Kinetics of the Oxidation of Uranium(IV) Ions by Halogens in Aqueous Solution. Part I. Iodine and Bromine

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The reaction $U^{4+} + 2H_2O + I_2 \longrightarrow UO_2^{2+} + 2I^- + 4H^+$ obeys the rate expression $-d[I_2]/dt = k_2'[U^{IV}][I_2][H^+]^{-2}$, with $k_2' = 8{\cdot}9 \times 10^{-4}$ l mol^{-1} s^{-1} at 40 °C and $I = 1{\cdot}0$M. The rate of reaction decreases with increasing $[I^-]$ and the results fit the expression $-d[I_2]/dt = k_8[U^{IV}][I_2] + k_9[U^{IV}][I_3^-]$, where $k_8 = 9{\cdot}9 \times 10^{-2}$ and $k_9 = 1{\cdot}9 \times 10^{-2}$ l mol^{-1} s^{-1} at 40 °C, $[H^+] = 0{\cdot}10$M, and $I = 1{\cdot}0$M. Activation energies and entropies of activation for the two paths are: for k_8, $E_a = 17{\cdot}3 \pm 2{\cdot}6$ kcal mol^{-1}, $\Delta S^\ddagger = -9{\cdot}1 \pm 1{\cdot}5$ cal K^{-1} mol^{-1}; and for k_9, $E_a = 19{\cdot}9 \pm 1{\cdot}2$ kcal mol^{-1}, $\Delta S^\ddagger = -4{\cdot}6 \pm 0{\cdot}3$ cal K^{-1} mol^{-1}. The effect on the rate of added SO_4^{2-}, F^-, Cl^-, Br^-, N_3^-, and NCO^- ions is also reported. The reaction $U^{4+} + Br_2 + 2H_2O \longrightarrow UO_2^{2+} + 2Br^- + 4H^+$ has been confirmed as obeying the rate expression $-d[U^{IV}]/dt = k_3[U^{IV}][Br_2]$, with $k_3 = 1{\cdot}16 \times 10^{-3}$ l mol^{-1} s^{-1} at 25 °C, $[H^+] = 0{\cdot}70$M, and $I = 3{\cdot}0$M. The activation energy and entropy for this reaction are $E_a = 23{\cdot}3 \pm 5{\cdot}0$ kcal mol^{-1} and $\Delta S^\ddagger = 1{\cdot}99 \pm 0{\cdot}05$ cal K^{-1} mol^{-1}.

THE oxidations (1) of uranium(IV) to uranium(VI) ion

$$U^{4+} + 2H_2O + X_2 \longrightarrow UO_2^{2+} + 2X^- + 4H^+ \quad (1)$$

by halogens are examples of complementary reactions in which the oxidation states of uranium and the halogen molecule both change by two units. The kinetics of the reaction of bromine with uranium(IV) ions have been investigated by Gordon and Andrewes;[1] we have confirmed their results and extended the work to determine the activation energy for the reaction.

EXPERIMENTAL

Uranium(VI) perchlorate was prepared by fuming $UO_2(NO_3)_2,6H_2O$ (AnalaR) repeatedly with 60% perchloric

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[1] G. Gordon and A. Andrewes, *Inorg. Chem.*, 1964, **3**, 1733.

acid until the brucine test [2] for nitrate gave a negative result. Uranium(IV) perchlorate solutions were prepared by electrolytic reduction of solutions of uranium(VI) perchlorate in perchloric acid at 0 °C by use of a mercury-pool cathode and a platinised titanium anode, the course of the electrolysis being followed by titration. Uranium(IV) ion concentrations were determined by adding a known excess of standard cerium(IV) sulphate solution to an aliquot portion of the U^{IV} solution, allowing a few minutes for the reaction to go to completion, and then estimating the excess of Ce^{IV} iodometrically. The acid concentration of the U^{IV} solution was determined by passing an aliquot portion down a cation-exchange resin in the acid form, estimating the total acid concentration in the eluent by sodium hydroxide titration, and then subtracting from this the amount of acid that had been generated on the resin by the known amount of U^{4+} in solution.

Sodium perchlorate was prepared by neutralising a slurry of sodium carbonate (AnalaR) with 60% perchloric acid. Sodium perchlorate concentrations were determined by evaporating a known volume of solution to dryness and weighing the solid.

Aqueous iodine solutions were obtained by shaking iodine (AnalaR) with distilled water for 24 h and then filtering off undissolved solid. Concentrations were determined by direct titration at 0 °C with sodium thiosulphate, sodium starch glycollate being used as indicator. Typically, concentrations of *ca.* 10^{-3}M could be obtained in this way. Aqueous bromine solutions were obtained by shaking the approximate quantity of bromine with water. Bromine concentrations were determined by adding aliquot portions to an excess of sodium iodide solution and titrating the iodine liberated with standard sodium thiosulphate solution.

The AnalaR chemicals Na_2SO_4, NaCl, KI, and KBr and reagent grade chemicals NaF, NaN_3, and NaCNO were used without purification.

The reactions of iodine and bromine with uranium(IV) ions are both moderately slow so they were both followed by manual spectrophotometric measurements with a Unicam SP 500 spectrophotometer with thermostatted cell-block. Absorbances at 464 nm corresponding to the isosbestic point for I_2 and I_3^- (U^{IV} and U^{VI} absorb negligibly) and 649 nm corresponding to U^{IV} were used to follow the courses of the reactions of U^{IV} with I_2 and of U^{IV} with Br_2 respectively.

The ionic strength of reactant solutions was maintained at 1·0M for runs with U^{IV} and I_2 and at 3·0M (so that comparison with previous work [1] would be possible) for those with U^{IV} and Br_2, sodium perchlorate being used as the inert electrolyte.

RESULTS

The Uranium(IV) *Perchlorate–Iodine Reaction.*—The rate expression was determined as follows. Runs were performed with $[U^{IV}]$ in *ca.* 10—100-fold excess over $[I_2]$. Plots of log $(OD_t - OD_\infty)$ against t (where OD_t and OD_∞ are optical densities at time t and ∞, with $\infty = ca.\ 7t_{\frac{1}{2}}$) were linear to more than 80% reaction. Pseudo-first-order rate constants, k_1, derived from the slopes of such plots, were obtained at a variety of uranium(IV) ion concentrations and then log k_1 was plotted against log $[U^{IV}]$ to give a straight line of slope 0·98 ± 0·07.

The excellent linearity of the first-order plots and the slope of 0·98 for the plot of log k_1 against log $[U^{IV}]$ established that the reaction was of the first order in $[I_2]$ and $[U^{IV}]$ respectively. Some additional runs were carried out in which neither iodine nor uranium(IV) ions were present in great excess, and for these conditions the second-order plots of log $([U^{IV}]/[I_2])$ against t were linear, thus confirming that the reaction was of the second order. The rate expressions are thus (2) for an excess of uranium(IV) ion or (3) in general. Results are given in Table 1.

$$-d[I_2]/dt = k_1[I_2] \qquad (2)$$

$$-d[I_2]/dt = k_2[U^{IV}][I_2] \qquad (3)$$

TABLE 1

Pseudo-first-order (k_1) and second-order rate constants (k_2) for the uranium(IV) ion–iodine reaction. $[H^+] =$ 0·05M; I = 1·0M; t = 40 °C

$10^4[U^{IV}]_0$/M	$10^4[I_2]_0$/M	$10^4k_1/s^{-1}$	10^2k_2/l mol^{-1} s^{-1}
214	2·623	39·8	18·50
107	2·623	19·5	18·20
53·6	2·623	9·52	17·80
26·8	2·623	4·27	18·50
8·58	3·98		17·40
8·46	4·65		18·90
8·63	4·93		17·80
			Average: 18·20 ± 0·57

The second-order rate constant, k_2, was then measured at various acid concentrations, with a variety of initial uranium(IV) ion and iodine concentrations and both pseudo-first-order and second-order conditions. Results are in Table 2. A plot of log k_2 against log $[H^+]$ was approximately linear and yielded a best straight line of slope −1·94 ± 0·60, from which it can be deduced that the order of reaction with respect to $[H^+]$ is −2·0. The rate expression should therefore be written as (4). Values of

$$-d[I_2]/dt = k_2'[U^{IV}][I_2][H^+]^{-2} \qquad (4)$$

k_2' calculated by use of this equation are in Table 2. A significant deviation occurred at the lowest acid concentration. Similar deviations have been observed for the reactions of U^{IV} with Br_2 and with Cl_2 [1,3] (though at different $[H^+]$) and are not understood and cannot be rationalised by use of a two-part expression involving orders in $[H^+]$ other than −2.

TABLE 2

Second-order rate constants for the uranium(IV) ion–iodine reaction as a function of $[H^+]$. I = 1·0M; t = 40 °C

No. of runs	$[H^+]$/M	10^2k_2/l mol^{-1} s^{-1}	$10^4k_2'$/mol l^{-1} s^{-1}
7	0·05	18·20	4·55
4	0·10	10·20	10·20
3	0·15	4·20	9·45
3	0·20	2·67	11·68
3	0·30	1·08	9·72
			Average: 8·92 ± 2·15

Effect of Anions other than Perchlorate on the Rate of the Uranium(IV) *Ion–Iodine Reaction.*—The effect on the rate of the uranium(IV)–iodine reaction of adding F^-, Cl^-, Br^-, SO_4^{2-}, N_3^-, and NCO^- ions separately, at constant ionic strength, was investigated. It was assumed that HN_3 and HF were completely undissociated at the acid concentrations employed in this study. The results are in Table 3.

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[2] F. Feigl, 'Spot Tests in Inorganic Analysis,' Elsevier, Amsterdam, 1958, p. 328.

[3] A. Adegite and M. H. Ford-Smith, following paper.

The acid dependence of the rate of the uranium(IV) ion–iodine reaction in the presence of sulphate ions was investigated. The results (Table 4) were obtained at $[SO_4^{2-}] = 0{\cdot}03$M, when nearly all the reaction is proceeding via uranium(IV)–sulphate complex ions (see Discussion section). A plot of log k_2 against log $[H^+]$ was linear with a slope of $-2{\cdot}34 \pm 0{\cdot}05$, which confirms that rate $\propto [H^+]^{-2}$ in the presence as well as in the absence of sulphate ions. It is noteworthy that in the presence of sulphate ions the result at $[H^+] = 0{\cdot}05$M is no longer discrepant.

TABLE 3

10^2k_2/l mol^{-1} s^{-1} for the uranium(IV) ion–iodine reaction as a function of various anion concentrations. $[H^+] = 0{\cdot}10$M; $I = 1{\cdot}0$M; $t = 40$ °C

	F^-	Cl^-	Br^-	I^-	SO_4^{2-}	N_3^-	CNO^-
[Anion]/M	a	b	b	c	d	d	e
0·0	10·2	10·2	10·2	10·2	10·2	10·2	10·2
0·001	9·0				13·4	6·1	
0·002					15·2		
0·003	6·0						
0·004	4·0				19·8		
0·005		9·9		4·26		5·8	
0·008					23·4		
0·010	0·32		10·0	3·32	20·4	5·5	
0·016							11·5
0·020		9·70	10·2	2·62	14·4	5·1	
0·030					9·2		
0·040							15·6
0·050		9·0	7·6	2·23	4·6	4·8	19·2

	a	b	c	d	e
$10^2[U^{IV}]_0$/M	1·018	1·072	1·072	1·018	1·017
$10^4[I_2]_0$/M	4·019	4·019	5·464	4·564	4·019

TABLE 4

Second-order rate constants in the presence of sulphate ions as a function of $[H^+]$. $[SO_4^{2-}] = 0{\cdot}03$M; $I = 1{\cdot}0$M; $t = 25$ °C; $[U^{IV}]_0 = 8{\cdot}30 \times 10^{-3}$M; $[I_2]_0 = 5{\cdot}93 \times 10^{-4}$M

$[H^+]$/M	10^2k_2/l mol^{-1} s^{-1}	10^4k_{14}/mol l^{-1} s^{-1}
0·05	37·0	9·3
0·10	9·2	9·2
0·15	3·1	7·0
0·20	1·8	7·2

The temperature dependence of the rate of the uranium(IV)–iodine reaction was investigated in both the absence and presence of iodide ions; results are in Table 5.

TABLE 5

Observed second-order rate constants (10^2k_2/l mol^{-1} s^{-1}) for the uranium(IV) ion–iodine reaction at various iodide concentrations and temperatures. $[H^+] = 0{\cdot}10$M; $I = 1{\cdot}0$M; $[U^{IV}]_0 = 7{\cdot}13 \times 10^{-3} - 1{\cdot}513 \times 10^{-2}$M; $[I_2]_0 = 5{\cdot}62$—$5{\cdot}79 \times 10^{-4}$M

t/°C $[I^-]$/M	24·8	30·8	40·0	45·1	50·1
0	3·85	5·25	10·20	17·80	36·3
0·001					33·0
0·004		2·83			
0·005			4·27	11·40	19·35
0·008		2·08			
0·01		1·84	3·32	8·30	14·50
0·02		1·17	2·62	5·93	10·13
0·04				4·90	
0·05			2·23	4·55	7·23

The Uranium(IV) *Perchlorate–Bromine Reaction.*—A rate expression and rate constants for this reaction have been obtained by Gordon and Andrewes,[1] but Arrhenius parameters had not been measured. Using a constant acid concentration and reaction mixtures in which neither U^{IV} nor Br_2 was in great excess, we obtained good straight lines when log ($[U^{IV}]/[Br_2]$) was plotted against time. The slopes yielded the values for the second-order rate constant k_3 in the rate expression (5) at four different temperatures (Table 6). We adopted the published [1] rate expression (6) to calculate values of k_3' (Table 6).

$$-d[U^{IV}]/dt = k_3[U^{IV}][Br_2] \qquad (5)$$

$$-d[U^{IV}]/dt = k_3'[U^{IV}][Br_2][H^+]^{-2} \qquad (6)$$

TABLE 6

Second-order rate constants for the uranium(IV) ion–bromine reaction. $[H^+] = 0{\cdot}70$M; $I = 3{\cdot}0$M; $[U^{IV}]_0 = 4{\cdot}7 \times 10^{-3}$—$9{\cdot}5 \times 10^{-2}$M; $[Br_2]_0 = 2{\cdot}0$—$3{\cdot}7 \times 10^{-2}$M

No. of runs	t/°C	10^3k_3/l mol^{-1} s^{-1}	$10^4k_3'$/mol l^{-1} s^{-1}
6	25·0	1·16 ± 0·24	5·69 ± 1·18
	25·0	1·08 ± 0·13 [a]	5·30 ± 0·64
1	34·1	5·03	24·6
1	40·0	9·60	47·0
1	50·0	30·4	149

[a] From ref. 1.

A plot of log k_3 against $1/T$ was linear and from the slope and intercept we calculate $E_a = 23{\cdot}3 \pm 5{\cdot}0$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1{\cdot}99 \pm 0{\cdot}05$ cal K^{-1} mol^{-1}. Table 6 shows that our results for 25 °C are in satisfactory agreement with those of Gordon and Andrewes.[1]

DISCUSSION

The complementary reaction between uranium(IV) ions and iodine could proceed either by the two-electron (bimolecular) path (7) or by a number of one-electron paths, *e.g.*, (8) and (9) or (10) and (11). The mechanism comprising reactions (8) and (9) is kinetically indistinguishable from the two-electron path (7), both producing second-order kinetics with $k_2 = k_a$ for reaction (7) and $k_2 = k_bk_d/(k_c + k_d)$ for (8) + (9). If one makes the assumption $k_c \gg k_d$, which gives $k_2 = k_bk_d/k_c$, then it can be shown that mechanism (8) + (9) requires k_d to be unusually but not impossibly large. The equilibrium constant for reaction (8) ($= k_b/k_c$) is calculated to be 8×18^{-8} at 25 °C from the electrode-potential data of equations (12) and (13). (The uranium $E°$ value is from

$$U^{IV} + I_2 \xrightarrow{k_a} U^{IV} + 2I^- \qquad (7)$$

$$U^{IV} + I_2 \underset{k_c}{\overset{k_b}{\rightleftharpoons}} U^V + I_2^- \qquad (8)$$

$$U^V + I_2^- \xrightarrow{k_d} U^{VI} + 2I^- \qquad (9)$$

$$2U^V \xrightarrow{k_e} U^{IV} + U^{VI} \qquad (10)$$

$$U^{IV} + I_2^- \xrightarrow{k_f} U^V + 2I^- \qquad (11)$$

$$U^V + e^- \longrightarrow U^{IV};\ E° = +0{\cdot}62\ V \qquad (12)$$

$$I_2 + e^- \longrightarrow I_2^-;\ E° = +0{\cdot}2\ V \qquad (13)$$

the literature;[4] we have calculated the value of the I_2–I_2^- E° and arrive at the same result as that published by Higginson and his co-workers.[5]) Combination of this calculated value of $k_b/k_c = 8 \times 10^{-8}$ with the observed value of $k_2 = 3{\cdot}9 \times 10^{-2}$ l mol^{-1} s^{-1} at $[H^+] = 0{\cdot}05$M gives $k_d = 5 \times 10^6$ l mol^{-1} s^{-1}.

The mechanism involving reactions (8), (10), and (11) leads to an extremely complicated rate expression. However the rate of reaction (10) is known [6] to be quite slow, with $k_c = 436$ l mol^{-1} s^{-1} at $[H^+] = 1{\cdot}0$M, and this suggests that this mechanism is implausible. We conclude that it is probable that the expected two-electron mechanism does operate in the reaction of uranium(IV) with iodine.

Because $E^\circ = +0{\cdot}54$ V for the Br_2–Br_2^- half-cell reaction (calculated; in substantial agreement with the value of $+0{\cdot}478$ V calculated by Carter and Davidson [7]) while the observed rate of the uranium(IV) ion–bromine reaction is not much greater than that for the uranium(IV) ion–iodine reaction, there is less reason to prefer the two-electron over the one-electron path for the bromine reaction since k_d is not required to be unusually large.

Dependence of Rate of Reaction on Acidity.—Both the iodine and bromine reactions have rates $\propto [H^+]^{-2}$. We adopt the customary rationalisation of this acid dependence and deduce that, in the absence of terms which are independent of $[H^+]$ or which contain $[H^+]^{-1}$, the species U^{4+} and $U(OH)^{3+}$ react much more slowly than $U(OH)_2^{2+}$ with iodine and bromine as shown by the reactions (14)—(17). Unfortunately, while K_1 has been measured [4]

$$U^{4+} + H_2O \overset{K_1}{\rightleftharpoons} U(OH)^{3+} + H^+ \qquad (14)$$

$$U(OH)^{3+} + H_2O \overset{K_2}{\rightleftharpoons} U(OH)_2^{2+} + H^+ \qquad (15)$$

$$U(OH)_2^{2+} + I_2 \xrightarrow{k_4} UO_2^{2+} + 2I^- + 2H^+ \qquad (16)$$

$$U(OH)_2^{2+} + Br_2 \xrightarrow{k_5} UO_2^{2+} + 2Br^- + 2H^+ \qquad (17)$$

where $k_4 = k_2'/K_1K_2$ and $k_5 = k_3'/K_1K_2$

at a variety of temperatures and ionic strengths, only one early and uncertain measurement of K_1K_2 $(= 5 \times 10^{-3}$ mol^2 l$^{-2})$ has been reported.[4] (If this value is to be believed, then $K_2 > K_1$, which is improbable.) Using this value for K_1K_2, uncorrected for temperature and ionic-strength differences, we obtain $k_4 = 0{\cdot}178$ l mol^{-1} s^{-1} at 40 °C and $k_5 = 0{\cdot}106$ l mol^{-1} s^{-1} at 25 °C.

Dependence of Rate of Reaction on the Concentration of Added Anions.—We attribute the changes in rate, listed in Table 3, accompanying the replacement of ClO_4^- by other anions to the formation of inner-sphere complexes by U^{IV} and/or I_2 with these anions, with the complexed and uncomplexed species reacting at different rates.

Iodide. The observed decrease in rate with increasing iodide-ion concentration is consistent with the mechanism (18)—(20). Linear plots of $k_2(1 + K_4[I^-])$ against $[I^-]$

$$I_2 + I^- \overset{K_4}{\rightleftharpoons} I_3^- \qquad (18)$$

$$U^{IV} + I_2 \xrightarrow{k_8} \text{Products} \qquad (19)$$

$$U^{IV} + I_3^- \xrightarrow{k_9} \text{Products} \qquad (20)$$

were obtained at four temperatures with intercept $= k_8$ and slope $= k_9K_4$, to give the results shown in Table 7.

TABLE 7

Analysis of changes in the second-order rate constant for the uranium(IV) ion–iodine reaction with changes in $[I^-]$ and temperature

t/°C	K_4/l mol^{-1} [a]	10^2k_8/ l mol^{-1} s^{-1}	10^2k_9/ l mol^{-1} s^{-1}
24·8		3·9	
30·8	602·6	6·98	0·80
40·0	466·5	9·90	1·89
45·1	411·0	23·8	3·70
50·1	364·2	43·0	5·37

[a] From ref. 4.

Plots of log k_8 and log k_9 against $1/T$ were linear; from the slopes and intercepts we calculate the Arrhenius parameters listed in Table 8. These values of E_a and $\Delta S^\ddagger$ must include the (unknown) ΔH° and ΔS° values for hydrolysis of the uranium(IV) ion.

Treatment of the observed data in terms of mechanism (21) and (22), with $k_6 = 3{\cdot}98 \times 10^{-2}$ and $k_7 = 2{\cdot}9 \times 10^7$ l mol^{-1} s^{-1} at 40 °C, is kinetically indistinguishable from the $I_2 + I_3^-$ treatment but we think the latter explanation is more plausible.

$$U(OH)_2^{2+} + I_2 \xrightarrow{k_6} \text{Products} \qquad (21)$$

$$U(OH)^{3+} + HOI \xrightarrow{k_7} \text{Products} \qquad (22)$$

TABLE 8

Arrhenius parameters for the uranium(IV) ion–iodine reaction

Reaction	E_a/kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}
$U^{IV} + I_2(k_8)$	$17{\cdot}3 \pm 2{\cdot}6$	$-9{\cdot}1 \pm 1{\cdot}5$
$U^{IV} + I_3^-(k_9)$	$19{\cdot}9 \pm 1{\cdot}2$	$-4{\cdot}6 \pm 0{\cdot}3$

Sulphate. The effect of added sulphate ions is to increase the rate of the $U^{IV} + I_2$ reaction at low $[SO_4^{2-}]$ and to decrease the rate at higher $[SO_4^{2-}]$. It was assumed that the rate expression (23) was applicable.

$$\text{Rate} = k_2[U^{IV}][I_2] = k_8[U^{4+}][I_2] + k_{12}[USO_4^{2+}][I_2] + k_{13}[U(SO_4)_2][I_2] \qquad (23)$$

Concentrations of U^{4+}, USO_4^{2+}, and $U(SO_4)_2$ were computed at each $[SO_4^{2-}]$ and these, together with the rate data, are illustrated in the Figure. By use of a computer and a multiple regression program the values $k_{12} = 0{\cdot}330 \pm 0{\cdot}002$ and $k_{13} = 0{\cdot}016 \pm 0{\cdot}015$ l mol^{-1} s^{-1} were calculated to give optimum agreement with the

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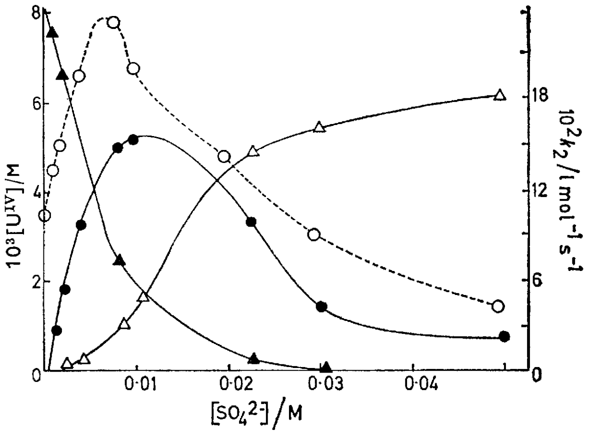
[4] 'Stability Constants of Metal-ion Complexes', 2nd edn., The Chemical Society, London, 1964.

[5] E. A. M. Wetton and W. C. E. Higginson, *J. Chem. Soc.*, 1965, 5890.

[6] H. G. Heal and J. G. N. Thomas, *Trans. Faraday Soc.*, 1949, **45**, 11.

[7] P. R. Carter and N. Davidson, *J. Phys. Chem.*, 1952, **56**, 877.

experimental results. A comparison of experimental and calculated second-order rate constants is shown in Table 9; the average discrepancy of 6·5% between experimental and calculated rate constants suggests that the assumed rate expression is satisfactory.



Change in the rate of the uranium(IV)–iodine reaction and calculated concentration of complexed and uncomplexed U^{IV} species in solution with changing sulphate-ion concentration; (△), $[U(SO_4)_2]$; (●), $[U(SO_4)^{2+}]$; (▲), $[U^{4+}]$; and (○), $10^2k_2/l\ mol^{-1}\ s^{-1}$

Fluoride, chloride, bromide, azide, and cyanate. Data for the effect of these anions on the rate of the reaction are reported in Table 3, but there is insufficient information in the literature about the relevant equilibrium constants for much useful comment. Chloride and bromide ions have little effect on the rate; this suggests that the species I_2Cl^- and I_2Br^- react with U^{IV} at rates similar to that of I_2 since they are present in significant amounts at the higher anion concentrations. (At $[X^-] = 0·05$M the iodine was complexed to the following approximate[4] extents: 5% I_2F^-; 8% I_2Cl^-; 40% $I_2N_3^-$, and 90% I_2Br^-.)

TABLE 9

Comparison of calculated and observed second-order rate constants $k_2/l\ mol^{-1}\ s^{-1}$ for the uranium(IV) ion–iodine reaction at various sulphate-ion concentrations. $[U^{IV}]_0 = 6·9$—$8·5 \times 10^{-3}$M; $[I_2]_0 = 4·56 \times 10^{-4}$M; $[H^+] = 0·10$M; $I = 1·0$M; $t = 40$ °C; $k_8 = 10·2 \times 10^{-2}$, $k_{12} = 0·330$, $k_{13} = 0·016\ l\ mol^{-1}\ s^{-1}$

$[SO_4^{2-}]/M$	10^2k_2 (obs)	10^2k_2 (calc)	% Difference
0	10·2	10·2	0
0·001	13·4	11·8	11·7
0·002	15·2	15·0	1·2
0·004	19·8	18·8	5·0
0·008	23·4	22·7	2·9
0·01	20·4	22·5	10·2
0·02	14·4	14·1	2·2
0·03	9·2	8·1	12·0
0·04	4·6	4·6	6·7

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