Kinetics and Mechanism of the Oxidation of Uranium(III) by Aqueous Acidic Solutions of Iodine and Bromine

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The rates of oxidation of U^{3+} by I_2 and Br_2 in aqueous acidic solutions have been investigated. For the iodine reaction the rate equation is (i) where $k_1 = (3.92 \pm 0.78) \times 10^5$ dm^3 mol^{-1} s^{-1} and $k_2 = (0.31 \pm 0.02) \times 10^5$ dm^3

$$\text{Rate} = -d[I_2]_T/dt = k_1[U^{3+}][I_2] + k_2[U^{3+}][I_3^-] \qquad \text{(i)}$$

mol^{-1} s^{-1} at 25 °C and $I = 1.0$ mol dm^{-3} Li[ClO$_4$]. The corresponding activation parameters are $\Delta H_1^\ddagger = 3.2 \pm 0.4$ kcal mol^{-1}, $\Delta S_1^\ddagger = -11.0 \pm 1.0$ cal K^{-1} mol^{-1}, $\Delta H_2^\ddagger = 3.9 \pm 0.4$ kcal mol^{-1}, and $\Delta S_2^\ddagger = -12.6 \pm 1.5$ cal K^{-1} mol^{-1}. The rate is unaffected by acid for the range $[H^+] = 0.05$—0.5 mol dm^{-3}, but added Cl^- increases the rate. For the bromine reaction the rate equation is (ii) where $k_{Br} = (7.2 \pm 0.8) \times 10^6$ dm^3 mol^{-1} s^{-1} at

$$\text{Rate} = -d[Br_2]/dt = k_{Br}[U^{3+}][Br_2] \qquad \text{(ii)}$$

$I = 1.0$ mol dm^{-3}, 25 °C, and $[H^+] = 0.1$ mol dm^{-3}. Activation parameters are $\Delta H^* = 3.1 \pm 0.3$ kcal mol^{-1} and $\Delta S^* = -21.2 \pm 2.3$ cal K^{-1} mol^{-1}. The rate is unaffected by acid in the range $[H^+] = 0.1$—0.5 mol dm^{-3} or by bromide in the range $[Br^-] = 0.004$—0.2 mol dm^{-3}. On employing Marcus theory, an excellent correlation has been obtained between the rates of uranium(III) reduction of some oxidants, including iodine and bromine, and the free energies of these reactions. Since these other non-halogen reactions go *via* the outer-sphere mechanism, it is concluded that at least the first step in the two-step oxidation of U^{3+} by Br_2, I_2, or $[I_3]^-$ is outer sphere. The homonuclear exchange rate constant k_{ex} for $U^{3+} + U^{4+}$ is deduced to be 1.66 ± 0.16 dm^3 mol^{-1} s^{-1}.

SINCE Espenson and Wang published their results on the kinetics of the reduction of some penta-amminecobalt(III) complexes [1,2] and some chromium(III) complexes,[3] there have been a number of kinetic studies of reactions in which U^{3+} is the reducing ion. Newton and his co-workers reported [4,5] the reactions of this powerful reducing ion with $[UO_2]^{2+}$, $[UO_2]^+$, and *cis*-$[Co(NH_3)_4(OH_2)_2]^{3+}$, and more recently Ekstrom *et al.*[6] reported the reduction of V^{3+}, $[VO]^{2+}$, and Fe^{3+}. Here we report the results of our kinetic investigation of the reaction (1). Although it was previously reported [7-9]

$$2U^{3+} + X_2 \longrightarrow 2U^{4+} + 2X^- \qquad (1)$$
$$(X = I \text{ or } Br)$$

that both Br_2 and I_2 oxidize the expected uranium product U^{4+} to $[UO_2]^{2+}$, the rates of these reactions are extremely slow and do not compete with or provide complications to the fast reduction of these halogens by U^{3+}. On the basis of Marcus theory,[10] attempts have been made to correlate the rate constants of the different uranium(III) reactions with the free energies of the reactions.

EXPERIMENTAL

Materials.—Uranium(III) solutions were prepared by zinc-amalgam reduction of uranium(VI) perchlorate solutions containing the desired amounts of acid (generally 0.1 mol dm^{-3} HClO$_4$) and Li[ClO$_4$] solution. Uranium(VI) perchlorate was prepared by fuming $[UO_2][NO_3]_2 \cdot 6H_2O$ (AnalaR grade) with concentrated perchloric acid until the brucine test for nitrogen was negative.[11] As a result of the extremely rapid reaction of U^{3+} with oxygen, the zinc-amalgam reduction was effected in serum bottles in which oxygen was excluded by continuously passing argon which had been previously scrubbed in chromium(II) towers. Solutions of U^{3+} were kept under an argon atmosphere and transferred to the Durrum–Gibson stopped-flow syringes employing anaerobic techniques. Concentrations of the uranium(III) solutions were determined using reported values [2,5] of the absorption coefficients (ε 1 620 and 154 dm^3 mol^{-1} cm^{-1} at 350 and 522 nm). Because of the low solubility of iodine, aqueous solutions of tri-iodide prepared by dissolution of resublimed iodine in potassium iodide (AnalaR) were employed. Bromine solutions were similarly made by shaking pure bromine with water until a substantial amount of it had dissolved. The concentrations of the tri-iodide and bromine solutions were determined by titration against standardized sodium thiosulphate. Lithium perchlorate, prepared by the usual methods from lithium carbonate and HClO$_4$, was employed to maintain a constant ionic strength. Where necessary, allowance was always made for any added sodium iodide or sodium bromide.

Kinetics.—Rates of the $U^{3+} + [I_3]^-$ reaction were monitored at 400 nm under pseudo-first-order conditions with uranium(III) concentrations in large excess over total iodine concentrations. Under these conditions, absorbance changes were due to total iodine being consumed during the course of the reaction. Although, both U^{3+} and $[I_3]^-$ absorb in this region (ε 208 and 6 750 dm^3 mol^{-1} cm^{-1} respectively), the absorbance change due to U^{3+} consumed is very small compared to the absorbance due to the $[I_3]^-$. This was confirmed by the non-dependence of the rate constants on wavelength in the 380—420 nm region. The rate of the $U^{3+} + Br_2$ reaction was monitored at 350 nm following changes in the absorbance of U^{3+} which is the predominant absorbing species for the concentrations

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employed. Some runs were made with bromine concentrations in large excess over U^{3+}, and others under direct second-order conditions. Rate constants from both sets of measurements were in reasonable agreement.

RESULTS

Stoicheiometry.—The ratio of moles of U^{3+} to $[I_3]^-$ or Br_2 consumed was determined by spectrophotometric measurement of absorbance changes as $[I_3]^-$ was added to excess of U^{3+}. Two moles of U^{3+} were consumed per mol of halogen or trihalide. This confirms that the reduction of the halogens by U^{3+} is much faster than by U^{4+}, and hence there is no interference from absorbance changes due to the latter reduction.

TABLE 1

Rate constants for the $U^{3+} + [I_3]^-$ reaction at $I = 1.0$ mol dm^{-3} Li[ClO$_4$] and $[I_2]_T = 1.0 \times 10^{-5}$—$2.0 \times 10^{-5}$ mol dm^{-3}

θ_c / °C	$10^5[U^{3+}]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$10^3[I^-]$ / mol dm^{-3}	$10^3[Cl^-]$ / mol dm^{-3}	$10^{-5}k_0$ / dm^3 mol^{-1} s^{-1}
25	11.7	0.1	2.0		1.62
	36.6	0.1	2.0		1.84
	37.5	0.1	2.0		1.36
	48.8	0.1	2.0		1.57
	52.0	0.1	2.0		1.47
	73.2	0.1	2.0		1.88
	75.5	0.1	2.0		1.65
	97.6	0.1	2.0		1.70
	73.4	0.05	2.0		1.62
	60.0	0.20	2.0		1.48
	78.5	0.30	2.0		1.40
	68.2	0.40	2.0		1.68
	68.2	0.50	2.0	1.0	1.60
	32.9	0.1	2.0	2.5	1.70
	26.4	0.1	2.0	5.0	1.83
	47.4	0.1	2.0	10.0	2.03
	27.7	0.1	20.0		2.37
	56.0	0.1	40.0		0.54
	56.0	0.1	160.0		0.43
	56.0	0.1	200.0		0.35
	56.0	0.1	2.0		0.33
41	56.0	0.1	8.0		2.45
	56.0	0.1	10.0		1.20
	56.0	0.1	40.0		1.16
	56.0	0.1	160.0		0.60
	56.0	0.1	2.0		0.45
20	56.0	0.1	8.0		1.36
	56.0	0.1	10.0		0.63
	56.0	0.1	40.0		0.55
	56.0	0.1	80.0		0.35
	56.0	0.1	80.0		0.31
	56.0	0.1	160.0		0.28
5	56.0	0.1	2.0		0.77
	56.0	0.1	8.0		0.40
	56.0	0.1	10.0		0.33
	56.0	0.1	40.0		0.21
	56.0	0.1	80.0		0.19
	56.0	0.1	120.0		0.18

Rate Data for the Uranium(III) + *Iodine Reaction*.—Pseudo-first-order plots were linear to more than 90% completion of reaction. From such plots, pseudo-first-order rate constants were obtained, and thence the second-order rate constants at different initial concentrations of reactants. From these, and the stoicheiometric results, the rate law for the reaction is as in (2). Values of k_0 were

$$\frac{-\frac{1}{2}d[U^{III}]}{dt} = \frac{-d[I_3]^-}{dt} = k_0[U^{3+}][I_3]^- \qquad (2)$$

determined for different initial concentrations of U^{3+}, total iodine ($[I_3]^- + [I_2]$), H^+, Cl^-, I^-, and temperature and the results are shown in Table 1. It is evident that k_0 is independent of the concentration of acid and U^{3+}, increases with Cl^-, but decreases with I^-.

Analysis of the effect of added iodide. Among the different equilibria that can be set up in acid solutions containing iodide and iodine, the most viable (in terms of effect on rate) is the rapid equilibrium (3). Thus, the decreasing

$$I_2 + I^- \overset{K_3}{\rightleftharpoons} [I_3]^- \qquad (3)$$

value of k_0 as $[I^-]$ increases is due to the slower oxidation rate by $[I_3]^-$ compared with molecular I_2. Therefore, rate equation (2) must be modified as in (4). From (4), one

$$\text{Rate} = k_0[U^{III}][I_2]_T = k_1[U^{3+}][I_2] + k_2[U^{3+}][I_3^-] \qquad (4)$$

$$[I_2]_T = [I_2] + [I_3^-] \qquad (5)$$

obtains (6) where K_3 is the equilibrium constant for (3) and

$$k_0(1 + K_3[I^-]) = k_1 + k_2K_3[I^-] \qquad (6)$$

k_1 and k_2 are the bimolecular rate constants for the oxidation of U^{3+} by I_2 and $[I_3]^-$ respectively. Plots of the left-hand side of equation (6) against $[I^-]$ should be linear with gradient and intercepts of k_1 and k_2K_3 respectively. Such plots at different temperatures are shown in Figure 1, and the values of k_1 and k_2 and the employed values of K_3 are given as functions of temperature in Table 2. The corresponding activation parameters obtained from plots of log(log k/T) against $1/T$ are: $\Delta H_1^‡ = 3.2 \pm 0.4$ kcal mol^{-1}, $\Delta S_1^‡ = -11.0 \pm 1.0$ cal K^{-1} mol^{-1}, $\Delta H_2^‡ = 3.9 \pm 0.4$ kcal mol^{-1}, and $\Delta S_2^‡ = -12.6 \pm 1.5$ cal K^{-1} mol^{-1}.*

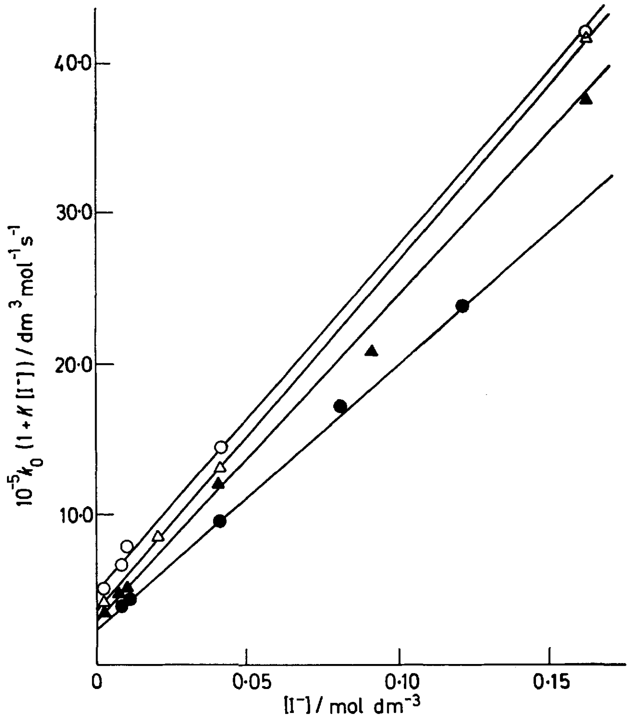

FIGURE 1 Effect of iodide ion on the $U^{3+} + I_2$ reaction: plots of $k_0(1 + K[I^-])$ against $[I^-]$ at 5 (●), 20 (▲), 25 (△), and 41 °C (○)

Effect of Cl^-. Table 1 shows that k_0 increases slightly as

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* 1 cal = 4.184 J.

[Cl$^-$] increases. In the absence of any information regarding the complex-formation constant for [UCl]$^{2+}$, the slight catalysis by Cl$^-$ is attributed to a higher rate of oxidation by [I$_2$Cl]$^-$ compared to [I$_3$]$^-$ or I$_2$. (It is considered unlikely that the formation constant for [UCl]$^{2+}$ will be much different from 1.08 dm^3 mol^{-1}, the value for $U^{4+} + Cl^- \rightleftharpoons [UCl]^{3+}$.[12]) Plots of k_0 against [Cl$^-$] were linear, and from these the rate equation (7) is deduced with $k_1 = (1.64 \pm 0.02) \times 10^5$ dm^3 mol^{-1} s^{-1} and $k_3 = (7.39 \pm 0.15) \times 10^6$

$$\text{Rate} = k_1[U^{3+}][I_2] + k_3[U^{3+}][I_2][Cl^-] \qquad (7)$$

dm^6 mol^{-2} s^{-1}. An alternative interpretation, fully amplified below, is that the chloride catalysis is the often observed effect of adding anions to reactions of the outer-sphere type.

TABLE 2

Variation of k_1, k_2, and K_3 with temperature for the U^{3+} + iodine reaction

θ_c/°C	K_3 * / dm^3 mol^{-1}	$10^{-5}k_1$ / dm^3 mol^{-1} s^{-1}	$10^{-5}k_2$ / dm^3 mol^{-1} s^{-1}
5.0	113.2	2.35 ± 0.27	0.16 ± 0.01
20.0	836.6	3.19 ± 0.27	0.26 ± 0.01
25.0	74.48	3.92 ± 0.97	0.31 ± 0.01
41.0	577.2	5.11 ± 0.34	0.40 ± 0.01

* Obtained from the data of M. Davies and E. Gwynne, *J. Amer. Chem. Soc.*, 1952, **74**, 2748.

TABLE 3

Second-order rate constants (k_4) for the U^{3+} + Br$_2$ reaction at I = 1.0 mol dm^{-3} Li[ClO$_4$]

θ_c/°C	$10^5[U^{3+}]$/mol dm^{-3}	$10^5[Br_2]$/mol dm^{-3}	[H$^+$]/mol dm^{-3}	$10^3[Br^-]$/mol dm^{-3}	$10^{-6}k_4$/dm^{3}mol^{-1}s^{-1}
12.0	5.40	0.86	0.10		0.58
	7.80	6.40	0.10		0.59
	13.4	10.20	0.10		0.53
	13.4	10.20	0.10		0.56
17.0	8.48	3.20	0.10		0.66
	13.57	3.20	0.10		0.65
	13.57	6.40	0.10		0.60
	8.48	6.40	0.10		0.66
	8.48	12.80	0.10		0.67
	13.57	12.80	0.10		0.61
25.0	0.85	0.93	0.10		0.72
	1.11	1.25	0.10		0.82
	1.11	1.25	0.10		0.73
	1.11	2.50	0.10		0.75
	0.85	4.70	0.10		0.78
	0.85	7.00	0.10		0.74
	0.85	9.30	0.15		0.73
	2.70	1.14	0.25		0.79
	2.70	1.14	0.36		0.71
	2.70	1.14	0.45		0.75
	2.70	1.14	0.45	4.00	0.79
	2.50	2.50	0.45	8.00	0.71
	2.50	2.50	0.45	16.00	0.66
	2.50	2.50	0.45	32.00	0.83
	2.50	2.50	0.45	100.00	0.69
	2.4	12.3	0.45	200.00	0.70
31	8.10	4.40	0.10		0.83
	8.10	4.40	0.10		0.90
	8.10	8.80	0.10		0.90
	15.17	8.80	0.10		0.86
	8.10	13.20	0.10		0.90

Rate Data for the Uranium(III) + *Bromine Reaction*.—The agreement between second-order rate constants obtained from pseudo-first-order plots in which [Br$_2$] > [U^{3+}], and those obtained when [Br$_2$]$_0$ and [U^{3+}]$_0$ differed only slightly, confirms the rate equation (8). The magnitude of k_4 and the reported value for the corresponding

$$\text{Rate} = \frac{-\frac{1}{2}d[U^{3+}]}{dt} = \frac{-d[Br_2]}{dt} = k_4[U^{3+}][Br_2] \qquad (8)$$

reaction of bromine with U^{4+} show that reaction (1) (X = Br) is *ca.* 10^9 times faster than the rate of oxidation of U^{4+} by bromine. The independence of k_4 of [Br$_2$]$_0$ confirms this. Values of k_4 as functions of [U^{3+}]$_0$, [Br$_2$]$_0$, [H$^+$], [Br$^-$], and temperature are shown in Table 3. The results show that k_4 is not dependent on the concentration of acid or bromide. From plots of $\log(k_4/T)$ against $1/T$, the activation parameters obtained for this reaction were $\Delta H_4^\ddagger = 3.1 \pm 0.3$ kcal mol^{-1} and $\Delta S_4^\ddagger = -21.2 \pm 2.3$ cal K^{-1} mol^{-1}.

DISCUSSION

The form of the rate laws obtained for these systems suggest a bimolecular interaction between U^{3+} and the oxidants. These reactions are non-complementary redox processes, and by comparison with similar systems that have been previously investigated such as $V^{2+} + X_2$ (X = I, Br, or Cl),[13] $V^{3+} + X_2$ (X = I or Br),[14,15] $Ti^{3+} + X_2$ (X = I or Cl),[16,17] $Fe^{2+} + Br_2$, $[M^{II}L]^{2-} + X_2$ (L = ethylenediaminetetra-acetate; M = Fe, Co, or Mn; X = I or Br),[18-21] and $[VO]^{2+} + Cl_2$,[22] the reaction probably proceeds by a series of univalent changes with the production of [I$_2$]$^{-\cdot}$ or [Br$_2$]$^{-\cdot}$ as reactive intermediates. The suggested paths could therefore be written as (9)—(11). In the above scheme, path (10) is

$$U^{3+} + X_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} U^{4+} + [X_2]^{-\cdot} \qquad (9)$$

$$U^{3+} + [X_3]^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} U^{4+} + [X_2]^{-\cdot} + X^- \qquad (10)$$

$$U^{3+} + [X_2]^{-\cdot} \xrightarrow{k_7} U^{4+} + 2X^- \qquad (11)$$

kinetically indistinguishable from (9) for X = Br, and $k_7 \gg k_{-5}$ and $k_7 \gg k_{-6}$. Hence, applying the steady-state approximation to [X$_2$]$^{-\cdot}$, the rate equation derived from (9)—(11) becomes identical with the empirical rate laws (4) and (8). It should be noted that the expected inhibition by U^{4+} will not occur here since $\Delta G^\ominus$ for reactions (9) and (10) are very favourable.[17]

The alternative scheme to equations (9)—(11) is a two-electron transfer process represented by equations

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(12)—(14). This alternative is rejected on the grounds

$$U^{3+} + X_2 \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} U^V + 2X^- \qquad (12)$$

$$U^V + U^{III} \xrightarrow{k_9} 2U^{IV} \qquad (13)$$

$$2U^V \xrightarrow{k_{10}} U^{VI} + U^{IV} \qquad (14)$$

that independent measurements [2-4] of k_9 and k_{10} show that they are much smaller than either k_0 or k_4. In addition, reaction (12) involves the conversion of an aqua-ion (U^{3+}) to an oxo-cation ($[UO_2]^+$) and kinetic studies of such systems {for instance, $V^{3+} + X_2$ ($X = I$ or Br),[14,15] $[VO]^{2+} + Cl_2$,[22] and oxidation of U^{4+} to $[UO_2]^{2+}$ by X_2 ($X = Cl$, Br, or I) [7-9]} have shown that k_8 should be strongly acid dependent. Our results (Tables 1 and 3) show that both k_0 and k_4 which are equivalent to k_8 are acid independent, and thus provide an empirical basis for the rejection of the two-electron path.

The problem of whether these reactions proceed by the outer-sphere or inner-sphere mechanisms has to be resolved on the basis of indirect evidence since a binuclear intermediate [23] or the immediate products [24] of the reaction cannot be identified because both U^{3+} and U^{4+} are substitution-labile.* An additional complication is that the mechanism involves two consecutive reactions, $U^{3+} + X_2$ and $U^{3+} + [X_2]^{-\cdot}$ [equations (9)—(11)]. The two reactions need not be of the same mechanism, as has been demonstrated for $Cr^{2+} + Cl_2$.[25,26] Here, $Cr^{2+} + Cl_2$ [equivalent to (9)] is inner-sphere only, while $Cr^{2+} + [X_2]^{-\cdot}$ proceeds by both the inner-sphere and the outer-sphere mechanisms.[26] Our choice of mechanism for the oxidation of U^{3+} by X_2 is based on the correlation of rate with free energy employing Marcus theory.[10] Marcus's equation for a series of reactions that proceed by the same mechanism is (15) where k_{11}

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \qquad (15)$$

and k_{22} are the homonuclear electron-exchange rates for the reducing and oxidizing ions (here, U^{3+} and X_2 respectively), k_{12} and K_{12} are the rate and equilibrium constants for the redox reactions respectively, and $\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2)$ with Z being the collision frequency for the uncharged species, generally taken as 10^{11} dm^3 mol^{-1} s^{-1}. Equation (15) could be written as (16). Thus, in a series of reactions of different

$$\log k_{12} - 0.5 (\log k_{22} + \log f) = 0.5 \log K_{12} + 0.5 \log k_{11} \qquad (16)$$

oxidants with the same reducing ion, and providing the reactions proceed by the same mechanism, a plot of the left-hand side of equation (16) against $\log K_{12}$ should be linear with gradient and intercept of 0.5 and 0.5 $\log k_{11}$ respectively.

It has been shown that the oxidations of U^{3+} by V^{3+} and Fe^{3+} most probably proceed by the outer-sphere mechanism.[6] Similarly, the reductions of $[Ru(NH_3)_6]^{3+}$ by aqua-ions [27] and U^{3+} (ref. 28) also proceed by the outer-sphere mechanism. Consequently, as a means of employing Marcus theory to probe the mechanism of oxidation of U^{3+} by I_2, $[I_3]^-$, and Br_2, equation (16) was applied to provide correlations of the rates of these reactions. However, in applying this equation, some of the kinetic and thermodynamic parameters that appear in the equation have not been experimentally determined, and hence estimated values reported by other workers were employed. For the halogen species, k_{22} reported by Woodruff and Margerum [21] for the reactions $I_2 + [{}^*I_2]^- \longrightarrow [I_2]^- + {}^*I_2$ and $Br_2 + [{}^*Br_2]^- \longrightarrow [Br_2]^- + {}^*Br_2$ were used; k_{22} for $[{}^*I_3]^- + [I_2]^{-\cdot} + I^- \longrightarrow [{}^*I_2] + I^- + [I_3]^-$ ($[{}^*I_3]^- + [I_3]^{2-} \longrightarrow$) was assumed to be the same as that for the $I_2 + [{}^*I_2]^- \longrightarrow [I_2]^- + {}^*I_2$ reaction, this assumption having been made earlier.[21] The reduction potential for $[I_3]^- + e^- \longrightarrow [I_2]^{-\cdot} + I^-$ ($[I_3]^-$– $[I_3]^{2-}$ couple) was

TABLE 4

Values of the kinetic (at 25 °C) and thermodynamic parameters employed in the correlation of rates with equilibrium constants using Marcus theory in the reactions of U^{3+} with some oxidants

Oxidant	k_{22} / dm^3 mol^{-1} s^{-1}	k_{12} / dm^3 mol^{-1} s^{-1}	$\log K_{12}$ [a]	$\log f$	Ref. b	Ref. c
I_2	8.5×10^4	3.9×10^5	12.51	−2.29	21	*d*
$[I_3]^-$ [e]	8.5×10^4	3.1×10^4	9.64	−1.36	21	*d*
Br_2	29	7.2×10^5	19.27	−4.52	21	*d*
Fe^{3+}	4	3.9×10^5	23.66	−6.54	*f*	6
V^{3+}	1.0×10^{-2}	84.7	6.25	−0.41	*g*	6
$[Ru(NH_3)_6]^{3+}$	8.2×10^2	1.0×10^5	12.35	−1.99	*h*	28

[a] $\log K_{12}$ was calculated from $E^\ominus$ values obtained from refs. 29 and 35. [b] For k_{22}. [c] For k_{12}. [d] This work. [e] See text for comments on quoted values of k_{22} and K_{12}. [f] W. L. Reynolds and R. W. Lumry, 'Mechanisms of Electron Transfer,' The Ronald Press, New York, 1966, p. 34. [g] K. V. Krishnamurty and A. C. Wahl, *J. Amer. Chem. Soc.*, 1958, **80**, 5921. [h] T. J. Meyer and M. Taube, *Inorg. Chem.*, 1968, **7**, 2369.

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* It is assumed that both U^{3+} and U^{4+} have substitution characteristics similar to the substitution-labile lanthanoid ions.

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calculated from the estimated value of the reduction potential for the I_2^-–$[I_2]^{-\bullet}$ couple[29] and the equilibrium constant for the formation of $[I_3]^-$. The values of the various parameters employed in the application of equation (16) are presented in Table 4.

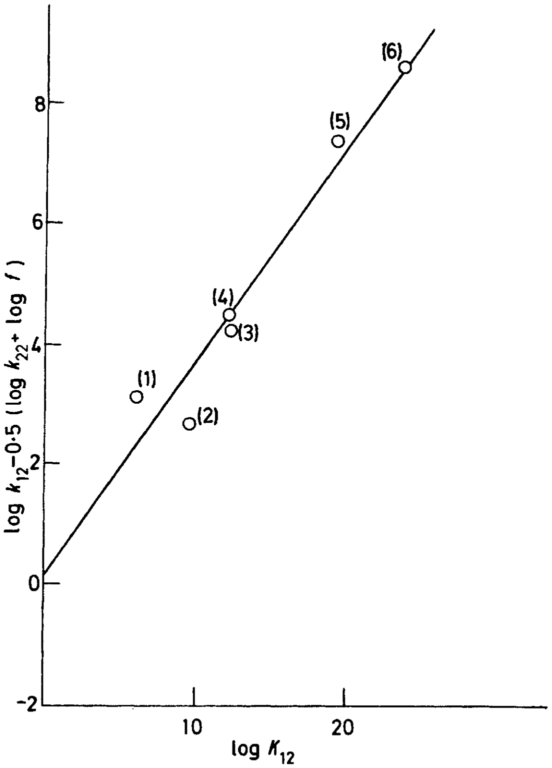

FIGURE 2 Correlation of rates of oxidation of U^{3+} using Marcus theory: plots of log k_{12} −0.5 (log k_{22} + log f) against log K_{12}. (1) V^{3+}, (2) $[I_3]^- \longrightarrow [I_2]^{-\bullet} + I^-$, (3) $I_2 \longrightarrow [I_2]^{-\bullet}$, (4) $[Ru(NH_3)_6]^{3+}$, (5) $Br_2 \longrightarrow [Br_2]^{-\bullet}$, and (6) Fe^{3+}

Plots of the left-hand side of equation (16) against log K_{12} were linear (Figure 2), and of gradient and intercept of 0.36 ± 0.04 and 0.11 ± 0.02 respectively. The gradient is less than the theoretical value of 0.5. Apart from reasons advanced by Marcus[30] which could account for a lower value of the gradient, the approximations and assumptions outlined above may also contribute to the deviation from the theoretically expected value. A gradient of similarly low magnitude has been previously reported by Fulton and Newton[31] for some redox reactions involving actinoid ions. However, in spite of the deviation of the gradient, the linearity of the curve is evidence of, at least, a qualitative agreement with Marcus theory, and suggests that the reactions under test most probably proceed by the same mechanism. Since there are strong arguments in favour of the outer-sphere mechanism for the $U^{3+} + Fe^{3+}$ and $U^{3+} + V^{3+}$ reactions (the acid-independent path, which was the considered path in this correlation),[6] one can reasonably conclude that the first step [equation (9)] in the reduction of I_2, $[I_3]^-$, and Br_2 by U^{3+} proceeds by the outer-sphere mechanism. This conclusion is further supported by the observed catalysis of the $U^{3+} + I_2$ reaction by Cl^-, because added anions have been shown[32] to have greater catalytic effects on the rates of outer-sphere redox reactions than those which are inner sphere. There is no evidence from this work to distinguish between the outer-sphere and the inner-sphere mechanism in the second path, *viz.* the oxidation of U^{3+} by $[X_2]^{-\bullet}$.

From the intercept of the linear plot of Figure 2, k_{11} for the exchange reaction (17) is equal to 1.66 ± 0.16

$$^*U^{3+} + U^{4+} \longrightarrow {}^*U^{4+} + U^{3+} \qquad (17)$$

$dm^3\,mol^{-1}\,s^{-1}$. This value is lower than the experimentally determined value for the $Pu^{3+} + Pu^{4+}$ exchange ($k_{11} = 200\ dm^3\,mol^{-1}\,s^{-1}$ for the acid-independent path)[33] where a 5*f* electron is involved, but much higher than that for the $Eu^{2+} + Eu^{3+}$ exchange ($k_{11} = 1.0 \times 10^{-7}\ dm^3\,mol^{-1}\,s^{-1}$)[34] where the more embedded 4*f* electron is being transferred. The low value for k_{11} for the $U^{4+} + U^{3+}$ exchange suggests that the large thermodynamic driving force, $\Delta G^\ominus$ ($E^\ominus$ for the U^{4+}–U^{3+} couple is −0.63 V),[35] in the oxidation of U^{3+} is primarily responsible for the high rates of the reactions.

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