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Kinetics and Mechanism of the Oxidation of Europium(II) by Aqueous Solution of Iodine and Triiodide

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The rates of reduction of I_2 *and* I_3^- *by* Eu^{2+} *have been measured in aqueous solutions. The data are consistent with the rate equation: Rate =* $-d/dt\,[I_2]_{\mathrm{Total}} = k_1[Eu^{2+}][I_2] + k_2[Eu^{2+}][I_3^-]$ *with* $k_1 = (6.14 \pm 0.19) \times 10^3 M^{-1} sec^{-1}$, $k_2 = (0.37 \pm 0.05) \times 10^3 M^{-1} sec^{-1}$ *at* $I = 1.0M$ $(LiClO_4)$, $[H^+] = 0.1M$, $t = 25$ *°C. The corresponding activation parameters are* $\Delta H_1^* = (3.4 \pm 0.6)$ *kcal* mol^{-1}, $\Delta S_1^* = -(29.8 \pm 5.4)$ *cal* mol^{-1} deg^{-1}, $\Delta H_2^* = (5.0 \pm 0.6)$ *kcal* mol^{-1}, $\Delta S_2^* = -(30.0 \pm 3.1)$ *cal* mol^{-1} deg^{-1}. *The proposed mechanism is a series of univalent changes with* $\cdot I_2^-$ *as a reaction intermediate. The activation parameters are compared with those obtained for other halogen reactions. The data give no conclusive distinction between the inner sphere or the outer sphere mechanism for these reactions.*

Introduction

In previous publications, we have tried to elucidate the kinetics and mechanism of oxidation of aqua-ions by aqueous solutions of halogens. From such studies, we had been able to conclude that most of these reactions occur by univalent changes involving $\cdot X_2^-$(X = Cl, Br, I) as reactive intermediates. Examples of such systems are the non-complementary redox reactions between VO^{2+}, Ti^{3+} and aqueous solutions of chlorine [1, 2]. For such non-complementary systems as typified by (1),

$$2M^{n+} + X_2 = 2M^{(n+1)+} + 2X^- \tag{1}$$

the suggested electron transfer paths are:

$$M^{n+} + X_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^{(n+1)+} + \cdot X_2^- \tag{2}$$

$$M^{n+} + \cdot X_2^- \xrightarrow{k_2} M^{(n+1)+} + 2X^- \tag{3}$$

We have demonstrated [1, 2] that kinetic reversibility is only observed if $\Delta G^\circ > O$ for the first step, *i.e.* equation (2), and empirical evidence for this is an observed inhibition by $M^{(n+1)+}$. The $VO^{2+} + Cl_2$, $VO^{2+} + Br_2$ and $Fe^{2+} + Br_2$ systems typify this [1, 3, 4]. In others, where $\Delta G^\circ < O$ for equation (2), there is no inhibition by $M^{(n+1)+}$, and other evidence has to be sought to confirm the mechanism. The (U^{3+} + $I_2|I_3^-$) and ($Ti^{3+} + Cl_2$) reactions are good examples of such systems [2, 5]. In some others, particularly where the final metal ion is $M^{(n+2)+}$, and the $M^{(n+1)+}$ is unstable, it is uncertain whether such reactions occur by the paths (2) and (3) or by a direct two-electron transfer process. The oxidation of U(IV) to U(VI) by X_2 provides good examples of such sytems [6–8]. It is only in the $Fe^{II} + Cl_2$ reaction where Fe^{IV} was identified as an intermediate [9], that evidence of a direct two-electron transfer step was found.

Another point of mechanistic interest in halogen reactions is the relative reactivity of X_2 and X_3^- when they oxidize a common reducing ion. In most reactions $k_{X_3^-} < k_{X_2}$, the difference in rate being generally due to differences in the activation enthalpies. The $U^{4+} + I_2$, $V^{2+} + X_2$ (X = I, Br), and $M^{II}\,EDTA^{2-} + X_2$ (M = Fe, Co, Mn, X = Br, I) reactions are cases where this has been found [8, 10, 11].

Finally, the question of the inner sphere or outer sphere mechanism has only been resolved in a few of the halogen reactions. The obstacles to this are two-fold: (a) lability of the final products and hence, inability to use the more definitive product criteria to distinguish between the two types of activated complexes and (b), the possibility that in reactions that proceed by a series of univalent changes, X_2 and $\cdot X_2^-$ might react with the aqua-ions by formation of the same or different types of activated complexes (outer sphere or binuclear complexes). This problem is made evident in the $Cr^{2+} + X_2$ reaction [12], where 75% of the reaction product is $CrCl^{2+}$, and 25% Cr^{3+}. It was only after pulse raldiolysis studies [12b] of the $\cdot X_2^- + Cr^{2+}$ reaction that the explanation for this could be provided.

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We have studied the reaction between Eu^{2+} and I_2 in solutions containing different amounts of iodide, in the hope of relating our findings to the three mechanistic points of interest outlined above.

Experimental

Materials

Eu^{3+} solutions were made by dissolving a known weight of Eu_2O_3 in a known excess of perchloric acid. The excess acid was determined by ion exchange chromatography using DOWEX 50-X2 in the hydrogen form and assuming that the europium ions in solution exist as Eu^{3+}. The results obtained from this agree with those obtained by calculating the excess acid from the stoicheiometry of the reaction (4):

$$Eu_2O_3 + 6H^+ = 2Eu^{3+} + 3H_2O \qquad (4)$$

Europous solutions were made from these solutions by zinc amalgam reduction of the Eu^{3+} solutions. Concentrations of the Eu^{2+} solutions were determined by adding a known volume of the Eu^{2+} solution into excess deaerated triiodide solution and determining the excess triiodide by titration against $Na_2S_2O_3$.

Since iodine has a low solubility in water, iodine solutions were made by dissolving solid iodine in a known concentration of iodide solutions, and the concentrations of the triiodide solutions were determined by titration against $Na_2S_2O_3$. $LiClO_4$ and NaI were all B.D.H. (AR) grade, and were used without further purification.

Kinetics

Rates of reaction were monitored at 400nm by following absorbance changes due to triiodide. The rates were too fast for manual measurements and hence a Durrum–Gibson stopped flow spectrophotometer with fully thermostated cell compartments was employed for the kinetic studies. All solutions were prepared under an inert atmosphere maintained by bubbling argon previously scrubbed in chromous towers into the reactant solutions contained in capped serum bottles. In order to prevent loss of iodine during the deaeration of the solutions, the small amount (usually 0.1–0.2 ml) of triiodide was not added into the deaerated solutions containing all other reagents until the kinetic runs were about to start, and a blanket of argon was maintained over the solution. Ionic strength was maintained constant at 1.0*M* using $LiClO_4$.

Results

The order of the reaction was determined by working under pseudo first order conditions with Eu^{2+} concentrations in at least twenty-fold excess over the total iodine ($[I_2]$ + $[I_3^-]$) concentrations. The linearity of pseudo-first order plots up to more than 90% reaction confirms that the reaction is first order in iodine. From such plots, pseudo first order and hence, second order rate constants were obtained as functions of Eu(II) concentrations. The constancy of the second order rate constants with $[Eu^{2+}]_o$ confirms that reaction is also first order in $[Eu^{2+}]$. The second order rate constants were also determined at different acid concentrations, iodide concentrations and temperatures, and values obtained are presented in Table I.

TABLE I. Rate Constants (k_o) for the $Eu^{3+} + I_3^-$ Reaction. I = 1.0*M* $LiClO_4$ $[H^+]$ = 0.10*M*.

T °C	$10^4[Eu^{2+}]$	$10^3[I^-]$	$10^{-3}k_o(M^{-1}\ sec^{-1})$
25	2.35	2.0	3.58
25	4.70	2.0	3.49
25	9.40	2.0	3.54
25	7.05	2.0	3.53
25	7.05[a]	2.0	3.44
25	7.05[b]	2.0	3.65
25	7.05	1.0	3.58
25	7.05	10.0	1.07
25	7.05	20.0	0.72
25	7.05	30.0	0.62
25	7.05	40.0	0.55
25	7.05	50.0	0.51
25	7.05	60.0	0.49
41	4.70	1.0	5.16
41	4.70	2.5	3.73
41	4.70	5.0	2.66
41	4.70	10.0	1.77
41	4.70	15.0	1.42
28	4.70	1.0	3.94
28	4.70	10.0	1.24
28	4.70	20.0	0.83
28	4.70	40.0	0.64
18	4.70	1.0	2.54
18	4.70	10.0	0.79
18	4.70	20.0	0.59
18	4.70	40.0	0.48
18	4.70	60.0	0.32

[a] Contains 0.5*M*$[H^+]$. [b] Contains 1.0*M*$[H^+]$.

The results show that the second order rate constant (k_o) is independent of $[H^+]$, but decreases as $[I^-]$ increases. The obvious rationalization of this result is that since the equilibrium reaction (5)

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (5)$$

is very rapid compared to the observed rate of the reaction, the decreasing rate with increasing iodide concentration is due to the fact that I_3^- reacts with Eu^{2+} more slowly than does I_2. The results were therefore analysed in the light of this. Thus the rate of the reaction is given by (6):

$$\text{Rate: } -d/dt\,[I_2]_T = k_o[Eu^{2+}][I_2]_T = k_1[Eu^{2+}][I_2] + k_2[Eu^{2+}][I_3^-] \qquad (6)$$

where $[I_2]_T = [I_2] + [I_3^-]$.

From equation (6), one obtains (7):

$$K_o(1 + K[I^-]) = k_1 + k_2\,K[I^-] \qquad (7)$$

where K is the equilibrium constant for the formation of I_3^- (equation 5). From plots of the L.H.S. of equation (7) *versus* $[I^-]$, k_1 and k_2 can be obtained. The values of k_1, k_2 computed from such plots and the values of K employed in the computation are shown in Table II. From plots of log k/T *versus* 1/T, values of the activation parameters were computed as follows:

$\Delta H_1^* = (3.43 \pm 0.60)$ kcal mol^{-1}
$\Delta S_1^* = (-29.8 \pm 5.4)$ cal mol^{-1} deg^{-1}
$\Delta H_2^* = (5.0 \pm 0.6)$ kcal mol^{-1}
$\Delta S_2^* = (-30.0 \pm 3.1)$ cal mol^{-1} deg^{-1}.

TABLE II. Variation of k_1, k_2 and K_3 with Temperature in the Europium(II) + Iodine Reaction.

t (°C)	K_3[a]	$10^{-3}k_1$	$10^{-3}k_2$
18	871	4.45 ± 0.03	0.36 ± 0.01
25	747.8	6.14 ± 0.19	0.37 ± 0.05
28	722.8	6.70 ± 0.31	0.43 ± 0.15
41	577.2	8.08 ± 0.29	0.67 ± 0.43

[a]Values of K_3 obtained from data in Reference 13.

Discussion

The $Eu^{2+} + I_2|I_3^-$ reaction is a non-complementary reaction and therefore could proceed by a direct two-electron transfer to form Eu^{4+} as shown in equations (8) and (9):

$$Eu^{2+} + I_2, I_3^- \rightleftharpoons Eu^{4+} + 2I^-\ (3I^-) \qquad (8)$$

$$Eu^{4+} + Eu^{2+} \longrightarrow 2Eu^{3+} \qquad (9)$$

This path is very unlikely because it involves removal of two electrons from the well-embedded 4*f* orbital, and the activation energy for this process should be much higher than obtained in this work. It is therefore suggested that the reaction occurs by a series of univalent changes involving $^{\bullet}I_2^-$ as an intermediate, as depicted in equations (10) and (11):

$$Eu^{2+} + I_2(I_3^-) \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} Eu^{3+} + I_2^-(I_2^- + I^-) \qquad (10)$$

$$Eu^{2+} + I_2^- \xrightarrow{k_{11}} Eu^{3+} + 2I^- \qquad (11)$$

There is no observed inhibition by Eu^{3+} because $\Delta G^o < O$ for equation (10), and hence, this step is not reversible in the kinetic sense. Estimates [14, 15] of E° for the $I_2|^{\bullet}I_2^-$ couple give it as (0.1–0.2))V while E° for the $Eu^{3+}|Eu^{2+}$ couple is –0.43. Thus, $k_{11} \gg k_{-10}$ and hence the rate equation derived from equations (10) and (11) will be the simple bimolecular rate expression as observed in these studies with $k_{10} = k_1$ or k_2 depending on whether I_2 or I_3^- is the reactant. Reaction paths (10) and (11) will place Eu^{2+} alongside with V^{2+}, Ti^{3+}, VO^{2+}, U^{3+} which are all one-electron reductants with halogens [1, 2, 3, 5].

The higher reactivity of I_2 compared to I_3^- is obviously due to the higher value of ΔH^* in the $Eu^{2+} + I_3^-$ reaction. This higher value of $\Delta H^*_{I_3^-}$ is general in all reactions where I_3^- has been found to oxidize a reducing ion more slowly than I_2. Examples are the reactions of V^{2+}, U^{3+}, $[M^{II}(EDTA)]^{2-}$(M = Fe or Co), $[Fe^{II}(CyEDTA)]^{2-}$, U^{4+} with I_2 and I_3^-. The reason for this difference is that the path (10) for I_3^- involves the breaking of one bond to form $^{\bullet}I_2^-$ and I_3^- while no bond is broken when I_2 is the reactant. It is significant to note that ΔS^* for both I_2 and I_3^- are about the same showing that charge considerations are not important in their reactions with Eu^{2+}. However, the values of ΔS^* obtained in this reaction are the lowest (most negative) so far reported in the reactions of I_2 or I_3^- with metal ions (Table III). Since the electron to be transfered is from the least exposed and hence, most inacessible orbital, the 4*f* orbital, it seems reasonable to attribute the very negative values of ΔS_1^* and ΔS_2^* in this system to a considerable lower probability of transferring electrons from the inner 4*f* orbitals to the acceptor orbitals of the oxidant. This explanation is consistent with the fact that the 4*f* orbitals are generally not available for bonding and hence, have little orbital overlap with those of the oxidants.

TABLE III. Values of Entropies of Activation for Different Reactions in which I_2 or I_3^- is the Oxidant.

Reductant	ΔS^* (I_2)	ΔS^* (I_3^-)	Reference
V^{2+}	–14.1	–21	9
$Co^{II}CyDTA^{2-}$	– 7.3	– 9	11
$Co^{II}EDTA^{2-}$	+ 1	+ 5	11
$Fe^{II}CyDTA^{2-}$	– 5	+28	11
$Fe^{II}EDTA^{2-}$	– 5	+15	11
U^{3+}	–11	–12.6	5
U^{4+}	– 9.1	– 4.6	8
Eu^{2+}	–29.8	–30	This work

The question of distinction between the inner sphere or the outer sphere mechanism, for at least, the first step in the Eu^{2+} reduction of I_2 and I_3^- cannot be made from our data. However, comparison of the rate constants for these reactions with those of V^{2+} ($k_{I_2} = 7.5 \times 10^3$, $k_{I_3^-} = 9.7 \times 10^2$ M^{-1} sec^{-1})

[10], which are related to the outer sphere mechanism shows that the Eu^{2+} reactions are slower. Since Eu^{2+} is a thermodynamically better reducing agent than V^{2+}, this tends to suggest that Eu^{2+} reactions, in view of Marcus' theory [16], proceed by a different mechanism, *i.e.* the inner sphere mechanism. This conclusion is in itself not sufficiently convincing because the very low homonuclear electron exchange rate constant [17] for Eu^{2+} might also account for this lower rate of reduction of I_2 and I_3^- by Eu^{2+}, and hence, the possibility of the Eu^{2+} + I_2, I_3^- reactions going by the outer sphere mechanism cannot be completely ruled out on the basis of this rate comparison.

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