caged carbocation radical [pathway (d)] for the haemin-catalysed oxidation. The latter pathway should be justified as the one-electron reduction potential of oxoiron should be high enough to facilitate extensive charge transfer during the epoxidation.

The results of this work indicate that for most of the alkenes studied a mechanism involving only charge transfer from the $>C=C<$ bond to the Ru^{IV}=O moiety could not explain the entire experimental findings. For example, there is only a very small dependence of the rate constants on the E° of the Ru^{IV}=O/Ru^{III}-OH couple of [Ru^{IV}(terpy)L(O)]²⁺. In the oxidation of *para*-substituted styrenes the span in the rate constants from 4-methyl- to 4-fluoro-styrene is less than three-fold despite a large difference in the σ^+ of the *para* substituent. The 1e or 2e reduction potential of Ru^{IV}=O is pH dependent. Thus, the reaction Ru^{IV}=O + e → Ru^{III}=O could occur at a very negative potential despite the high E° value of 1.13 V *vs.* SCE for [Ru^{IV}(terpy)(dcbipy)O]²⁺ at pH 1.0. Furthermore, Ru^{III}=O is a very high-energy intermediate. The reduction of Ru^{IV}=O to Ru^{III} is usually accompanied by breakage of the oxygen-ruthenium π bond together with co-ordination of a Lewis acid (A) on the oxygen atom as in Scheme 2. Thus pathway (c) is unlikely to be responsible for the alkene oxidation by Ru^{IV}=O. Pathway (b) is excluded on the basis of the kinetic data for the oxidation of *para*-substituted styrenes. However, the redox potential of the Ru^{IV}=O oxidant does affect alkene oxidation. For example, *trans*-[Ru^{IV}LO(MeCN)]²⁺ (L = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)¹⁶ with a much lower E° than that of [Ru^{IV}(terpy)(dcbipy)O]²⁺ is inert towards styrene and norbornene even at 50 °C. The mechanism in Scheme 3 is proposed. Both the pre-association of Ru^{IV}=O and alkene to form a precursor complex and charge transfer from $>C=C<$ to Ru=O affect the overall reaction rate.

Table 5 Oxidation of organic substrates by Bu^tO₂H catalysed by [Ru^{II}(terpy)(dcbipy)(H₂O)] [CF₃SO₃]₂ in acetone*

Substrate	Product	Turnover (% yield)	t/h
Cyclohexane	Cyclohexanol	128 (18)	4
	Cyclohexanone	87 (13)	
Adamantane	Adamantan-1-ol	87 (14)	4
	Adamantan-2-ol	19 (3)	
	Adamantan-2-one	9 (1.4)	
Methylcyclohexane	1-Methylcyclohexanol	25 (5.4)	4
	3-Methylcyclohexanone	11 (2.4)	
	4-Methylcyclohexanone	29 (6.4)	
	2- + 3- + 4-Methylcyclohexanol	33 (7.3)	
Norbornene	<i>exo</i> -2,3-Epoxynorbornane	183 (37)	4
Styrene	Styrene oxide	17 (3.2)	3
	Benzaldehyde	221 (40)	
Cyclooctene	Cyclooctene oxide	73 (15)	6

* Reaction conditions: 0.002 mmol catalyst, 1.4 mmol Bu^tO₂H, 0.2 g(solid)/0.5 cm³(liquid) substrate in acetone (2 cm³). Yield based on amount of Bu^tO₂H consumed.

cis-Stilbene has been used as a probe to study the mechanism of epoxidation,¹⁷ but here benzaldehyde was found to be the major product. We cannot confirm whether the oxidation occurring within the precursor complex [Ru^{IV}=O, >C=C<] can be rationalized by the concerted pathway (a) or the step-wise process (c). However, these pathways could simply represent extremes and the reaction may well be intermediate in character or proceed by more than one pathway.

Catalytic oxidation of hydrocarbons. Recently ruthenium-catalysed oxidation of alkanes with *tert*-butyl hydroperoxide has been reported using *cis*-[Ru^{II}L₂(H₂O)₂]²⁺ complexes as catalysts (L = substituted 2,2'-bipyridine or 1,10-phenanthroline).^{3b} The efficiencies of these catalysts have prompted us to continue similar investigations on [Ru^{II}(terpy)(dcbipy)(H₂O)]²⁺. The results are summarized in Table 5.

The ruthenium complex was found to be a highly active catalyst for both oxygenation of alkanes and alkenes. No oxidation product was detected in the absence of the catalyst. The recovery of the catalyst after the oxidation reactions was studied by ultraviolet-visible spectroscopy. The results indicated that over 96% of the catalyst was regenerated even after stirring the complex with Bu^tO₂H and organic substrate (*e.g.* norbornene) for 1 d. This robust oxidative catalyst thus offers the advantage of producing high product turnover numbers. For example a mixture of 0.002 mmol of the complex with 7 mmol of Bu^tO₂H and 1 g of norbornene in acetone (4 cm³) produced a 40% yield of norbornene oxide and a catalytic turnover number of > 1000. With aromatic alkenes like styrene, the carbonyl products were detected in high yields along with some epoxides.

The catalytic oxidation of alkanes was also found to be efficient. For the oxidation of cyclohexane the total turnovers of cyclohexanol and cyclohexanone are well over 200 after 4 h. Addition of Bu^tO₂H and cyclohexane similarly increases the turnover number to over 1000 after 8–10 h. The oxidation probably involves the formation of a cyclohexyl radical intermediate. This is because when an excellent atom donor or radical scavenger such as bromotrichloromethane was used as the cosolvent with acetone (1:10) in the cyclohexane oxidation, cyclohexyl bromide was detected in high yield.

The selectivity of this new [Ru^{II}(terpy)(dcbipy)(H₂O)]²⁺ complex has also been tested in the oxygenation of adamantane and methylcyclohexane. The alkane oxidation occurs preferentially at the tertiary C–H bond. The ratio of the tertiary to secondary hydrogen abstraction was found to be 9.3:1 for adamantane and 3.4:1 for methylcyclohexane respectively (after statistical correction for the number of C–H bonds for both types). These ratios are within the range expected for a radical pathway.

Alternative oxidants like iodosylbenzene(PhIO) and *m*-

chloroperoxybenzoic acid have also been used; however, only trace amounts of products were detected in each case.

Here we can almost eliminate the possibility of the Ru^{IV}=O oxo species as the active intermediate for the following reasons. (1) By ultraviolet-visible spectrophotometry, no immediate oxidation of Ru^{II} to Ru^{IV}=O by Bu^tO₂H was found in acetone. (2) The complex [Ru^{IV}(terpy)(dcbipy)O]²⁺ does not react with saturated hydrocarbons at room temperature. This contradicts the active oxygenation observed in the catalytic system. (3) The complex [Ru^{IV}(terpy)(dcbipy)O]²⁺ selectively oxidizes the 3° (C–H) bond of adamantane in contrast to the catalytic system where both the 2° and 3° (C–H) bonds are oxidized.

Conclusion

We have demonstrated that a stable and robust Ru^{IV}=O oxidant can be obtained with the ligand dcbipy. Oxidation of alcohols and alkenes by Ru^{IV}=O cannot be explained solely by a charge-transfer mechanism. The complex [Ru^{II}(terpy)(dcbipy)(H₂O)]²⁺ appears to be a stable catalyst for the oxidation of alkanes by Bu^tO₂H.

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