Kinetics and Mechanism of the Oxidation of Iodide by *trans*-Dioxoruthenium(VI)

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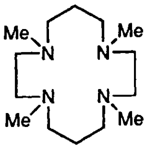
The kinetics of reduction of *trans*-[Ru(tmc)O$_2$]$^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) by iodide has been studied in aqueous acidic solution. The reaction has the following stoichiometry: *trans*-[Ru^{VI}(tmc)O$_2$]$^{2+}$ + 3I$^-$ + 2H$^+$ $\longrightarrow$ *trans*-[Ru^{IV}(tmc)O(OH$_2$)]$^{2+}$ + I$_3^-$. The rate law is $-d[Ru^{VI}]/dt = (k_a + k_b[H^+])[Ru^{VI}][I^-]$ with $k_a = 0.041 \pm 0.013$ dm^3 mol^{-1} s^{-1} and $k_b = 18.5 \pm 0.2$ dm^6 mol^{-2} s^{-2} at 25.0 °C and 0.1 mol dm^{-3} ionic strength. For k_a $\Delta H^‡ = 42.9 \pm 9.4$ kJ mol^{-1} and $\Delta S^‡ = -131 \pm 40$ J K^{-1} mol^{-1}, while for k_b, $\Delta H^‡ = 36.9 \pm 2.9$ kJ mol^{-1} and $\Delta S^‡ = -97 \pm 10$ J K^{-1} mol^{-1}. A mechanism involving oxygen-atom transfer from Ru^{VI} to iodide is consistent with the data.

In recent years a number of *trans*-dioxoruthenium(VI) species containing macrocyclic tertiary amine, pyridine and porphyrin ligands have been synthesized.[1] Studies on the reactions of this class of complexes with organic substrates indicate that they are potent oxidants which react through a variety of pathways including one-electron transfer, oxygen-atom transfer, hydrogen atom or hydride abstraction.[1,2] Less is known, however, about their reactivities toward simple inorganic substrates. We report here the kinetics of reduction of *trans*-[Ru^{VI}(tmc)O$_2$]$^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) by iodide. This complex is a mild oxidant which is particularly stable due to the macrocyclic tertiary amine ligand tmc, hence it is a suitable candidate for kinetic studies. It reacts by an outer-sphere one-electron pathway with substitution-inert ruthenium(II) reducing agents.[3] In the oxidation of substitution-labile Fe^{2+}(aq), however, it is suggested that an inner-sphere one-electron mechanism is involved with a binuclear Ru–O–Fe species as transition state.[4] On the other hand, the oxidation of PPh$_3$ to PPh$_3$O undoubtedly involves oxygen-atom transfer.[5] Although the oxidations of iodide by transition-metal complexes have been extensively studied,[6] most are outer-sphere one-electron reactions. In the present study with an oxoruthenium species as oxidant there are obviously additional pathways such as inner-sphere one-electron transfer and oxygen-atom transfer to iodide.

Experimental

Materials.—The complex *trans*-[Ru^{VI}(tmc)O$_2$][PF$_6$]$_2$ was prepared by a literature method.[7] The ionic strength was maintained with sodium trifluoroacetate. All chemicals were of reagent grade. Water for kinetic experiments was distilled twice from alkaline permanganate.

Kinetics.—The kinetics of the reaction was determined using a Hewlett-Packard 8452A diode-array spectrophotometer. The concentrations of iodide were at least in 10-fold excess of that of Ru^{VI}. The rate of the reaction was measured by monitoring the appearance of I$_3^-$ at 353 nm. Pseudo-first-order rate constants, k_{obs}, were obtained by non-linear least-squares fits of A_t *vs.* time t according to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, where A_0 and A_∞ are the initial and final absorbances, respectively. Second-order rate constants, k_2, were obtained from linear least-squares fits of k_{obs} *vs.* [I$^-$]. No difference in rate constants between reactions carried out in air and under argon were found, and most runs were done in air.



tmc

Products and Stoichiometry.—The amount of I$_3^-$ produced was determined spectrophotometrically at 353 nm by using known values of ε for I$_2$ and I$_3^-$ and the equilibrium constant for I$_2$ + I$^-$ $\rightleftharpoons$ I$_3^-$.[8] The molar absorption of coefficients of Ru^{VI} and Ru^{IV} are less than 5 × 10^2 dm^3 mol^{-1} cm^{-1} at this wavelength. One mol of I$_3^-$ was found to be produced per mol of Ru^{VI} consumed. The product resulting from the reduction of Ru^{VI} was determined as follows. A known amount of Ru^{VI} was allowed to react with an excess of iodide. The resulting solution was loaded onto Sephadex-SP C-25 cation-exchange resin. By eluting with 0.2 mol dm^{-3} HClO$_4$ and examining the UV/VIS spectrum of the solution *trans*-[Ru^{IV}(tmc)O(OH$_2$)]$^{2+}$ [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 420 (150), 280 (1600) and 210 (9800)][3,9] was found to be produced quantitatively.

Results and Discussion

Spectral Changes and Stoichiometry.—Rapid spectral changes were observed when a solution of Ru^{VI} was mixed with an excess of iodide in acidic solution. A well defined isosbestic point at 268 nm was maintained through the course of the reaction (Fig. 1). The final solution was found to contain 1 mol of Ru^{IV} and 1 mol of I$_3^-$ per mol of Ru^{VI} used (see Experimental section). Thus the overall reaction can be represented by equation (1).

$$[Ru^{VI}(tmc)O_2]^{2+} + 3I^- + 2H^+ \longrightarrow [Ru^{IV}(tmc)O(OH_2)]^{2+} + I_3^- \quad (1)$$

Kinetics.—The kinetics of the reaction was followed at 353 nm (λ_{max} of I$_3^-$). In the presence of at least 10-fold excess of I$^-$, clean pseudo-first-order kinetics was observed for over three half-lives. Representative data are collected in Table 1. The pseudo-first-order rate constants, k_{obs}, were independent of [Ru^{VI}] from 2.5 × 10^{-5} to 1 × 10^{-4} mol dm^{-3}, but depended linearly on [I$^-$], even at concentrations of I$^-$ up to 2000 times that of Ru^{VI}. Thus the experimentally determined rate law is as in equation (2).

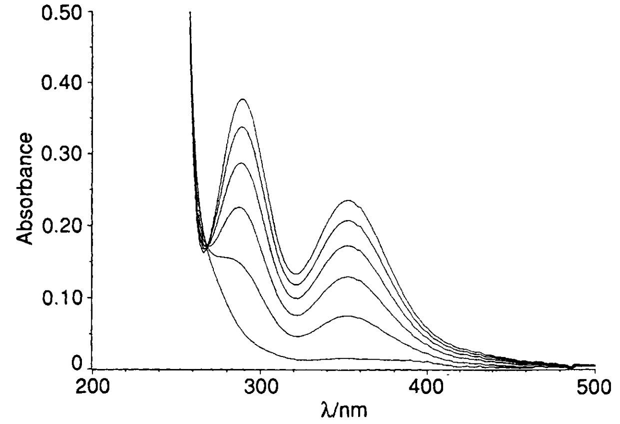


Fig. 1 Spectral changes during the reaction of $[\mathrm{Ru^{VI}(tmc)O_2}]^{2+}$ (5×10^{-5} mol dm^{-3}) with $\mathrm{I^-}$ (5×10^{-4} mol dm^{-3}) in 0.01 mol dm^{-3} $\mathrm{CF_3CO_2H}$ (I = 1.0 mol dm^{-3}) at 25 °C. The lowest curve is the initial spectrum taken *ca.* 10 s after mixing. Spectra were recorded at 500 s intervals

Table 1 Representative rate constants for the oxidation of iodide by $[\mathrm{Ru(tmc)O_2}]^{2+}$ *

T/K	I/mol dm^{-3}	$[\mathrm{H^+}]$/ mol dm^{-3}	$[\mathrm{I^-}]$/ mol dm^{-3}	k_{obs}/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}
298	0.1	0.10	1.0×10^{-3}	1.94×10^{-3}	1.92
	0.1	0.10	2.0×10^{-3}	3.88×10^{-3}	
	0.1	0.10	3.0×10^{-3}	6.14×10^{-3}	
	0.1	0.10	8.0×10^{-3}	1.52×10^{-2}	
	0.1	0.10	1.0×10^{-2}	1.95×10^{-2}	
	0.1	6.0×10^{-2}	1.0×10^{-3}	7.39×10^{-4}	1.20
	0.1	6.0×10^{-2}	5.0×10^{-3}	6.08×10^{-3}	
	0.1	6.0×10^{-2}	8.0×10^{-3}	9.23×10^{-3}	
	0.1	6.0×10^{-2}	1.0×10^{-2}	1.17×10^{-2}	
	0.1	2.0×10^{-2}	1.0×10^{-3}	4.65×10^{-4}	0.437
	0.1	2.0×10^{-2}	3.0×10^{-3}	1.25×10^{-3}	
	0.1	2.0×10^{-2}	8.0×10^{-3}	3.49×10^{-3}	
	0.1	2.0×10^{-2}	1.0×10^{-2}	4.37×10^{-3}	
	0.1	2.0×10^{-3}	1.0×10^{-3}	1.59×10^{-4}	0.0733
	0.1	2.0×10^{-3}	5.0×10^{-3}	4.84×10^{-4}	
	0.1	2.0×10^{-3}	8.0×10^{-3}	6.45×10^{-4}	
	0.1	2.0×10^{-3}	1.0×10^{-2}	8.40×10^{-4}	
	0.1	1.0×10^{-4}	1.0×10^{-3}	4.45×10^{-5}	0.027
	0.1	1.0×10^{-4}	5.0×10^{-3}	1.30×10^{-4}	
	0.1	1.0×10^{-4}	8.0×10^{-3}	2.03×10^{-4}	
	0.1	1.0×10^{-4}	1.0×10^{-2}	2.48×10^{-4}	
	0.01	1.0×10^{-4}	1.0×10^{-2}	7.40×10^{-4}	
	0.025	1.0×10^{-4}	1.0×10^{-2}	5.62×10^{-4}	
	0.05	1.0×10^{-4}	1.0×10^{-2}	4.16×10^{-4}	
	0.08	1.0×10^{-4}	1.0×10^{-2}	3.39×10^{-4}	
	0.10	1.0×10^{-4}	1.0×10^{-2}	2.48×10^{-4}	
290	0.1	1.0×10^{-4}			0.0181
298	0.1	1.0×10^{-4}			0.0270
305	0.1	1.0×10^{-4}			0.0426
312	0.1	1.0×10^{-4}			0.0682
318	0.1	1.0×10^{-4}			0.0876
290	0.1	4.0×10^{-2}			0.50
298	0.1	4.0×10^{-2}			0.715
305	0.1	4.0×10^{-2}			1.10
312	0.1	4.0×10^{-2}			1.43
318	0.1	4.0×10^{-2}			2.17

* Ionic strength was maintained with $\mathrm{Na(O_2CCF_3)_2}$; $[\mathrm{Ru^{VI}}]$ = 5.0×10^{-5}–1.0×10^{-4} mol dm^{-3}. Each value is the average of at least two determinations. Results are reproducible to within 5%.

$$-\mathrm{d}[\mathrm{Ru^{VI}}]/\mathrm{d}t = k_2[\mathrm{Ru^{VI}}][\mathrm{I^-}] = k_{obs}[\mathrm{Ru^{VI}}] \tag{2}$$

The effect of the ionic strength of the reaction rate was investigated from I = 0.01 to 0.1 mol dm^{-3} at $[\mathrm{I^-}]$ = 0.01 mol dm^{-3} and pH 4.0. As expected for a reaction between ions of opposite charges, k_2 decreases with increasing ionic strength; a plot of log k_{obs} *versus* $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ is linear with slope = -3.0 ± 0.2 and intercept = -2.8 ± 0.1.

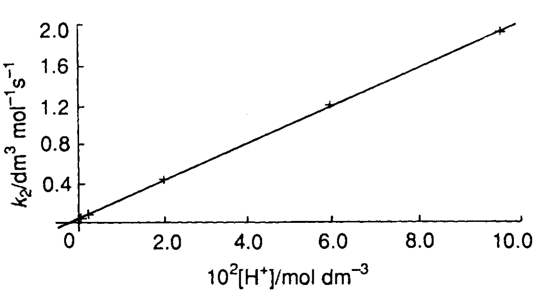


Fig. 2 Plot of k_2 *vs.* $[\mathrm{H^+}]$ at 25.0 °C and I = 0.1 mol dm^{-3}

The effect of acid on the rate constants was investigated in the concentration range $[\mathrm{H^+}]$ = 0.0001–0.10 mol dm^{-3}: k_2 was found to vary with $[\mathrm{H^+}]$ according to equation (3) (Fig. 2). At

$$k_2 = k_a + k_b[\mathrm{H^+}] \tag{3}$$

298 K and I = 0.1 mol dm^{-3} values of k_a and k_b are 0.041 ± 0.013 dm^3 mol^{-1} s^{-1} and 18.5 ± 0.2 dm^6 mol^{-2} s^{-2} respectively.

Activation parameters were obtained from plots of ln(k/T) *versus* $1/T$ according to the Eyring equation. For k_a, $\Delta H^{\ddagger}$ = 42.9 ± 9.4 kJ mol^{-1} and $\Delta S^{\ddagger}$ = -131 ± 40 J K^{-1} mol^{-1}, while for k_b, $\Delta H^{\ddagger}$ = 36.9 ± 2.9 kJ mol^{-1} and $\Delta S^{\ddagger}$ = -97 ± 10 J K^{-1} mol^{-1}.

Mechanism.—The one-electron outer-sphere oxidation of iodide has been studied for many complexes under conditions where the reverse reaction is negligible.[6] The stoichiometry is as in equation (4) the rate law is as in (5) and the general

$$2\mathrm{M_{ox}} + 2\mathrm{I^-} \longrightarrow 2\mathrm{M_{red}} + \mathrm{I_2} \tag{4}$$

$$-\mathrm{d}[\mathrm{M_{ox}}]/\mathrm{d}t = 2k_1[\mathrm{M_{ox}}][\mathrm{I^-}] + 2k_2[\mathrm{M_{ox}}][\mathrm{I^-}]^2 \tag{5}$$

mechanism is shown in Scheme 1.

$$\mathrm{M_{ox}} + \mathrm{I^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M_{red}} + \mathrm{I^{\bullet}} \tag{6}$$

$$\mathrm{M_{ox}} + 2\mathrm{I^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{M_{red}} + \mathrm{I_2^{\bullet -}} \tag{7}$$

$$\mathrm{M_{ox}} + \mathrm{I_2^{\bullet -}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{M_{red}} + \mathrm{I_2} \tag{8}$$

$$\mathrm{I^{\bullet}} + \mathrm{I^-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{I_2^{\bullet -}} \tag{9}$$

Scheme 1

Our results differ from the general rate law (5) in two important aspects. First, the reaction is dependent on $[\mathrm{H^+}]$. Secondly, it is strictly first order in iodide concentration even when $[\mathrm{I^-}]$ is 2000 $[\mathrm{Ru^{VI}}]$. A clue to the possible mechanism for this reaction may be obtained by estimating the rate constant (k_{12}) for the one-electron outer-sphere oxidation of iodide by $\mathrm{Ru^{VI}}$ using the Marcus cross-relation[10] (neglecting work terms) (10), The value of $K_{12} = 9.5 \times 10^{-14}$, the equilibrium constant

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{\frac{1}{2}} \tag{10}$$

$$\log f_{12} = (\log K_{12})^2/4\log(k_{11}k_{22}/10^{22}) \tag{11}$$

for the reaction, is calculated from the reduction potentials for the $\mathrm{Ru^{VI}}$–$\mathrm{Ru^{V}}$ (0.56 V)[11] and the $\mathrm{I^{\bullet}}$–$\mathrm{I^-}$ (1.33 V)[12] couples. A value of 1×10^5 dm^3 mol^{-1} s^{-1} is used for k_{11}, the self-exchange rate for Ru^{VI}–Ru^{V}; k_{22}, the self-exchange rate[12] for I$^•$–I$^-$, is taken as 1×10^9 dm^3 mol^{-1} s^{-1}. The value of k_{12} obtained in this manner is 7×10^{-3} dm^3 mol^{-1} s^{-1}. Although this calculated value is over two orders of magnitude lower than the experimental value measured in 0.1 mol dm^{-3} H$^+$, it is only about 10 times smaller than k_a, the rate constant for the proton-independent path; hence an outer-sphere one-electron pathway cannot be ruled out based on this calculation.

A one-electron pathway which accommodates the acid

$$\mathrm{O{=}Ru^{VI}{=}O + H^+ \rightleftharpoons O{=}Ru^{VI}{=}OH} \qquad (12)$$

$$\mathrm{O{=}Ru^{VI}{=}OH + I^- \rightleftharpoons O{=}Ru^{V}{=}OH + I^{\bullet}} \qquad (13)$$

$$\mathrm{O{=}Ru^{VI}{=}O + I^- \rightleftharpoons O{=}Ru^{V}{=}O + I^{\bullet}} \qquad (14)$$

$$\mathrm{O{=}Ru^{V}{=}O + H^+ \rightleftharpoons O{=}Ru^{V}{=}OH} \qquad (15)$$

$$\mathrm{O{=}Ru^{V}{=}OH + O{=}Ru^{V}{=}O + H^+ \longrightarrow O{=}Ru^{VI}{=}O + O{=}Ru^{IV}{-}OH_2} \qquad (16)$$

$$\mathrm{O{=}Ru^{VI}{=}O + I^{\bullet} \overset{fast}{\rightleftharpoons} products} \qquad (17)$$

Scheme 2

dependence is shown in Scheme 2. In this mechanism, oxidation of I$^-$ by both O=Ru^{VI}=OH and O=Ru^{VI}=O accounts for the presence of protonated and non-protonated paths. The dioxoruthenium(V) species is known to disproportionate rapidly in acidic solutions.[3] This mechanism is, however, discarded for the following reasons. No evidence of protonation of the ruthenium(VI) species is seen even in presence of 10 mol dm^{-3} H$^+$.[3] Moreover, no acid dependence was observed for the outer-sphere reduction of the complex by Ru^{II} (ref. 3) and the inner-sphere reduction by Fe^{II}.[4]

A mechanism that is consistent with all experimental observations involves a two-electron pathway as shown in Scheme 3. According to this mechanism the rate law is as in

$$\mathrm{O{=}Ru^{VI}{=}O + I^- \overset{\mathit{K}}{\rightleftharpoons} O{=}Ru^{IV}{-}OI} \qquad (18)$$

$$\mathrm{O{=}Ru^{IV}{-}OI + H_3O^+ \xrightarrow{\mathit{k}_5} O{=}Ru^{IV}{-}OH_2 + HOI} \qquad (19)$$

$$\mathrm{O{=}Ru^{IV}{-}OI + H_2O \xrightarrow{\mathit{k}_6} O{=}Ru^{IV}{-}OH + HOI} \qquad (20)$$

$$\mathrm{O{=}Ru^{IV}{-}OH + H^+ \longrightarrow O{=}Ru^{IV}{-}OH_2} \qquad (21)$$

$$\mathrm{HOI + I^- + H^+ \xrightarrow{fast} I_2 + H_2O} \qquad (22)$$

Scheme 3

equation (23) which is in accord with the experimental rate law

$$\text{Rate} = K(k_6 + k_5[\mathrm{H^+}])[\mathrm{Ru^{VI}}][\mathrm{I^-}] \qquad (23)$$

where $k_a = Kk_6$ and $k_b = Kk_5$. This mechanism involves oxygen-atom transfer from dioxoruthenium(VI) to I$^-$, which is analogous to oxidation of PPh$_3$ to PPh$_3$O.[5] A similar mechanism has also been proposed for the oxidation of I$^-$ by MnO$_4^-$.[13]

The one-electron pathway is uphill by 0.77 V. On the other hand, from the redox potentials[7,14] of half-reactions (24) and (25) the two-electron O-atom-transfer pathway is uphill only by

$$\mathrm{HOI + H^+ + 2e \longrightarrow I^- + H_2O};\ E^\circ = 0.985\ \mathrm{V} \qquad (24)$$

$$\mathrm{O{=}Ru^{VI}{=}O + 2e + 2H^+ \longrightarrow O{=}Ru^{IV}{-}OH_2};\ E^\circ = 0.90\ \mathrm{V} \qquad (25)$$

about 0.1 V, hence this pathway is energetically much more favourable than the one-electron pathway.

The outer-sphere one-electron oxidation[12] of I$^-$ by [Os(phen)$_3$]$^{3+}$ (phen = 1,10-phenanthroline) has $\Delta H^‡ = 57.3$ kJ mol^{-1} and $\Delta S^‡ = -17$ J K^{-1} mol^{-1}. The much more negative $\Delta S^‡$ values (-131 and -97 J K^{-1} mol^{-1} respectively for the non-protonated and protonated paths) observed in the present case (where the oxidant is also cationic) provide further evidence that a different mechanism is operating. The increase in $\Delta S^‡$ in going from the non-protonated to the protonated path can be explained by the release of water molecules by the proton in the transition state.

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