Kinetics of Reaction of Vanadium(IV) with Chlorine in Aqueous Solutions

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The kinetics of the reaction $2[VO]^{2+} + Cl_2 + 2H_2O \longrightarrow 2[VO_2]^+ + 2Cl^- + 4H^+$ have been studied in aqueous solutions at 25 °C, with hydrogen-ion concentration in the range 0·10—1·0M and an ionic strength of 1·0M. In the initial stages of the reaction, and for conditions in which $[V^{IV}]_0 \gg [Cl_2]_0$, without any initial addition of V^V, the reaction follows the rate law $-\frac{1}{2}d[V^{IV}]/dt = -d[Cl_2]/dt = k_0'[V^{IV}][Cl_2]/[H^+]$ where $k_0' = 5·32 \pm 0·39$ s^{-1} at 25 °C. The reaction is strongly inhibited by vanadium(V), and hence marked deviation from the rate law is observed as the reaction progresses. Chloride ion also decreases the rate. The results are consistent with a mechanism involving $[Cl_2]^{-\bullet}$ as a transient intermediate. From the analysis of the Cl^- dependence of the apparent second-order rate constant obtained under conditions in which the rate law is valid, the rate constant for the V^{IV}–HOCl reaction is estimated as $19·60 \pm 0·03$ l mol^{-1} s^{-1} at 25 °C. Rate constants for the reaction of $[Cl_2]^{-\bullet}$ with V^{IV} and V^V are estimated to be $5·1 \times 10^7 \leqslant k_{-1} \leqslant 1·3 \times 10^{11}$ and $4·1 \times 10^5 \leqslant k_2 \leqslant 1·2 \times 10^9$ l mol^{-1} s^{-1}, respectively.

THE kinetics of redox reactions involving transition-metal ions of d^1 configuration have received some attention recently.[1-4] Such ions, when they are the reducing ions, provide good examples of reaction paths proceeding by a series of one-electron changes in non-complementary redox reactions. Inhibition by the immediate product of the reaction, *viz.* the metal ion with the d^0 configuration, and concomitant production of highly reactive unstable intermediates (evidence for their existence is often deduced from the kinetics of the system), provide unequivocal evidence for such mechanisms.

Reaction (1) is a prototype of such redox reactions,

$$2[VO]^{2+} + Cl_2 + 2H_2O \rightleftharpoons 2[VO_2]^+ + 2Cl^- + 4H^+ \quad (1)$$

$[VO]^{2+}$ and Cl_2 being the one-electron reductant and two-electron oxidant respectively. Should this reaction proceed by the general mechanism outlined above, the radical anion $[Cl_2]^{-\bullet}$ will be produced as the transient intermediate, and inhibition by $[VO_2]^+$ would be observed if the rates of reaction of $[VO]^{2+}$ and $[VO_2]^+$ with $[Cl_2]^{-\bullet}$ are comparable. Recently[3] Dreyer and Gordon published their results on this system as well as the oxidation of $[VO]^{2+}$ by HOCl, the molecular aqueous-hydrolysis product of Cl_2. Their experiments were conducted under pseudo-first-order conditions, in which Cl_2 was always in excess, and in a medium of very high Cl^- concentration. Their technique was such that for reactions in which $[H^+] \leqslant 0·20$M only the latter 50% of the reaction could be followed, and for $[H^+] \geqslant 0·20$M they observed deviation from second-order kinetics but did not investigate the cause of this deviation.* In this work, kinetic findings for reaction (1) are reported for $[H^+]$ in the range 0·1—1·0M and at an ionic strength of 1·0M, with and without initial addition of vanadium(V).

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* 1M = 1 mol dm^{-3}.

[1] D. R. Rosseinsky, *Chem. Rev.*, 1972, **72**, 215 and refs. therein.

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

[3] K. Dreyer and G. Gordon, *Inorg. Chem.*, 1972, **11**, 1174.

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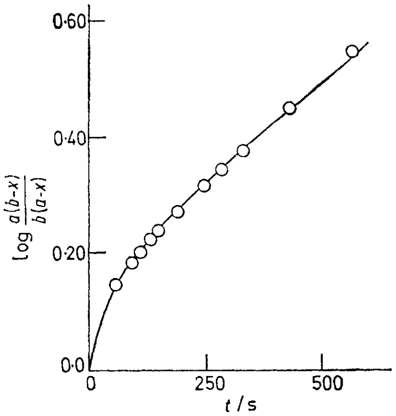
EXPERIMENTAL

Vanadium(IV) solutions were prepared by the method described by Higginson and Sykes.[5] Ammonium trioxovanadate(V) was dissolved in sodium hydroxide. The resulting solution was acidified with perchloric acid, and the V^{V} was reduced to V^{IV} with sodium sulphite. Ammonium carbonate was added to precipitate the hydrated $V_2O_4 \cdot H_2O$. The latter was washed to remove any sulphate and dissolved in perchloric acid to obtain vanadium(IV) perchlorate. The concentrations of V^{IV} in solution were determined by titration against standardized permanganate solutions. Excess of acid in solution was determined by the cation-exchange method. Total cation concentration was first determined, the free acid in solution being the total cation concentration less twice the V^{IV} concentration. The methods of preparation and analysis of chlorine solutions and sodium perchlorate have been reported earlier.[6]



Rate curve for the V^{IV}–Cl_2 reaction at 25 °C: $[V^{IV}] = 1 \cdot 03 \times 10^{-3}$, $[Cl_2] = 1 \cdot 31 \times 10^{-3}$, $[H^+] = 0 \cdot 4$, and $I = 1 \cdot 0$M

The course of the reaction was followed by monitoring the V^{V} concentrations at 350 nm. At this wavelength, and in the concentration ranges employed in the kinetic runs, neither Cl_2(aq) nor V^{IV} has any significant absorbance. For runs which were sufficiently slow to be followed manually, the course of the reaction was followed with a Unicam SP 500 spectrophotometer with a thermostatted cell compartment, but for the faster runs (those in which V^{IV} was in large excess), a Durrum–Gibson stopped-flow spectrophotometer was used. The ionic strength was maintained constant at $I = 1 \cdot 0$M with sodium perchlorate.

RESULTS

The reaction was assumed to follow second-order kinetics with rate defined as in equation (2). Plots of log ($[V^{IV}]/[Cl_2]$) against time showed smoothly decreasing gradients

$$-\frac{1}{2}\frac{d[V^{IV}]}{dt} = -\frac{d[Cl_2]}{dt} = k_0[V^{IV}][Cl_2] \qquad (2)$$

(Figure) which suggest that at least one of the products of the reaction might be inhibiting the reaction. Vanadium(V) was therefore initially added to the reaction medium and the results (the reaction became slower and second-order plots deviated much earlier from linearity than when there was no initial addition of V^{V}) showed that V^{V}, indeed, inhibits the reaction and that it could be primarily responsible for the marked deviation of the second-order plots from linearity. The rate of the reaction was also followed under pseudo-first-order conditions with $[V^{IV}]_0 \gg [Cl_2]_0$. Pseudo-first-order plots were linear up to 50—60% completion of reaction, after which deviations from linearity were also observed. Apparent second-order rate constants (k_0) were obtained from the initial gradient of the curves, and the values obtained as functions of initial concentrations of reactants, hydrogen ion, chloride, and V^{V} are shown in Table 1.

TABLE 1

Values of rate constants for the vanadium(IV)–chlorine reaction at various $[V^{IV}]$, $[Cl_2]$, $[H^+]$, and $[Cl^-]$, 25 °C, and $I = 1 \cdot 0$M (all concentrations are expressed in mol l^{-1})

Run	$10^3[V^{IV}]$	$10^3[Cl_2]$	$[H^+]$	$10^3[Cl^-]$	k_0/ l mol^{-1} s^{-1}
(1)	2·68	0·58	0·10	0·0	51·5
(2)	3·36	0·58	0·10	0·0	52·25
(3)	4·48	0·58	0·10	0·0	54·0
(4)	5·60	0·58	0·10	0·0	49·3
(5)	2·69	0·62	0·10	0·0	49·4
					Mean 51·3 ± 1·6
(6)	2·60	0·57	0·20	0·0	27·2
(7)	0·31	0·39	0·20	0·0	27·6
					Mean 27·4
(8)	3·01	1·40	0·30	0·0	18·9
(9)	2·60	0·57	0·30	0·0	17·4
(10)	2·60	0·54	0·30	0·0	18·5
(11)	1·03	1·29	0·30	0·0	20·4
(12)	1·03	1·27	0·30	0·0	16·0
(13)	0·26	0·48	0·30	0·0	18·6
(14)	0·39	0·48	0·30	0·0	20·5
(15) *	3·02	1·40	0·30	0·0	18·6
(16)	3·02	1·40	0·30	0·0	18·8
(17)	3·02	1·40	0·30	0·0	18·5
(18)	3·02	1·40	0·30	0·0	18·4
					Mean 18·4 ± 1·3
(19)	0·10	1·35	0·40	0·0	10·5
(20)	0·10	1·31	0·40	0·0	14·1
					Mean 12·3
(21)	0·10	1·27	0·50	0·0	9·2
(22)	0·10	1·35	0·60	0·0	7·4
(23)	0·10	1·35	0·80	0·0	6·7
(24)	0·10	1·59	1·00	0·0	5·5
(25)	3·02	1·40	0·30	2·0	12·3
(26)	3·02	1·40	0·30	4·0	10·3
(27)	3·02	1·40	0·30	6·0	8·3
(28)	3·02	1·40	0·30	8·0	7·5
(29)	3·02	1·40	0·30	12·0	6·6

* Runs (15)—(18) contained initially added V^{V} of concentration in the range $1 \cdot 0$—$4 \cdot 0 \times 10^{-4}$M.

Inhibition by V^{V}.—The observed inhibition by V^{V} suggests that the reaction proceeds according to equations (3) and (4).

$$V^{IV} + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} V^{V} + [Cl_2]^{-\cdot} \qquad (3)$$

$$V^{IV} + [Cl_2]^{-\cdot} \xrightarrow{k_2} V^{V} + 2Cl^- \qquad (4)$$

Applying the steady-state hypothesis to $[Cl_2]^{-\cdot}$, rate equation (5) is derived. If $[Cl_2]_0 \gg [V^{IV}]_0$ and $[V^{V}] \gg$

$$-\frac{1}{2}\frac{d[V^{IV}]}{dt} = -\frac{d[Cl_2]}{dt} = \frac{k_1k_2[V^{IV}]^2[Cl_2]}{k_{-1}[V^{IV}] + k_2[V^{IV}]} \qquad (5)$$

$[V^{IV}]_0$, equation (5) reduces to a pseudo-second-order

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[5] W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 1964, **68**, 612.

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

equation in $[V^{IV}]$ as in (6) where $p = k_1k_2/k_{-1}$. A plot of

$$-\frac{d[Cl_2]}{dt} = p[V^{IV}]^2 \qquad (6)$$

$1/[V^{IV}]_0$ against t should be linear and of gradient p under these conditions. The curves were, indeed, linear for more than 80% completion of reaction, thereby confirming that the rate equation (5) appropriately describes the rate behaviour of this system. In the initial stages of the reaction, for runs in which there is no addition of V^V, *i.e.* where $[V^{IV}] \gg [V^V]$, equation (5) reduces to simple second-order rate equation with $k_1 = k_0$. Thus, the linear portion of the second-order and pseudo-first-order plots correspond to this situation, and by substituting the obtained values of k_0 for k_1 values of the ratio $k_2 : k_{-1}$ were obtained * from the determined values of p (Table 2).

TABLE 2

Values of p ($= k_1k_2/k_{-1}$) under conditions in which the reaction is pseudo-second order in $[V^{IV}]$ at 25 °C and I = 1·0M (all concentrations are expressed in mol l^{-1})

$10^2[V^{IV}]$	$10^2[Cl_2]$	$10^2[V^V]$	p/ l mol^{-1} s^{-1}	R	k_0/ l mol^{-1} s^{-1}	$[H^+]$
0·45	2·26	3·05	0·275	0·010	27·4	0·20
0·38	3·62	1·94	0·122	0·010	12·3	0·40
0·38	3·14	1·94	0·123	0·017	7·39	0·60
0·44	2·92	3·60	0·099	0·015	6·74	0·80

Effect of Hydrogen Ion on the Rate.—From Table 1, k_0 decreases as $[H^+]$ increases. A plot of log k_0 against log $[H^+]$ was linear and of gradient $(-1{\cdot}0 \pm 0{\cdot}1)$. Thus the rate equation in the initial stages of the reaction, when inhibition by V^V is not significant, is as in (7), with $k_0' = 5{\cdot}32 \pm 0{\cdot}39$ s^{-1} in the range $0{\cdot}10 \leqslant [H^+] \leqslant 1{\cdot}0$M.

$$-\frac{1}{2}\frac{d[V^{IV}]}{dt} = \frac{k_0'}{[H^+]}[V^{IV}][Cl_2] \qquad (7)$$

DISCUSSION

The inhibition of the reaction by V^V and the attendant complexity of the rate law suggest that the reaction of Cl_2 with $[VO]^{2+}$ in aqueous solution most probably proceeds by a series of one-electron changes in which $[Cl_2]^{-\cdot}$ is a reactive intermediate. The chlorine radical anion has been proposed as an intermediate in the Mn^{III} catalysis of oxidation [9] of oxalate by $[MnO_4]^-$, the chloride-catalysed oxidation [10] of Tl^I by Mn^{III}, Co^{III} oxidation of Cl^-,[11] and the reduction [12] of aqueous solutions of halogens by V^{2+}. Such halogen-ion radicals have been identified in the photolysis [13] and pulse radiolysis [14] of aqueous halide solutions. The rates of their disproportionation [13] and oxidation reactions with aqua- [15] and metal-complex [16] ions have been measured. It is therefore suggested that the paths represented by (3) and (4) are the most likely for this reaction.

Estimates of the redox potential for the Cl_2–$[Cl_2]^{-\cdot}$ couple, based on many assumptions about the thermodynamic parameters for the chlorine atom, have been reported by different workers.[15-18] From these estimates, and the $E^\ominus$ for the $[VO_2]^+$–$[VO]^{2+}$ couple,[19] the equilibrium constant (K) for reaction (3) can be calculated. Since $K = k_1/k_{-1}$, and from the present results k_1 and $k_2 : k_{-1}$ are known, independent values of k_2 and k_{-1} can be calculated, and the results along with the $E^\ominus$ estimates for the Cl_2–$[Cl_2]^{-\cdot}$ couple are in Table 3. It appears that there is no basis to prefer one estimate of $E^\ominus$ for the Cl_2–$[Cl_2]^{-\cdot}$ couple to another and, therefore, only the range of magnitudes of k_{-1} and k_2 could be fixed from these data. Thus, $5{\cdot}1 \times 10^7 < k_{-1} \leqslant 1{\cdot}3 \times 10^{11}$ and $4{\cdot}1 \times 10^5 \leqslant k_2 < 1{\cdot}2 \times 10^9$ l mol^{-1} s^{-1}. Although these estimated values of k_2 lie within the range of possible values for bimolecular reactions in solutions, the upper limit of 10^9 l mol^{-1} s^{-1} is at least two orders of magnitude higher than measured rate constants reported for the oxidation [15] of Fe^{2+}, Co^{2+}, and Mn^{2+} by $[Cl_2]^{-\cdot}$. It is considered unlikely that $[VO]^{2+}$ could be a specially favoured reductant towards $[Cl_2]^{-\cdot}$ because of the structural rearrangement that should accompany the oxidation of $[VO]^{2+}$ to $[VO_2]^+$, and, therefore, an estimate of 0·43 V for the Cl_2–$[Cl_2]^{-\cdot}$ couple is rather too low.

TABLE 3

Values of k_2 and k_{-1} from different estimates of $E^\ominus$ for the Cl_2–$[Cl_2]^{-\cdot}$ couple. R = 0·01, $[H^+]$ = 0·20M, k_1 = 27·42 l mol^{-1} s^{-1}, 25 °C, I = 1·0M

E/V	K	k_{-1}/l mol^{-1} s^{-1}	k_2/l mol^{-1} s^{-1}	Ref.
0·60	$1{\cdot}7 \times 10^{-7}$	$1{\cdot}6 \times 10^8$	$1{\cdot}6 \times 10^6$	18
0·64	$5{\cdot}4 \times 10^{-7}$	$5{\cdot}1 \times 10^7$	$4{\cdot}1 \times 10^5$	16
0·43	$2{\cdot}2 \times 10^{-10}$	$1{\cdot}3 \times 10^{11}$	$1{\cdot}3 \times 10^9$	15
0·475	$7{\cdot}9 \times 10^{-9}$	$3{\cdot}5 \times 10^9$	$3{\cdot}4 \times 10^7$	17

Alternative paths which could explain the observed inhibition by V^V are (8) and (9). Although paths (8) and

$$V^{IV} + Cl_2 \rightleftharpoons V^V + Cl^- + Cl \qquad (8)$$

$$V^{IV} + Cl \longrightarrow V^V + Cl^- \qquad (9)$$

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* An alternative method of obtaining R ($= k_2 : k_{-1}$) is to use the integrated form of equation (5) as given by Sykes,[7] and previously employed by Ashurst and Higginson [8] in the Fe^{II}–Fe^{III} reaction. This method involves estimating the appropriate value of R that would give a linear plot for a rather complicated equation. When this approach was adopted for this system the linearity of the curve obtained was not sensitive to values of R for up to 70% completion of reaction. The apparent unsuitability of this method is due to the complications arising from the composite nature of the reaction. The oxidizing species, Cl_2 and HOCl, both of which are present in the solution, react at comparable rates with $[VO]^{2+}$, and, therefore, the rate of the reaction is also dependent on $[Cl^-]$. Thus, in the latter stages of the reaction, sufficient Cl^- has been formed to have an effect on the rate, and, hence, a unique value of R could not be obtained from this method.

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(9) are kinetically equivalent to (3) and (4), the latter are preferred because of the high complexing constant [15a] (10^5 l mol^{-1}) for reaction (10). Moreover, since paths (3)

$$\mathrm{Cl} + \mathrm{Cl}^- \longrightarrow [\mathrm{Cl}_2]^{-\cdot} \qquad (10)$$

and (4) do not require total fission of the Cl–Cl bond, they should lead to a lower activation energy and should therefore be preferred to (8) and (9). The observed decrease in rate with initial addition of Cl^-, although consistent with this path, cannot be exclusively attributed to reaction (8), nor can it be a basis for preferring paths (8) and (9) to (3) and (4) because of more evident reasons (which are discussed later) that explain the decrease in rate with initial addition of Cl^-.

A two-electron-transfer process with initial disproportionation of $\mathrm{V^{IV}}$ to $\mathrm{V^{III}}$ and $\mathrm{V^{V}}$ could also explain the observed inhibition by $\mathrm{V^{V}}$ but it is considered unlikely because of the following reasons. (*i*) The disproportionation (11) is thermodynamically unfavourable and con-

$$2\mathrm{V^{IV}} \rightleftharpoons \mathrm{V^{V}} + \mathrm{V^{III}} \qquad (11)$$

centration of $\mathrm{V^{III}}$ will be too low to explain the observed rates of reaction.* (*ii*) The mechanism of reaction (12)

$$2\mathrm{V^{III}} + \mathrm{Cl}_2 \rightleftharpoons 2\mathrm{V^{IV}} + 2\mathrm{Cl}^- \qquad (12)$$

is complex. In a direct kinetic investigation [20] of reaction (12) it was not certain that a direct two-electron transfer from $\mathrm{V^{III}}$ to Cl_2 occurs. The rate of the reaction is comparable to that [21] of $\mathrm{V^{III}}$–$\mathrm{V^{V}}$, and, hence, both $\mathrm{V^{V}}$ and Cl_2 would compete for the $\mathrm{V^{III}}$. (*iii*) If the disproportionation (11) is a fast equilibrium, then reaction (12) would be rate determining. The rate of oxidation of $\mathrm{V^{IV}}$ by Cl_2 as determined in this work is much lower than that [20] of reaction (12).

The rate constants obtained from the initial rates decrease as $[\mathrm{H}^+]$ and also $[\mathrm{Cl}^-]$ increase. The inverse first order with respect to $[\mathrm{H}^+]$ is consistent with the results of other systems in which oxidation of an aqua-ion by a halogen results in formation of an oxo-ion.[6,22] Electron transfer in such systems is preceded by hydrolysis of the aqua-ion to species which are structurally intermediate between the reactant and product ions. Thus for the $[\mathrm{VO}]^{2+}$–Cl_2 reaction the following activation steps are suggested to explain the observed rate decrease with $[\mathrm{H}^+]$ and $[\mathrm{Cl}^-]$.

$$[\mathrm{VO}]^{2+} + \mathrm{H_2O} \underset{\text{fast}}{\overset{k_v}{\rightleftharpoons}} [\mathrm{VO(OH)}]^+ + \mathrm{H}^+ \qquad (13)$$

$$\mathrm{Cl_2} + \mathrm{H_2O} \underset{\text{fast}}{\overset{k_{\mathrm{Cl}}}{\rightleftharpoons}} [\mathrm{VO_2}]^+ + \mathrm{H}^+ + \mathrm{Cl_2}]^{-\cdot} \qquad (14)\dagger$$

$$[\mathrm{VO(OH)}]^+ + \mathrm{Cl_2} \xrightarrow{k_3} [\mathrm{VO_2}]^+ + \mathrm{H}^+ + [\mathrm{Cl_2}]^{-\cdot} \qquad (15)$$

$$[\mathrm{VO}]^{2+} + \mathrm{HOCl} \xrightarrow{k_4} [\mathrm{VO(OCl)}]^+ + \mathrm{H}^+$$

$$[\mathrm{VO(OH)}]^+ + [\mathrm{Cl_2}]^{-\cdot} \xrightarrow{\text{fast}} [\mathrm{VO_2}]^+ + \mathrm{H}^+ + 2\mathrm{Cl}^- \qquad (17)$$

$$\begin{aligned}\text{Rate} &= k_3[\mathrm{VO(OH)}^+][\mathrm{Cl_2}] + k_4[\mathrm{VO}^{2+}][\mathrm{HOCl}] \\ &= k_0\Sigma[\mathrm{V^{IV}}]\Sigma[\mathrm{Cl_2}] \qquad (18)\end{aligned}$$

where

$$\Sigma[\mathrm{V^{IV}}] = \frac{[\mathrm{VO}^{2+}]}{[\mathrm{H}^+]}([\mathrm{H}^+] + K_{\mathrm{V}}) \qquad (19)$$

$$\Sigma[\mathrm{Cl_2}] = \frac{[\mathrm{Cl_2}]}{[\mathrm{H}^+][\mathrm{Cl}^-]}([\mathrm{H}^+][\mathrm{Cl}^-] + K_{\mathrm{Cl}}) \qquad (20)$$

From equations (15)—(20), (21) follows. Thus if the

$$\begin{aligned}&k_0([\mathrm{H}^+] + K_{\mathrm{V}})([\mathrm{H}^+][\mathrm{Cl}^-] + K_{\mathrm{Cl}}) \\ &\qquad = k_3K_{\mathrm{V}}[\mathrm{H}^+][\mathrm{Cl}^-] + k_4K_{\mathrm{Cl}}[\mathrm{H}^+] \qquad (21)\end{aligned}$$

left-hand side of equation (21) is plotted against $[\mathrm{Cl}^-]$, it should be linear with gradient and intercept $k_3K_{\mathrm{V}}[\mathrm{H}^+]$ and $k_4K_{\mathrm{Cl}}[\mathrm{H}^+]$, respectively. This graph was linear with $k_3K_{\mathrm{V}}[\mathrm{H}^+] = 0{\cdot}385$ mol l^{-1} s^{-1} and hence $k_3 = (1{\cdot}28 \pm 0{\cdot}03) \times 10^6$ l mol^{-1} s^{-1} at $[\mathrm{H}^+] = 0{\cdot}3$M, and if $K_{\mathrm{V}} = 10^{-6}$ mol l^{-1},[19] $k_4 = 19{\cdot}6 \pm 0{\cdot}33$ l mol^{-1} s^{-1}. This value of k_4 is in reasonable agreement with 14·08 l mol^{-1} s^{-1} obtained by direct measurement by Dreyer and Gordon.[3] The linearity of the curve obtained by applying equation (21), and the reasonable agreement between k_4 and the measured value by Dreyer and Gordon, confirm that inhibition by Cl^- is due to the decrease in the amount of HOCl present in the reaction medium as $[\mathrm{Cl}^-]$ increases.

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* From the $E^{\ominus}$ values [19] for the $\mathrm{V^{IV}}$–$\mathrm{V^{III}}$ and $\mathrm{V^{V}}$–$\mathrm{V^{IV}}$ couples, the equilibrium constant for reaction (11) is *ca.* 10^{-11} mol l^{-1} and therefore $[\mathrm{V^{III}}]$ would be *ca.* 10^{-8}—10^{-9}M for values of $[\mathrm{V^{IV}}]$ employed in this work. The second-order rate constant for the oxidation [20] of $\mathrm{V^{III}}$ by aqueous $\mathrm{Cl_2}$ is *ca.* 10^3 l mol^{-1} s^{-1}. Thus the rate obtained for the $\mathrm{V^{IV}}$–$\mathrm{Cl_2}$ reaction is much higher than predicted by the disproportionation (11).

† The value of $K_{\mathrm{Cl}} = 6{\cdot}4 \times 10^{-4}$ mol^2 l^{-2} (from ref. 3) was employed in the subsequent calculations.

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