Kinetics of the Oxidation of Uranium(IV) Ions by Halogens in Aqueous Solution. Part II.[1] Chlorine

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The rate of the reaction $U^{4+} + Cl_2 + 2H_2O \longrightarrow UO_2^{2+} + 2Cl^- + 4H^+$ is shown to obey the rate law $-d[U^{IV}]/dt = k[U^{IV}][Cl_2][H^+]^{-2}$. The rate constant decreases with increasing $[Cl^-]$ and the data are interpreted in terms of a mechanism involving two paths, $U(OH)_2^{2+} + Cl_2$ and $U(OH)^{3+} + HOCl$. Rate constants and Arrhenius parameters are calculated for the two paths.

In Part I [1] we reported the kinetics of the reaction of uranium(IV) ions with I_2 and Br_2. We now present results for the uranium(IV)–Cl_2 reaction, $U^{4+} + Cl_2 + 2H_2O \longrightarrow UO_2^{2+} + 2Cl^- + 4H^+$. Gordon and Feldman [2] have published a paper concerned mainly with the stoicheiometry of the reaction of U^{IV} with ClO_2^- in which they reported preliminary results for the kinetics of reaction of U^{IV} with HOCl, among other reactions.

EXPERIMENTAL

In addition to the chemicals described earlier,[1] we used AnalaR sodium chloride. Aqueous solutions of chlorine were prepared by bubbling chlorine gas from a cylinder through aqueous perchloric acid. Chlorine solutions were prepared freshly each day and concentrations were estimated iodometrically.

The course of the reaction was followed by manual measurement of the absorbance at 648 nm due to U^{4+} on a Unicam SP 500 spectrophotometer fitted with a thermostatted cell compartment. Neither U^{VI} nor Cl_2 in the concentrations used absorb significantly at 648 nm. Constant ionic strengths of 2·0 and 2·5M were used in the stoicheiometric and kinetic experiments respectively, sodium perchlorate being used as the inert electrolyte.

RESULTS

Stoicheiometry.—The stoicheiometry was determined by mixing known chlorine and uranium(IV) ion solutions in a volumetric flask, allowing the reaction to go to completion at 30 °C in a thermostat bath, and then estimating the concentration of the reactant which was originally in excess by titration. Results are in Table 1. The average

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[1] Part I, A. Adegite and M. H. Ford-Smith, preceding paper.

[2] G. Gordon and F. Feldman, *Inorg. Chem.*, 1964, **3**, 1728.

of five experiments gave $[Cl_2]_{consumed}/[U^{IV}]_{consumed} = 1{\cdot}15 \pm 0{\cdot}09$. That the result was significantly greater than unity is attributed by us to losses of chlorine owing to its volatility during the experiments.

TABLE 1

Determination of the stoicheiometry of the uranium(IV) ion–chlorine reaction. $t = 30$ °C; $I = 2{\cdot}0$M; $[Cl^-] = 0{\cdot}2$M; $[H^+] = 1{\cdot}0$M

$10^2[U^{IV}]_0$/M	$10^2[U^{IV}]_\infty$/M	$10^2[Cl_2]_0$/M	$10^2[Cl_2]_\infty$/M	$\frac{[Cl_2]_{consumed}}{[U^{IV}]_{consumed}}$
8·16	6·23	1·18	0·00	1·26
4·89	2·36	2·66	0·00	1·15
4·89	2·56	2·37	0·00	1·03
2·43	0·00	4·05	1·31	1·13
4·10	1·35	3·33	0·00	1·25
			Average:	1·15 ± 0·09

Spectra of reaction mixtures were run repeatedly on a Unicam SP 800 spectrophotometer. A typical example of such a series of spectra is shown in Figure 1. These spectra showed an isosbestic point at 312 nm and indicated that the reaction was simple and that no detectable long-lived intermediate was formed.

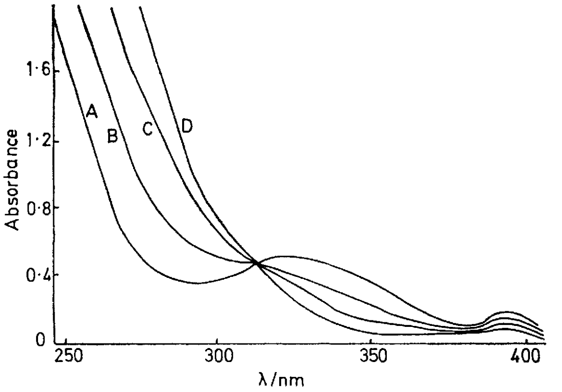

FIGURE 1 U.v. and visible spectral changes during the oxidation of uranium(IV) ion by Cl_2. $[U^{IV}] = 1{\cdot}952 \times 10^{-3}$M; $[Cl_2] = 1{\cdot}797 \times 10^{-3}$M; $[H^+] = 0{\cdot}5$M; $[Cl^-] = 0{\cdot}2$M; $I = 2{\cdot}0$M; $t = 25$ °C. A, 150; B, 900; and C, 2400 s after mixing; D, $[U^{IV}] = 1{\cdot}797 \times 10^{-3}$M, $[H^+] = 0{\cdot}5$M, $[Cl^-] = 0{\cdot}20$M

These preliminary experiments confirm that the reaction between chlorine and uranium(IV) ions can be written as (1) with the corresponding equation (2).

$$U^{4+} + Cl_2 + 2H_2O \longrightarrow UO_2^{2+} + 2Cl^- + 4H^+ \quad (1)$$

$$-d[U^{IV}]/dt = -d[Cl_2]/dt = d[UO_2^{2+}]/dt = -\tfrac{1}{2}d[Cl^-]/dt \quad (2)$$

Rate of the Uranium(IV) *Ion–Chlorine Reaction in Perchloric Acid.*—The order of the reaction with respect to $[U^{IV}]$ and $[Cl_2]$ was determined under pseudo-first-order conditions with $[Cl_2] > [U^{IV}]$. Good straight lines were obtained for up to *ca.* 90% reaction when $\log (OD_t - OD_\infty)$ was plotted against t and the slopes of the lines yielded k_1, the pseudo-first-order rate constant as a function of the Cl_2 concentration (in excess). Results are in Table 2. Log k_1 was then plotted against log $[Cl_2]$ to give a straight line of slope $0{\cdot}99 \pm 0{\cdot}06$. From the linearity of the first-order plots and the slope of unity for the plot of log k_1 against log $[Cl_2]$, the rate expression can be written as (3). Values of k_2 calculated by use of this expression from the pseudo-first-order data are in Table 2.

$$-d[U^{IV}]/dt = k_2[U^{IV}][Cl_2] \quad (3)$$

TABLE 2

Determination of the order of the reaction with respect to $[Cl_2]$. $[U^{IV}] = 3{\cdot}27 \times 10^{-3}$M; $[H^+] = 0{\cdot}5$M; $[Cl^-] = 0{\cdot}2$M; $I = 2{\cdot}0$M; $t = 30$ °C

$10^2[Cl_2]_0$/M	10^4k_1/s^{-1}	$10^2k_1/[Cl_2] = 10^2k_2$/l mol^{-1} s^{-1}
2·37	7·37	3·11
3·08	9·98	3·22
3·35	11·12	3·32
3·66	11·72	3·20
4·41	12·86	2·92
5·25	16·85	3·21

Having established that the reaction obeyed second-order kinetics, we performed runs with U^{IV} and Cl_2 concentrations approximately but not exactly equal, when the integrated form of the second-order rate expression was used. Second-order plots were usually linear to *ca.* 75% consumption of the species present in the smaller concentration and the slopes of such plots yielded the values of k_2 listed in Tables 3 and 4 which show the variations of k_2 with changing acid concentration and changing temperature and chloride-ion concentration respectively.

TABLE 3

Second-order rate constants for the uranium(IV) ion–chlorine reaction at various acid concentrations. $[Cl^-] = 0{\cdot}20$M; $I = 2{\cdot}50$M; $t = 30$ °C

$10^2[U^{IV}]$/M	$10^2[Cl_2]$/M	$[H^+]$/M	10^2k_2/l mol^{-1} s^{-1}		10^2k_0/mol l^{-1} s^{-1}
0·964	1·842	0·52	3·55	3·55	0·96
0·959	2·752	0·52	3·55		
0·886	1·616	0·62	3·17		1·22
0·449	0·703	0·81	2·38	2·51	1·65
1·989	3·005	0·81	2·18		
0·994	1·995	0·81	2·95		
0·483	0·758	0·81	2·67		
0·964	1·863	0·81	2·38		
0·658	0·851	1·00	1·60	1·77	1·77
0·327	0·226	1·00	1·93		
0·497	0·922	1·00	2·00		
0·794	1·690	1·00	1·63		
1·645	2·419	1·00	1·67		
0·889	1·721	1·22	1·00		1·49
0·795	1·419	1·53	0·61	0·67	1·57
0·795	1·345	1·53	0·72		
0·795	1·344	2·04	0·35	0·39	1·62
0·886	1·512	2·04	0·43		
				Average:	1·50 ± 0·09

The results in Table 3 show that k_2 decreases with increasing acid concentration. Figure 2 shows the plot of log k_2 against log $[H^+]$; all the points except those for the two lowest acid concentrations lie on a straight line of slope $-2{\cdot}07 \pm 0{\cdot}01$. This result shows that the rate expression should be written as (4). Figure 2 also shows a plot of k_2 against $[H^+]^{-2}$ which is accurately linear for the five highest acid concentrations and passes through the origin. Table 3 contains the calculated values of k_0, giving a weighted average result of $(1{\cdot}50 \pm 0{\cdot}09) \times 10^{-2}$ mol l^{-1} s^{-1} at 30 °C.

$$-d[U^{IV}]/dt = k_0[U^{IV}][Cl_2][H^+]^{-2} \quad (4)$$

Rate of Reaction in the Presence of Added Chloride Ion.—The rate of the uranium(IV) ion–chlorine reaction was found to decrease with increasing [Cl$^-$], as shown by the data in Table 4. The second-order rate constants for the reaction were measured at a variety of chloride-ion concentrations at four different temperatures. A plot of log k_2 against log [Cl$^-$] was linear with a slope of -0.50 ± 0.03, this being the apparent order of the reaction with respect to chloride concentration. These data are analysed in the Discussion section.

TABLE 4

Second-order rate constants for the uranium(IV) ion–chlorine reaction at different temperatures and chloride-ion concentrations. [H$^+$] = 1·0M; I = 2·50M

t/°C	10^2[U^{IV}]/M	10^2[Cl$_2$]/M	[Cl$^-$]/M	10^2k_2/ l mol^{-1} s^{-1}
30·0	0·658	0·851	0·20	1·60
	0·327	0·226	0·20	1·93
	0·497	0·922	0·20	2·00
	0·974	1·690	0·20	1·63
	1·645	2·419	0·20	1·67
	1·108	1·745	0·00	2·73
	1·080	1·818	0·50	1·12
	1·070	1·859	0·50	1·14
	1·070	1·859	1·00	0·87
	1·070	0·975	1·50	0·62
20·3	1·094	1·984	0·00	0·77
	1·094	2·038	0·20	0·36
	1·085	2·010	0·50	0·30
	1·085	2·159	1·00	0·24
	1·035	2·791	1·50	0·21
40·0	1·008	1·855	0·00	9·98
	1·008	1·895	0·00	10·19
	1·008	1·761	0·20	5.15
	1·008	1·835	0·50	4·87
	1·150	2·013	1·00	3·68
	1·104	1·758	1·50	3·53
50·0	1·102	2·006	0·00	31·25
	1·101	1·983	0·20	18·52
	1·101	1·887	0·50	17·50
	1·101	1·883	1·00	15·02
	1·101	2·037	1·50	11·64

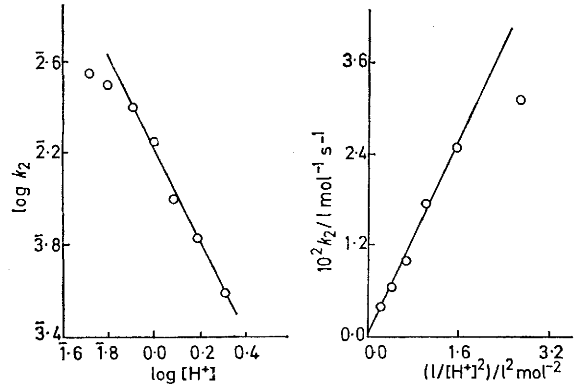

FIGURE 2 Dependence of the rate of the uranium(IV) ion–chlorine reaction on [H$^+$]

DISCUSSION

The data at the two lowest acid concentrations (0·52 and 0·62M) did not fit the rate expression (4). Similar discrepancies were found for the reactions of uranium(IV) ions with iodine[1] and bromine.[3] We have attempted to account for the acid dependence using a five-part rate expression of the type shown in equation (5) and estimating values of the parameters a—e using a

$$\text{Rate} = [\text{U}^{\text{IV}}][\text{Cl}_2]\{a + b[\text{H}^+]^m + c[\text{H}^+]^n + d[\text{H}^+]^p + e[\text{H}^+]^q\} \quad (5)$$

$$\text{where} \qquad -4 \leqslant m,n,p,q \leqslant +4$$

multiple regression computer program, but no improvement in the fit between calculated and observed rates was obtained compared with the use of the simple expression, Rate $\propto$ [H$^+$]$^{-2}$. (Values for the parameters a—e other than for -2, calculated by use of the computer program, were negative and/or had very large errors associated with them.) We are unable to explain the anomalously low rates of reaction at low [H$^+$] since neither specific salt effects (assuming that substitution of Na$^+$ for H$^+$ at a total ionic strength of 2·5M will not cause a change in the rate of reaction because of changed activity coefficients) nor possible polymerisation[4] of U$^{\text{IV}}$ seem able to account for the size of the observed anomaly.

The decreasing rate of reaction with increasing [Cl$^-$], when combined with Rate $\propto$ [H$^+$]$^{-2}$ suggests that the reaction paths (6)—(15) may be important, with other

$$\text{U}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{U(OH)}^{3+} + \text{H}^+ \qquad K_1 \quad (6)$$

$$\text{U(OH)}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{U(OH)}_2{}^{2+} + \text{H}^+ \qquad K_2 \quad (7)$$

$$\text{U}^{4+} + \text{Cl}^- \rightleftharpoons \text{UCl}^{3+} \qquad K_3 \quad (8)$$

$$\text{U(OH)}_2{}^{2+} + \text{Cl}^- \rightleftharpoons \text{U(OH)}_2\text{Cl}^+ \qquad K_4 \quad (9)$$

$$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^- \qquad K_5 \quad (10)$$

$$\text{Cl}_2 + \text{Cl}^- \rightleftharpoons \text{Cl}_3{}^- \qquad K_6 \quad (11)$$

$$\text{U(OH)}_2{}^{2+} + \text{Cl}_2 \xrightarrow{k_3} \text{UO}_2{}^{2+} + 2\text{Cl}^- + 2\text{H}^+ \quad (12)$$

$$\text{U(OH)}^{3+} + \text{HOCl} \xrightarrow{k_4} \text{UO}_2{}^{2+} + \text{Cl}^- + 2\text{H}^+ \quad (13)$$

$$\text{U(OH)}_2{}^{2+} + \text{Cl}_3{}^- \xrightarrow{k_5} \text{UO}_2{}^{2+} + 3\text{Cl}^- + 2\text{H}^+ \quad (14)$$

$$\text{U(OH)}_2\text{Cl}^+ + \text{Cl}_2 \xrightarrow{k_6} \text{UO}_2{}^{2+} + 3\text{Cl}^- + 2\text{H}^+ \quad (15)$$

possible paths such as $\text{U}^{4+} + \text{Cl}_2 \longrightarrow$, $\text{U(OH)}^{3+} + \text{Cl}_2 \longrightarrow$, $\text{U}^{4+} + \text{HOCl} \longrightarrow$, and $\text{U(OH)}_2{}^{2+} + \text{HOCl} \longrightarrow$ presumed to be negligibly important because they would give a different [H$^+$] dependence from that observed. The decrease in rate with increasing [Cl$^-$] can be explained, at least qualitatively, by supposing that $k_4 > k_3$ and/or k_5, $k_6 < k_3$. [In reactions (6)—(15) it is assumed that the rates of the hydrolyses (6), (7), and (10) and the chloride ion-complexing reactions (8), (9), and (11) are faster than reactions (12)—(15) and can therefore be represented by equilibrium constants. What evidence there is in the literature supports the validity of this assumption.]

The rate of the reaction can then be written as (16),

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[3] G. Gordon and A. Andrewes, *Inorg. Chem.*, 1964, **3**, 1733.
[4] S. Hietanen, *Acta Chem. Scand.*, 1956, **10**, 1531.

$$\begin{aligned}\text{Rate} &= k_2[\Sigma U^{IV}][\Sigma Cl_2] = k_3[U(OH)_2{}^{2+}][Cl_2] + k_4[U(OH)^{3+}][HOCl] + k_5[U(OH)_2{}^{2+}][Cl_3{}^-] + k_6[U(OH)_2Cl^+][Cl_2] \\ &= \frac{[U^{4+}][Cl_2]}{[H^+]^2[Cl^-]}(k_3K_1K_2[Cl^-] + k_4K_1K_5 + k_5K_1K_2K_6[Cl^-]^2 + k_6K_1K_2[Cl^-]^2) \qquad (16) \\ &= \frac{[U^{4+}][Cl_2]}{[H^+]^2[Cl^-]}(e + f[Cl^-] + g[Cl^-]^2)\end{aligned}$$

where $e = k_4K_1K_5$, $f = k_3K_1K_2$, and $g = (k_5K_1K_2K_6 + k_6K_1K_2K_4)$. [It should be noted that the paths $U(OH)_2Cl^+ + Cl_2 \longrightarrow$ and $U(OH)_2{}^{2+} + Cl_3{}^- \longrightarrow$ are kinetically indistinguishable.] Similarly, one can derive the expression (17). Equating (16) and (17) we obtain

$$\begin{aligned}\text{Rate} &= \frac{k_2[U^{4+}][Cl_2]}{[H^+]^3[Cl^-]}([H^+]^2 + K_1[H^+] + K_1K_2 + K_3[H^+]^2[Cl^-])([H^+][Cl^-] + K_5 + K_6[H^+][Cl^-]^2) \qquad (17) \\ &= \frac{k_2[U^{4+}][Cl_2]Y}{[H^+]^3[Cl^-]}\end{aligned}$$

equation (18). Three somewhat different methods were

$$\frac{k_2Y}{[H^+]} = e + f[Cl^-] + g[Cl^-]^2 \qquad (18)$$

used to obtain numerical values for *e*, *f*, and *g* from the data in Table 4. (*a*) Direct computation of *e*, *f*, and *g*. For various $[Cl^-]$ corresponding values of $k_2Y/[H^+]$ were calculated; a multiple regression computer program was then used to solve for *e*, *f*, and *g* in the resulting simultaneous equations. (*b*) Calculations of *e* from the $[Cl^-] = 0$ data, followed by calculating *f* and *g* at other $[Cl^-]$ by use of a multiple regression computer program. At $[Cl^-] = 0$, equation (18) simplifies to $k_2Y/[H^+] = e$ and the rate constant in the absence of added chloride ions yields a value for *e*. Using this fixed value, *f* and *g* were then computed from the data at other chloride-ion concentrations. (*c*) Fixing $g = 0$ [justified by the results obtained by methods (*a*) and (*b*)] and computing *e* and *f* by use of the multiple regression computer program. The results obtained by the three methods, using literature values [5] for the equilibrium constants uncorrected for ionic-strength differences, are in Table 5.

TABLE 5

Values of *e*, *f*, and *g* obtained by the three methods of calculation. $t = 30$ °C; $I = 2{\cdot}50$M

Parameter \ Method	(*a*)	(*b*)	(*c*)
$e/\text{mol}^2\ l^{-2}\ s^{-1}$	$4{\cdot}95 \times 10^{-5}$	$1{\cdot}27 \times 10^{-5}$	$(-3{\cdot}15 \pm 4{\cdot}57) \times 10^{-4}$
$f/\text{mol}\ l^{-1}\ s^{-1}$	$2{\cdot}10 \times 10^{-2}$	$(2{\cdot}08 \pm 0{\cdot}10) \times 10^{-2}$	$(2{\cdot}13 \pm 0{\cdot}05) \times 10^{-2}$
g/s^{-1}	$1{\cdot}80 \times 10^{-4}$	$(2{\cdot}23 \pm 15{\cdot}0) \times 10^{-4}$	0·00

The data obtained by method (*c*) are illustrated in Figure 3. The percentage of reaction proceeding by reaction (12) was calculated at each $[Cl^-]$ by use of the value of $f = 2{\cdot}13 \times 10^{-2}$ mol l^{-1} s^{-1} and the results are in Table 6.

Table 6 shows that under the conditions used (except $[Cl^-] = 0$) the reaction proceeds almost entirely *via* the $U(OH)_2{}^{2+} + Cl_2$ path, and the observed decrease in rate constant with increasing $[Cl^-]$ is due almost entirely to the formation of chloro-complexes (particularly UCl^{3+}) which react at negligible rates compared with the uncomplexed species. Clearly the assumption that $g = 0$ made in method (*c*) is justified, particularly by the results of method (*b*) calculations which indicate that *g* is zero within the limits of experimental and computational error. The best value for *e* is that obtained by method (*b*) by use only of the data for $[Cl^-] = 0$ when an appreciable percentage of the reaction proceeds *via* the $HOCl + UOH^{3+}$ path. All three methods of calculation give the same value of *f* within experimental error.

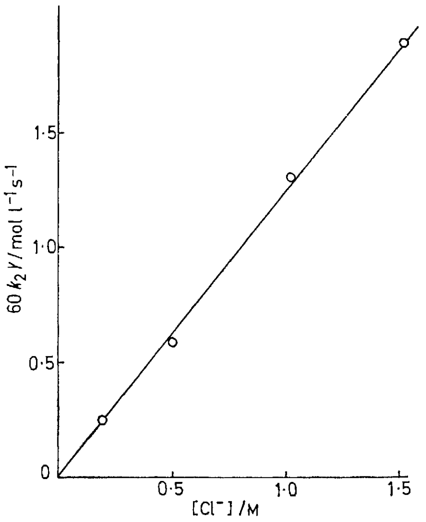

FIGURE 3 Plot of $60k_2Y$ against $[Cl^-]$

TABLE 6

Calculated percentage of reaction proceeding *via* the $U(OH)_2{}^{2+} + Cl_2$ path. $t = 30$ °C; $I = 2{\cdot}50$M; $f = 2{\cdot}13 \times 10^{-2}$ mol l^{-1} s^{-1}

$[Cl^-]$/M	Reaction/%	$[Cl^-]$/M	Reaction/%
0·0	78	1·0	99
0·2	95	1·5	102
0·5	112		

The correctness of the analysis is illustrated in Table 7 where a comparison is made between observed and calculated values of k_2 for all conditions. The average discrepancy between the two sets of figures is 7·8%, reducing to 4·0% if the data for $[H^+] = 0{\cdot}52$ and 0·62M are excluded.

From $e = 1{\cdot}27 \times 10^{-5}$ mol² l^{-2} s^{-1} and $f = 2{\cdot}13 \times 10^{-2}$ mol l^{-1} s^{-1} and literature values for the equilibrium constants [5] uncorrected for ionic-strength differences, we obtain the approximate values shown in equations (19)

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[5] 'Stability Constants of Metal-ion Complexes,' 2nd edn., The Chemical Society, London, 1964.

and (20) for the rate constants at 30 °C and $I = 2{\cdot}50\text{M}$,

$$\mathrm{U(OH)_2^{2+} + Cl_2}\!: \; k_3 = 4{\cdot}2 \text{ l mol}^{-1}\text{ s}^{-1} \qquad (19)$$

$$\mathrm{U(OH)^{3+} + HOCl}\!: \; k_4 = 0{\cdot}84 \text{ l mol}^{-1}\text{ s}^{-1} \qquad (20)$$

using $K_1 = 3 \times 10^{-2}$ mol l^{-1}, $K_1K_2 = 5 \times 10^{-3}$ mol^2 l^{-2}, $K_3 = 1{\cdot}08$ l mol^{-1}, and $K_5 = 4{\cdot}45 \times 10^{-4}$ mol^2 l^{-2}.

Gordon and Feldman[2] reported briefly that the second-order rate constant for the $\mathrm{U^{IV}}$ + HOCl reaction had the value 4·1 l mol^{-1} s^{-1} at 25 °C, $[\mathrm{H^+}] = 0{\cdot}25\text{M}$, and unspecified ionic strength. (The HOCl was prepared directly from $\mathrm{Cl_2O}$.) This gives the calculated value of $k_4 = 34$ l mol^{-1} s^{-1}. We are unable to account for the difference between our value of 0·84 and that derived from direct measurement, the difference being too large to be attributed solely to the effect of differences in ionic strength.

TABLE 7

Comparison of found and calculated k_2/l mol^{-1} s^{-1} at various $[\mathrm{H^+}]$ and $[\mathrm{Cl^-}]$. $e = 1{\cdot}27 \times 10^{-5}$ mol^2 l^2 s^{-1}; $f = 2{\cdot}13 \times 10^{-2}$ mol l^{-1} s^{-1}; $g = 0{\cdot}00$; $t = 30$ °C; $I = 2{\cdot}50\text{M}$

$[\mathrm{H^+}]$/M	$[\mathrm{Cl^-}]$/M	Found	Calculated	Difference/ %
0·52	0·20	3·55	4·37	23·1
0·62	0·20	3·17	4·13	30·0
0·81	0·20	2·51	2·45	2·4
1·00	0·20	1·77	1·63	8·0
1·22	0·20	1·00	1·01	1·0
1·53	0·20	0·67	0·68	1·5
2·04	0·20	0·39	0·40	2·6
1·00	0·00	2·73	2·85	4·4
1·00	0·50	1·13	1·09	3·5
1·00	1·00	0·87	0·85	2·3
1·00	1·50	0·62	0·66	6·5

The data at temperatures other than 30 °C contained in Table 4 were analysed by method (*b*) to give values of $K_1K_2k_3$ and k_4 at four temperatures, listed in Table 8. [The approximation had to be made that K_2 was independent of temperature because the doubtful literature value of K_2 was only measured at one temperature. The error introduced by this approximation is very small because only a small fraction of $\mathrm{U^{IV}}$ is present as $\mathrm{U(OH)_2^{2+}}$ under our experimental conditions.] log $K_1K_2k_3$ and log k_4 were plotted against $1/T$ to give straight lines and from the slopes and intercepts we calculated values for the activation energies and entropies of reaction, also listed in Table 8. These Arrhenius parameters for the two paths are *not* comparable because those for the $\mathrm{U(OH)_2^{2+} + Cl_2}$ path include $\Delta H°$ and $\Delta S°$ for the hydrolyses of $\mathrm{U^{4+}}$, reactions (6) and (7).

TABLE 8

Values of $K_1K_2k_3$ and k_4 at various temperatures and corresponding Arrhenius parameters

t/°C	$10^2K_1K_2k_3$/mol l^{-1} s^{-1}	k_4/l mol^{-1} s^{-1}
20·3	0·71	0·46
30·0	2·08	0·94
40·0	7·40	1·84
50·0	32·7	3·48
E_a/kcal mol^{-1}	24·2 ± 1·4	13·6 ± 0·3
$\Delta S^\ddagger$/cal K^{-1} mol^{-1}	11·2 ± 0·3	−15·8 ± 0·1

A comparison of the results for the oxidation of uranium(IV) ions by halogens is presented in Table 9, where the HOCl + $\mathrm{UOH^{3+}}$ contribution to the rate of the chlorine reaction has been eliminated, so making it possible to compare like with like.

TABLE 9

Comparison of the kinetics of oxidation of uranium(IV) ions by halogens at 40 °C

	$\mathrm{I_2}$ [b]	$\mathrm{Br_2}$ [c]	$\mathrm{Cl_2}$ [d]
k/mol l^{-1} s^{-1} [a]	$8{\cdot}9 \times 10^{-4}$	$4{\cdot}7 \times 10^{-3}$	$7{\cdot}4 \times 10^{-2}$
E_a/kcal mol^{-1}	17·3	23·3	24·2
$\Delta S^\ddagger$/cal K^{-1} mol^{-1}	−9·1	+2·0	+11·2

[a] Zeroth-order rate constant for the rate expression $-\mathrm{d}[\mathrm{U^{IV}}]/\mathrm{d}t = k[\mathrm{U^{IV}}][\mathrm{X_2}][\mathrm{H^+}]^{-2}$. [b] $I = 1{\cdot}0\text{M}$. [c] $I = 3{\cdot}0\text{M}$. [d] $I = 2{\cdot}5\text{M}$.

The acid dependence of the three reactions (21)—(23) are identical, with rate ∝ $[\mathrm{H^+}]^{-2}$, and this has been interpreted in terms of $k_c \gg k_a, k_b$ since under the

$$\mathrm{U^{4+} + X_2} \xrightarrow{k_a} \qquad (23)$$

$$\mathrm{UOH^{3+} + X_2} \xrightarrow{k_b} \qquad (24)$$

$$\mathrm{U(OH)_2^{2+} + X_2} \xrightarrow{k_c} \qquad (25)$$

conditions of our experiments $[\mathrm{U^{4+}}] > [\mathrm{UOH^{3+}}] > [\mathrm{U(OH)_2^{2+}}]$. The reason for this large difference in rate constants for the oxidation of the three $\mathrm{U^{IV}}$ species presumably lies in the fact that the uranium(VI) product is the oxo-ion $\mathrm{UO_2^{2+}}$ and the activation energy for the oxidation of $\mathrm{U(OH)_2^{2+}}$ (already containing two oxygen atoms more strongly bonded to uranium) to $\mathrm{UO_2^{2+}}$ will be less than that for $\mathrm{UOH^{3+}}$ or $\mathrm{U^{4+}}$. In other words, the reactant that most resembles the product species reacts the most rapidly. This phenomenon is quite well established in other studies involving the oxidation of aquo-ions to oxo-ions and the reduction of oxo-ions to aquo-ions.[6] An alternative explanation in terms of hydroxo-ligands bridging between oxidant and reductant does not explain the observations involving oxo-ions so simply. Interestingly, in the $\mathrm{U^{IV}}$ oxidations, the sole exception to the unreactivity of $\mathrm{U^{4+}}$ and $\mathrm{UOH^{3+}}$ is found with HOCl. This suggests that in the HOCl + $\mathrm{UOH^{3+}}$ reaction oxygen-atom transfer may take place, with the second oxygen atom in the product $\mathrm{UO_2^{2+}}$ being provided by HOCl. This would be analogous to the suggestion[7] that an oxygen-atom transfer mechanism operates in the oxidation of $\mathrm{SO_3^{2-}}$ by HOCl and means that the $\mathrm{UOH^{3+}}$ + HOCl reaction is inner sphere in character. The apparent unimportance of paths involving HOBr and HOI is doubtless due to the much lower concentrations of these species as compared with that of HOCl, as is shown by the equilibrium constants for $\mathrm{X_2}$ hydrolysis ($\mathrm{Cl_2}$, $3{\cdot}9 \times 10^{-4}$; $\mathrm{Br_2}$, $5{\cdot}8 \times 10^{-9}$; $\mathrm{I_2}$, $5{\cdot}4 \times 10^{-13}$ mol^2 l^{-2}).

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[6] A. G. Sykes, *Adv. Inorg. Radiochem.*, 1967, **10**, 153.

[7] J. Halpern and H. Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 380.

We have little evidence to distinguish between inner- and outer-sphere mechanisms for the $U(OH)_2^{2+} + X_2$ reactions. The relative rates of reaction of Cl_2, Br_2, and I_2 are in the 'expected' order $[k(Cl_2) > k(Br_2) > k(I_2)]$ in that they follow the order of equilibrium constants for the reactions $U^{IV} + X_2 \rightleftharpoons U^{VI} + 2X^-$. However a plot of $\Delta G^\ddagger$ against ΔG° for the three reactions is *not* obviously linear and the slope is very much less than that of 0·5 as required by Marcus theory of outer-sphere reactions.[8] This negative evidence indicates that at least some of the reactions proceed *via* an inner-sphere mechanism.

We have no evidence that the reactions proceed by other than a single-step two-electron change mechanism.

There is only one other example of the kinetics of oxidation of a metal ion by all three halogens being measured: that of Fe^{II} by chlorine,[9] bromine,[10] and iodine.[11] The data for Fe^{II} and U^{IV} oxidations by the halogens are compared in Table 10. Two major surprising features in the comparison are first that Fe^{2+} reacts much more rapidly with the halogens than does U^{4+} although the U^{IV} reactions are thermodynamically more favourable (E°: Fe^{3+}–Fe^{2+}, 0·77 V; UO_2^{2+},$4H^+$–U^{4+}, 0·33 V) and the Fe^{2+} reactions are non-complementary while the U^{IV} reactions *are* complementary, and secondly that the *variation* in rate constants from chlorine to iodine is very much greater with Fe^{2+} than with U^{4+}.

The increase in rate constant from I_2 to Cl_2 is caused by increasingly favourable $\Delta S^\ddagger$ terms for the U^{IV} reactions, and probably also for the Fe^{II} reactions, rather than decreasing activation energies. The trend in $\Delta S^\ddagger$ is presumably a reflection of the trend in ΔS° for the process $X_2 \longrightarrow 2X^-$.

TABLE 10

Comparison of kinetic data for the oxidation reactions of ion(II) and uranium(IV) with halogens

$$2Fe^{2+} + X_2 \longrightarrow 2Fe^{3+} + 2X^-$$

X_2	t/°C	k_2/l mol^{-1} s^{-1}	$[H^+]$/M	Relative k_2
I_2	25	$1·54 \times 10^{-4}$	1·0	1
Br_2	29·8	$7·6 \times 10^{-1}$	1·0	$5·1 \times 10^3$
Cl_2	30·0	$1·63 \times 10^2$	0·09	$1·1 \times 10^6$

$$U^{4+} + X_2 + 2H_2O \longrightarrow UO_2^{2+} + 2X^- + 4H^+$$

X_2	t/°C	k/mol l^{-1} s^{-1}	Relative k
I_2	40	$8·9 \times 10^{-4}$	1
Br_2	40	$4·7 \times 10^{-3}$	5·3
Cl_2	40	$7·4 \times 10^{-2}$	83

The reduced rates of reaction of U^{IV} compared with Fe^{II} might be a consequence of the fact that 5*f* and 3*d* electrons respectively have to be removed in their oxidations. If orbital overlap is required in the transition state then the presence of the electron in the less accessible *f* orbital might lead to reduced rates of reaction.

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[11] A. V. Hershey and W. C. Bray, *J. Amer. Chem. Soc.*, 1936, **58**, 1760.