Kinetics and Mechanism of the Oxidation of Titanium(III) by Aqueous Solutions of Chlorine

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The kinetics of the non-complementary redox reaction $2Ti^{3+} + Cl_2 + 2H_2O \longrightarrow 2[TiO]^{2+} + 2Cl^- + 4H^+$ have been studied in acid solution. Under the conditions $0{\cdot}10 \leqslant [H^+] < 1{\cdot}0$M, $0{\cdot}05 \leqslant [Cl^-] \leqslant 1{\cdot}0$M, and ionic strength of 1·0M, the reaction follows strictly second-order kinetics with an apparent second-order rate constant of 125·0 ± 8·0 l mol^{-1} s^{-1} at $[H^+] = 0{\cdot}5$, $[Cl^-] = 0{\cdot}5$, $I = 1{\cdot}0$M, and 30 °C. The rate decreases as $[H^+]$ and $[Cl^-]$ are independently increased, but addition of Ti^{IV} has no effect on the rate. The results are interpreted in terms of $[Ti(OH)]^{2+} + Cl_2$, $[TiCl]^{2+} + HOCl$, and $Ti^{3+} + HOCl$ as the important activation paths. The rate constant for the $Ti^{3+} + HOCl$ path is $(1{\cdot}02 \pm 0{\cdot}01) \times 10^4$ l mol^{-1} s^{-1}, with the activation parameters $\Delta H^{\ddagger} = 16{\cdot}0 \pm 0{\cdot}2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 12{\cdot}58 \pm 0{\cdot}6$ cal K^{-1} mol^{-1}. For the $[Ti(OH)]^{2+} + Cl_2$ path, electron transfer *via* a series of one-electron changes is suggested. The role of prior hydrolysis in the kinetics of oxidation of aqua-ions to oxo-cations by acid solutions of halogens is discussed.

THE kinetics and mechanisms of reactions involving titanium(III) as reducing agent have aroused some interest quite recently.[1,2] Titanium(III) is a sufficiently strong reducing ion to be oxidized by aqueous solutions of chlorine, bromine, and iodine. The redox potentials for reaction (1) are 1·26 (X = Cl), 0·99 (Br), and 0·44 V

$$2Ti^{3+} + 2H_2O + X_2 \longrightarrow 2[TiO]^{2+} + 2X^- + 5H^+ \quad (1)$$

(I). A detailed kinetic study of reaction (1) for the three halogens could provide an insight into some of the factors that affect the kinetic reactivity of the halogens in solution. The kinetics of oxidation of Ti^{III} by aqueous solutions of iodine have been reported by Johnson and Winstein.[3] Their results are consistent with rate equation (2). In this work we report our findings on a

$$\frac{1}{2}\frac{d[Ti^{III}]}{dt} = -\frac{d[I_2]}{dt} = k'\frac{[Ti^{III}][I_3^-]}{[H^+][I^-]} + \frac{k''[Ti^{III}][I_3^-]}{[H^+]} + \frac{k'''[Ti^{III}]}{[H^+]} \quad (2)$$

kinetic investigation of the oxidation of Ti^{III} by chlorine in aqueous acid solutions.

EXPERIMENTAL

Titanium(III) reacts [4] with perchlorate solutions, although quite slowly, and the reaction is sufficiently significant to make it inexpedient to use $Ti(ClO_4)_3$ as the source of Ti^{3+}. Titanium(III) chloride and a chloride medium are, therefore, commonly employed in studying Ti^{III} solution reactions.[1,2] Titanium(III) was prepared by dissolving titanium metal (99·8% pure) in properly deaerated, 4—6M hydrochloric acid.† The dissolution process continued for *ca.* 3—4 h and the temperature of the reaction mixture was kept at 50—70 °C. Nitrogen was continuously passed into the reaction mixture to maintain an inert atmosphere. The undissolved titanium metal was filtered off, and the filtrate was thoroughly flushed with nitrogen and kept in an atmosphere where the temperature was less than 0 °C. Concentrations of titanium were determined by adding a known excess of cerium(IV) sulphate to an aliquot portion of the Ti^{III} solution. The excess of cerium(IV) sulphate was determined by iodometry. The free acid in the titanium solution was determined by cation exchange using Amberlite 120 resin. Total cation was determined, the free acid being the total cation in the solution less three times the concentration of the titanium solution. Since the only anion in the solution was Cl$^-$, the total concentration of the cation was also the amount of Cl$^-$ present in solution. The total $[Cl^-]$ and free $[H^+]$ were both taken into account in making up the reaction medium to the required $[H^+]$ and $[Cl^-]$. Aqueous solutions of chlorine were prepared and their concentrations determined as previously described.[5] Sodium perchlorate, sodium chloride, and lithium chloride were all D.D.H. (AnalaR) and were used without further purification.

The kinetics of the reaction were followed using a Durrum–Gibson stopped-flow spectrophotometer in which the flow component was made of KEL-F. The course of the reaction was followed by monitoring changes in the absorbance of chlorine in the wavelength region 340—350 nm, where for the concentration range employed only chlorine has significant absorbance. The rate curves were all smooth showing that there were no complexities arising from side reactions of possible impurities (particularly iron [1b,2]) in the reaction system. All kinetic runs were carried out at an ionic strength of 1·0M maintained with lithium chloride and lithium perchlorate. To avoid the Ti^{III}–$[ClO_4]^-$ reactions, Ti^{III} solutions were added to HCl and when necessary perchlorate solutions were contained in the chlorine solutions. Both titanium and chlorine solutions were each maintained at a constant ionic strength of 1·0M.

RESULTS

Stoicheiometry.—Experiments in $[H^+] = 0{\cdot}5$, $[Cl^-] = 1{\cdot}0$, and $I = 1{\cdot}0$M, using both initial excess amounts of Ti^{III} and Cl$_2$, showed that the average stoicheiometry was 2·01 ± 0·06 mol of Ti^{III} consumed per mol of chlorine, and the equation for this reaction is therefore as in (1) (X = Cl).

Kinetics.—The reaction was shown to be first order in $[Ti^{III}]$, and also first order in $[Cl_2]$, as follows. Rates of reaction were measured under conditions in which $[Ti^{III}]_0$ was in at least 16—50-fold excess over $[Cl_2]_0$. Pseudo-first-order plots in $[Cl_2]$ were linear for more than 90% completion of reaction. Plots of log k' (k' being the pseudo-first-order rate constants obtained for each $[Ti^{III}]_0$) against log $[Ti^{III}]_0$

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† 1M = 1 mol dm^{-3}, 1 cal = 4·184 J.

[1] J. D. Ellis and A. G. Sykes, *J.C.S. Dalton*, (*a*) 1973, 537; (*b*) p. 2553.

[2] J. P. Birk and T. P. Logan, *Inorg. Chem.*, 1973, **12**, 580 and refs. therein.

[3] D. M. Yost and S. Zaharo, *J. Amer. Chem. Soc.*, 1926, **48**, 1181; C. E. Johnson and S. Winstein, *J. Amer. Chem. Soc.*, 1951, **73**, 2601.

[4] F. R. Duke and P. R. Quinney, *J. Amer. Chem. Soc.*, 1954, **76**, 3800; V. W. Cope, R. G. Miller, and R. T. M. Fraser, *J. Chem. Soc.* (*A*), 1967, 301.

[5] A. Adegite and M. F. Ford-Smith, *J.C.S. Dalton*, 1973, 138.

were linear and of gradient 1·09 ± 0·07, thus confirming that the reaction is also first order in $[\mathrm{Ti^{III}}]$. Apparent second-order rate constants, k_0, were obtained from the k' values. In addition, k_0 was also determined under conditions in which $[\mathrm{Ti^{III}}]_0$ and $[\mathrm{Cl_2}]_0$ did not differ significantly, and from the log $([\mathrm{Ti^{III}}]/[\mathrm{Cl_2}])$ against t plots k_0 was obtained (Table 1). The results show that at constant $[\mathrm{H^+}]$ and $[\mathrm{Cl^-}]$ the rate equation is as in (3) with $k_0 = (1{\cdot}25 \pm$

$$-\tfrac{1}{2}\frac{d[\mathrm{Ti^{III}}]}{dt} = -\frac{d[\mathrm{Cl_2}]}{dt} = k_0[\mathrm{Ti^{III}}][\mathrm{Cl_2}] \qquad (3)$$

$0{\cdot}08) \times 10^2$ l mol^{-1} s^{-1} at 30 °C, $[\mathrm{H^+}] = 0{\cdot}5$, $[\mathrm{Cl^-}] = 0{\cdot}5$, and $I = 1{\cdot}0$M.

TABLE 1

Rate constants for the $\mathrm{Ti^{III}}$–$\mathrm{Cl_2}$ reaction under different conditions at $[\mathrm{Cl^-}] = 0{\cdot}5$ and $I = 4{\cdot}0$M unless otherwise stated (all concentrations are expressed in mol l^{-1})

θ_c/°C	$10^2[\mathrm{Ti^{III}}]$	$10^3[\mathrm{Cl_2}]$	$[\mathrm{H^+}]$	$10^{-2}k_0$/l mol^{-1} s^{-1} obs.	$10^{-2}k_0$/l mol^{-1} s^{-1} calc.
30	1·21	0·75	0·50	1·21	
	1·92	0·75	0·50	1·22	
	2·56	0·75	0·50	1·10	
	3·20	0·75	0·50	1·22	
	3·84	0·75	0·50	1·40	
	1·13	1·22	0·50	1·30	
	0·25	2·10	0·50	1·30	
	0·34	2·10	0·50	1·22	
	0·34	3·20	0·50	1·26	
	0·85	3·20	0·50	1·25	
				Mean 1·25 ± 0·08	
	1·83	0·75	0.50		1·24 [a]
	1·83	0·75	0·50		1·18 [a]
	1·83	0·75	0·50		1·22 [a]
	1·83	0·75	0·50		1·20 [a]
	1·83	0·75	0·10	5·40	5·73
	1·83	0·75	0·20	2·90	2·93
	1·83	0·75	0·30	1·90	1·97
	0·93	1·60	0·60	0·89	1·19
	0·85	1·60	0·70	0·77	0·99
	0·93	1·60	0·80	0·74	0·74
	0·85	1·60	0.90	0·62	0·66
	0·85	1·60	1·00	0·54	0·60

θ_c/°C	$[\mathrm{Cl^-}]$	$10^{-2}k_0$/ l mol^{-1} s^{-1}	θ_c/°C	$[\mathrm{Cl^-}]$	$10^{-2}k_0$/ l mol^{-1} s^{-1}
30	0·20 [b]	1·47	15	0·10	0·66
	0·60	1·15		0·20	0·54
	0·80	1·04		0·40	0·49
	1·00	0·99		0·50	0·47
20·8	0·05	1·21	11	0·07	0·51
	0·10	1·14		0·17	0·50
	0·20	0·97		0·27	0·44
	0·30	0·85		0·37	0·43
	0·50	0·74		0·47	0·40
15	0·07	0·79			

[a] Concentrations of $\mathrm{Ti^{IV}}$ varying from $1{\cdot}0 \times 10^{-3}$ to $1{\cdot}0 \times 10^{-2}$M were initially added to the reaction medium. [b] In all runs investigating the effect of $[\mathrm{Cl^-}]$: $[\mathrm{H^+}] = 0{\cdot}50$, $[\mathrm{Ti^{III}}] = 0{\cdot}32 \times 10^{-2}$—$2{\cdot}40 \times 10^{-2}$, and $[\mathrm{Cl_2}] = 0{\cdot}75 \times 10^{-3}$—$0{\cdot}98 \times 10^{-3}$M.

Effect of Hydrogen Ions on the Rate.—The influence of $[\mathrm{H^+}]$ on the rate of reaction was investigated by determining k_0 at various $[\mathrm{H^+}]$. For $[\mathrm{H^+}] \leqslant 0{\cdot}5$M, HCl was varied, and a constant value of the ionic strength and $[\mathrm{Cl^-}]$ were maintained by adding the necessary aliquot portions of LiCl solution. For $[\mathrm{H^+}] > 0{\cdot}5$M, $\mathrm{HClO_4}$ was added to the chlorine solution such that $[\mathrm{H^+}]$ in the reaction mixture would be the expected amount and $[\mathrm{Cl^-}]$ would remain constant at 0·5M. The results (Table 1) show that k_0 decreases as $[\mathrm{H^+}]$ increases. A plot of log k_0 against log $[\mathrm{H^+}]$ was linear, of gradient −1·00 ± 0·01, thus confirming an order of −1·0 with respect to $[\mathrm{H^+}]$. Therefore in the range $0{\cdot}10 \leqslant [\mathrm{H^+}] \leqslant 1{\cdot}0$M, in which the kinetics were investigated, the rate equation is (4) with $k_\mathrm{T} = (0{\cdot}56 \pm 0{\cdot}03) \times 10^2$ s^{-1} at $[\mathrm{Cl^-}] = 0{\cdot}50$M, $I = 1{\cdot}0$M, and 30 °C.

$$\text{Rate} = k_\mathrm{T}[\mathrm{Ti^{III}}][\mathrm{Cl_2}]/[\mathrm{H^+}] \qquad (4)$$

Effect of Products.—The results presented in Table 1 show that added $\mathrm{Ti^{IV}}$ has no effect on the rate, but k_0 decreases as $[\mathrm{Cl^-}]$ increases.

Analysis of the Effects of Hydrogen Ion and Chloride on the Rate Constants.—A customary rationalization of the decrease in k_0 as both $[\mathrm{Cl^-}]$ and $[\mathrm{H^+}]$ increase is in terms of fast pre-equilibria which result in the formation of hydrolysed species and chloro-complexes of $\mathrm{Ti^{3+}}$ and $\mathrm{Cl_2}$. Equations (5)—(8) are therefore suggested as the relevant equilibrium steps that precede the activation paths (9)—(12). The Cl formed

$$[\mathrm{Ti(OH_2)_6}]^{3+} \overset{K_1}{\rightleftharpoons} [\mathrm{(H_2O)_5Ti(OH)}]^{2+} + \mathrm{H^+} \qquad (5)$$

$$\mathrm{Ti^{3+}} + \mathrm{Cl^-} \overset{K_2}{\rightleftharpoons} [\mathrm{TiCl}]^{2+} \qquad (6)$$

$$\mathrm{Cl_2} + \mathrm{H_2O} \overset{K_3}{\rightleftharpoons} \mathrm{HOCl} + \mathrm{H^+} + \mathrm{Cl^-} \qquad (7)$$

$$\mathrm{Cl_2} + \mathrm{Cl^-} \overset{K_4}{\rightleftharpoons} [\mathrm{Cl_3}]^- \qquad (8)$$

$$[\mathrm{Ti(OH)}]^{2+} + \mathrm{Cl_2} \xrightarrow{k_1} [\mathrm{TiO}]^{2+} + \mathrm{H^+} + [\mathrm{Cl_2}]^- \qquad (9)$$

$$[\mathrm{TiCl}]^{2+} + \mathrm{HOCl} \xrightarrow{k_2} [\mathrm{TiO}]^{2+} + \mathrm{H^+} + [\mathrm{Cl_2}]^- \qquad (10)$$

$$\mathrm{Ti^{3+}} + \mathrm{HOCl} \xrightarrow{k_3} [\mathrm{Ti(OH)}]^{3+} + \mathrm{Cl} + \mathrm{Ti} \qquad (11)$$

$$[\mathrm{Ti(OH)}]^{2+} + [\mathrm{Cl_3}]^- \xrightarrow{k_4} [\mathrm{Ti(OH)}]^{3+} + \mathrm{Cl^-} + [\mathrm{Cl_2}]^- \qquad (12)$$

in (11) most probably combines very rapidly with $\mathrm{Cl^-}$ to form $[\mathrm{Cl_2}]^{-\bullet}$, which subsequently also reacts very rapidly with $[\mathrm{Ti(OH)}]^{2+}$. Other possible steps such as $\mathrm{Ti^{3+}} + \mathrm{Cl_2}$, $[\mathrm{Ti(OH)}]^{2+} + \mathrm{HOCl}$, and $[\mathrm{Ti(OH)_2}]^+ + \mathrm{Cl_2}$ are considered unimportant because they would not be consistent with the form of acid dependence obtained. The rate equation for the system can, therefore, be written as (13). Since

$$\begin{aligned}\text{Rate} &= k_0\Sigma[\mathrm{Ti^{III}}]\Sigma[\mathrm{Cl_2}] = k_1[\mathrm{Ti(OH)^{2+}}][\mathrm{Cl_2}] + k_2[\mathrm{TiCl^{2+}}][\mathrm{HOCl}] + k_3[\mathrm{Ti^{3+}}][\mathrm{HOCl}] + k_4[\mathrm{Ti(OH)^{2+}}][\mathrm{Cl_3^-}] \\ &= \frac{[\mathrm{Ti^{3+}}][\mathrm{Cl_2}]}{[\mathrm{H^+}][\mathrm{Cl^-}]}(e[\mathrm{Cl^-}] + f + g[\mathrm{Cl^-}]^2) \qquad (13)\end{aligned}$$

where $e = k_1K_1 + k_2K_2K_3$, $f = k_3K_3$, and $g = k_4K_1K_4$

$\Sigma[\mathrm{Ti^{III}}] = [\mathrm{Ti^{3+}}] + [\mathrm{Ti(OH)^{2+}}] + [\mathrm{TiCl^{2+}}]$ and $\Sigma[\mathrm{Cl_2}] = [\mathrm{Cl_2}] + [\mathrm{HOCl}] + [\mathrm{Cl_3^-}]$, we obtain equation (14). Equating the right-hand side of expression (14) to that of (13) gives (15).

$$k_0[\mathrm{Ti^{III}}][\mathrm{Cl_2}] = k_0\frac{[\mathrm{Ti^{3+}}][\mathrm{Cl_2}]}{[\mathrm{H^+}]^2[\mathrm{Cl^-}]}([\mathrm{H^+}] + K_1 + K_2[\mathrm{H^+}][\mathrm{Cl^-}])([\mathrm{H^+}][\mathrm{Cl^-}] + K_3 + K_4[\mathrm{H^+}][\mathrm{Cl^-}]^2) \qquad (14)$$

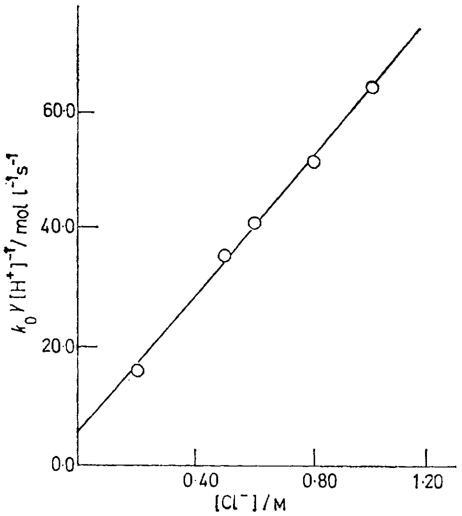
$$\frac{k_0}{[\mathrm{H^+}]}([\mathrm{H^+}] + K_1 + K_2[\mathrm{H^+}][\mathrm{Cl^-}])([\mathrm{H^+}][\mathrm{Cl^-}] + K_3 + K_4[\mathrm{H^+}][\mathrm{Cl^-}]^2) = \frac{k_0Y}{[\mathrm{H^+}]} = e[\mathrm{Cl^-}] + f + g[\mathrm{Cl^-}]^2 \qquad (15)$$

TABLE 2

Values of e, f, and k_3 at various temperatures for the Ti^{III}–Cl_2 reaction

θ_c/°C	e/s^{-1}	f/mol l^{-1} s^{-1}	$10^{-4}k_3$/ l mol^{-1} s^{-1}
30·0	58·54	4·65	1·02
20·8	40·98	1·48	0·43
15·0	24·53	0·97	0·35
11·0	22·11	0·29	0·15

In order to obtain values of e and f we assumed that g is small and hence $k_0Y/[H^+]$ is a linear function of $[Cl^-]$. Thus, a plot of $k_0Y/[H^+]$ against $[Cl^-]$ should be linear with slope e and intercept f. The plot was indeed linear (Figure), thus justifying the validity of the assumption. From the gradient and intercept, we obtain * $e = 58{\cdot}57 \pm 0{\cdot}03$ s^{-1} and $f = 4{\cdot}65 \pm 0{\cdot}02$ mol l^{-1} s^{-1}. Since $e = k_1K_1 + k_2K_2K_3$, it is not possible to obtain independent values for k_1 or k_2 from the gradient of the curve. However, from the value of f, k_3 was found to be $(1{\cdot}02 \pm 0{\cdot}10) \times 10^4$ l mol^{-2} s^{-1}. A further test of the appropriateness of equation (15), and hence the validity of our assumption (putting $g = 0$), was to substitute the values of e and f into (15) and then calculate k_0 for each $[H^+]$ at constant $[Cl^-]$. The results, which show a good agreement between the calculated and experimental value of k_0, are presented in the last column of Table 1. Values of e and f, and hence k_3, were determined for three other temperatures (Table 2). The activation parameters obtained for e and k_3 are $\Delta H^‡ = 8{\cdot}9 \pm 0{\cdot}1$ kcal mol^{-1} and $\Delta S^‡ = -21{\cdot}0 \pm 0{\cdot}8$ cal K^{-1} mol^{-1}, and $\Delta H^‡ = 16{\cdot}0 \pm 0{\cdot}2$ kcal mol^{-1} and $\Delta S^‡ = 12{\cdot}5 \pm 0{\cdot}6$ cal K^{-1} mol^{-1}, respectively.



Effect of chloride on the Ti^{III}–Cl_2 reaction. Plot of $k_0Y/[H^+]$ against $[Cl^-]$ [equation (15)] at $[H^+] = 0{\cdot}5$M, $I = 1{\cdot}0$M, and 30 °C

TABLE 3

Kinetic data for the oxidation of some metal aqua-ions to oxo-cations by aqueous acid solutions of halogens

Reaction	Order with respect to $[H^+]$	Principal reactant species	Ref.
$2V^{3+} + [I_3]^- + 2H_2O \longrightarrow 2[VO]^{2+} + 3I^- + 4H^+$	−1	$[V(OH)]^{2+} + [I_3]^-$	19
$2V^{3+} + Br_2 + 2H_2O \longrightarrow 2[VO]^{2+} + 2Br^- + 4H^+$	−1	$[V(OH)]^{2+} + Br_2$	20
$2[VO]^{2+} + Cl_2 + 2H_2O \longrightarrow 2[VO]^{2+} + 2Cl^- + 4H^+$	−1	$[VO(OH)]^+ + Cl_2$	7
		$[VO]^{2+} + HOCl$	7
$U^{4+} + Cl_2 + 2H_2O \longrightarrow [UO_2]^{2+} + 2Cl^- + 4H^+$	−2	$[U(OH)_2]^{2+} + Cl_2$	5
		$[U(OH)]^{3+} + HOCl$	5
$U^{4+} + Br_2 + 2H_2O \longrightarrow [UO_2]^{2+} + 2Br^- + 4H^+$	−2	$[U(OH)_2]^{2+} + Br_2$	*
$U^{4+} + I_2 + 2H_2O \longrightarrow [UO_2]^{2+} + 2I^- + 4H^+$	−2	$[U(OH)_2]^{2+} + I_2$	†
$2Ti^{3+} + [I_3]^- + 2H_2O \longrightarrow 2[TiO]^{2+} + 3I^- + 4H^+$	−1	$[Ti(OH)]^{2+} + [I_3]^-$	3
		$[Ti(OH)]^{2+} + I_2$	3
$2Ti^{3+} + Cl_2 + 2H_2O \longrightarrow 2[TiO]^{2+} + 2Cl^- + 4H^+$	−1	$[Ti(OH)]^{2+} + Cl_2$	‡
		$Ti^{3+} + HOCl$	‡

* G. Gordon and A. Andrews, *Inorg. Chem.*, 1964, **3**, 1933. † A. Adegite and M. H. Ford-Smith, *J.C.S. Dalton*, 1973, 134. ‡ This work.

DISCUSSION

Although it is uncertain whether Ti^{IV} exists as $[TiO]^{2+}$ or $[Ti(OH)_2]^{2+}$, that Ti^{III} exists predominantly as Ti^{3+} in acid solution is well established.[1] Therefore, oxidation of Ti^{III} to Ti^{IV} is accompanied by conversion of an aqua-ion to an oxo- or hydroxo-cation. Reactions in which aqua-ions are oxidized to oxo-cations by acid solutions of halogens seem to show similar hydrogen-ion dependences as obtained in this investigation. For the purpose of comparison, kinetic data are presented for such systems in Table 3. Three generalizations appear common to all. (*i*) Direct electron transfer does not occur between the aqua-ion and the halogen, *i.e.* activation paths of the form $M^{n+}(aq) + X_2 \longrightarrow$ activated complex are unimportant in these reactions. (*ii*) The

* Values of the equilibrium constants employed in this work are from literature reports, and they were used without correction for ionic-strength differences; $K_1 = 2{\cdot}8 \times 10^{-3}$ mol l^{-1} is from the data reported by Paris and Gregoire [6] at $I = 3{\cdot}0$M (KBr) and 25 °C. Since ΔH for the hydrolysis of Ti^{3+} has not been measured, it was assumed equal to 11·0 kcal mol^{-1}, that obtained by Furman and Gardner (*J. Amer. Chem. Soc.*, 1950, **72**, 1785) for hydrolysis of V^{3+}, an assumption made earlier by Ellis and Sykes.[1a] The constant $K_2 = 0{\cdot}07$ l mol^{-1} at 25 °C, and probably at zero ionic strength (H. J. Gardner, *Austral. J. Chem.*, 1967, **20**, 2057). Values of K_3 employed in the analysis were $4{\cdot}529 \times 10^{-4}$, $3{\cdot}443 \times 10^{-4}$, $2{\cdot}809 \times 10^{-4}$, and $2{\cdot}421 \times 10^{-4}$ mol^2 l^2 at 30, 20·8, 15, and 11 °C respectively. They were obtained from data reported by R. E. Connick and Y. T. Chia (*J. Amer. Chem. Soc.*, 1959, **81**, 1280). The constant $K_4 = 0{\cdot}19$ l mol^{-1} at zero ionic strength and 25 °C was from the work of J. Greensberg and B. R. Sundheim (*J. Chem. Phys.*, 1958, **29**, 1029). Variations of K_2 and K_4 with temperature have not been reported and, therefore, the values measured for 25 °C were used for all temperatures in this work.

[6] M. R. Paris and C. L. Gregoire, *Analyt. Chim. Acta*, 1968, **42**, 439.

[7] A. Adegite, *J.C.S. Dalton*, 1975, preceding paper.

precursor hydrolysed species formed before the electron-transfer steps contain the same number of oxygen atoms as the final products, *viz.* for $M^{n+} \longrightarrow [MO]^{(n-1)+}$ the hydrolysed species are $[M(OH)]^{(n-1)+}$ and for $M^{n+} \longrightarrow [MO_2]^{(n-2)+}$ the hydrolysed species are $[M(OH)_2]^{(n-2)+}$. (*iii*) It is uncertain whether such hydrolysed species are involved in the formation of inner-sphere activated complexes or intermediates, and therefore the generally observed inverse hydrogen-ion dependence is not necessarily evidence of an inner-sphere mechanism. It can therefore be suggested that the $[H^+]^{-1}$ or $[H^+]^{-2}$ dependences of the rate constants of these reactions are due to prior formation of hydroxo-complexes that are structurally very close to the products, and hence react with much lower activation energies than the aqua-ions or species that are more hydrolysed than the final products of the reaction. These hydroxo-complexes could then react with the halogens by either an outer- or inner-sphere mechanism.

As in the U^{IV}–Cl_2 and V^{IV}–Cl_2 reactions,[5,7] HOCl reacts with less hydrolysed metal-ion species than Cl_2. This is highly suggestive of an inner-sphere mechanism in which an oxygen atom is transferred from HOCl to the metal ion. The rate constant (k_3) for the Ti^{3+}–HOCl reaction is $1{\cdot}02 \times 10^4$ l mol^{-1} s^{-1}, which is in the range of the rate constant for substitution [1] into $[Ti(OH_2)_6]^{3+}$. Therefore, it is possible that this reaction, like the Ti^{3+}–$[VO_2]^+$ reaction, is substitution controlled. The oxidation of Ti^{III} by chlorine is a non-complementary reaction which could proceed by either a two-electron transfer as in (16) and (17) or by a series of univalent changes as in (18)

$$Ti^{III} + Cl_2 \underset{k_{-16}}{\overset{k_{16}}{\rightleftharpoons}} Ti^{V} + 2Cl^- \qquad (16)$$

$$Ti^{III} + Ti^{V} \xrightarrow{k_{17}} [(Ti^{IV})_2] \longrightarrow 2Ti^{IV} \qquad (17)$$

and (19). We did not observe the complicated kinetics which were partly associated with such dimeric titanium species as reported by Birk and Logan.[2] Moreover, if equation (16) were the slowest step, and hence rate determining, inhibition by Cl^- might be expected. Our results do show that added Cl^- decreases the rate of the reaction, but the analysis of the effect of added Cl^- on the rate confirms that the observed inhibition is primarily due to complexing reactions involving the formation of $[TiCl]^{2+}$ and $[Cl_3]^-$ and also the suppression of hydrolysis of Cl_2 to give HOCl, which reacts at a faster rate with Ti^{III} than Cl_2(aq). A similar interpretation had earlier been given to the observed decrease in rate by added Cl^- in the chlorine oxidation [5,9] of uranium(IV) and vanadium(IV).

Since both V^{IV} and Ti^{III} are d^1 metal ions and V^{IV} reactions proceed rigidly by one-electron changes [8] as attested by the V^{IV}–Ti^{III}, V^{IV}–Cl_2, and V^{IV}–Cr^{VI} reactions,[7,9,10] it is suggested that d^1 ions prefer not to react by two-electron-transfer processes which would entail transferring electrons from their completely filled penultimate orbitals. Therefore, the Ti^{III}–Cl_2 reaction most probably proceeds according to equations (18) and (19). Here $k_{19} \gg k_{18}$, and hence inhibition by Ti^{IV} is not observed. In general, in halogen reactions that proceed by the reactions (18) and (19), reversibility in the first step and expected product inhibition seems to depend on the free energy, $\Delta G^{\ominus}$, for the first step. If $E^{\ominus}$ for the M^{n+}–$M^{(n-1)+}$ couple is much less than that for X_2–$[X_2]^{-\cdot}$ (X = I, Br, or Cl), $\Delta G^{\ominus}$ for the first step will be less than zero, the first step in one-electron changes will not be reversible in the kinetic sense, and inhibition by M^{n+}, the oxidation product of the reaction, will not be observed. However, if the reverse is true, the first step will be reversible in the sense that M^{n+} will inhibit the reaction. The V^{IV}–Cl_2 and V^{IV}–Br_2 reactions ($E^{\ominus} = 1{\cdot}00$ V for the V^V–V^{IV} couple, 0·4—0·6 V, estimated for the Cl_2–$[Cl_2]^{-\cdot}$ and Br_2–$[Br_2]^{-\cdot}$ couples) [7,11-17] which are strongly inhibited by V^V, and Fe–Br_2 ($E^{\ominus} = 0{\cdot}77$ V for Fe^{3+}–Fe^{2+}), inhibited [18] by Fe^{III}, provide good examples of the latter case, while Ti^{III}–I_2, V^{III}–I_2, V^{III}–Br_2, and the present work are good examples [3,19,20] of the former.

$$Ti^{III} + Cl_2 \underset{k_{-18}}{\overset{k_{18}}{\rightleftharpoons}} Ti^{IV} + [Cl_2]^{-\cdot} \qquad (18)$$

$$Ti^{III} + [Cl_2]^{-\cdot} \xrightarrow{k_{19}} Ti^{IV} + 2Cl^- \qquad (19)$$

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