KINETICS AND MECHANISM OF THE REACTION BETWEEN PLUTONIUM(III) AND CHLORINE IN CHLORIDE SOLUTIONS

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Abstract—Oxidation of plutonium(III) to (IV) by chlorine in chloride solutions follows an apparently first order rate law with respect to both the reactants, and the rate is independent of acidity. At room temperature, and with 0.01 M initial plutonium concentration and about 0.025 M initial chlorine concentration, the specific reaction rate, k' increases from 0.04 to 2.8×10^{-2} min⁻¹, as the hydrochloric acid concentration of the medium changes from 1.5 to 8.0 M. In solutions having constant hydrochloric acid, k' increases at first linearly with initial chlorine concentration and finally approaches a limiting value for a given initial plutonium concentration. The limiting values in 7.0 M hydrochloric acid with 0.025 M of chlorine concentration are 0.6, 1.2 and more than 2.2×10^{-2} min⁻¹ respectively with 0.005, 0.01 and 0.02 M initial plutonium concentrations. The rate of oxidation is relatively very slow at room temperature in chloride free perchloric acid solutions, while in solutions containing mixture of hydrochloric and perchloric acids, it is markedly increased by chloride ion concentration for a given total molarity of the acid mixture as well as by the total molarity having fixed concentration of hydrochloric acid, showing thereby that the rate is influenced both by chloride ions as well as by ionic strength of the medium. Thermodynamic quantities of activation at 26°C have been calculated from the experimentally determined activation energy of the reaction, the average value of which is 16.0 ± 1.8 kcal/mole.

A mechanism is suggested according to which a transient species is assumed to be formed in steady state concentration by the action of Cl_3^- ions on Pu(III) ions, and the rate is determined by the reaction between these transient species and Pu(III) ions.

IT has recently been reported⁽¹⁾ that in chloride solutions, the oxidation of plutonium(III) to (IV) by chlorine follows an apparently first order rate law with respect to both reactants, the rate being independent of acidity but markedly dependent on chloride ion concentration of the solution. Moreover, the specific reaction rate gradually increases with the initial chlorine concentration and finally tends towards a constant value for a given initial plutonium(III) concentration. The higher the plutonium concentration, the higher is the value of the specific reaction rate. The present paper describes further work aimed at the determination of activation energy of the reaction in solutions having different hydrochloric acid concentrations and also at elucidating the mechanism. During the course of this work, it appeared that some of the reported numerical data⁽¹⁾ on specific reaction rates needed revision. Hence, a complete re-examination of the earlier work was also undertaken.

EXPERIMENTAL

The experimental technique followed in this work was the same as that described previously,⁽¹⁾ excepting that the purification procedures were effected on plutonium solutions which were taken directly from a stock prepared by dissolving plutonium metal in hydrochloric acid. In theearlier work,

⁽¹⁾ A. S. GHOSH MAZUMDAR, K. P. R. PISHARODY and R. N. SINGH, J. Inorg. Nucl. Chem. 24, 1617 (1962).

on the other hand, the plutonium solution was obtained by recovery from the end solutions resulting from various other experiments with this element. The following methods of purification were examined:

- (a) fluoride precipitation method following an oxidation reduction cycle;⁽²⁾
- (b) anion exchange method using Dowex-1 \times 4 resin;
- (c) hydrogen peroxide precipitation method⁽³⁾ from nitric acid solution (2-3 M); and
- (d) purification by method (b) followed by method (c) and final oxidation by ozone.



FIG. 1.—Variation of k' values with hydrochloric acid concentration. Plutonium purified by fluoride precipitation method following an oxidation reduction cycle (method a); \bigcirc purified by anion exchange resin (method b); \times purified by peroxide precipitation (method c); \blacksquare purified by method b, followed by method c and final oxidation by ozone (method d). * data from Reference 1.

From the nitric acid solutions obtained in methods (a), (b) and (c), the plutonium was precipitated as hydroxide and dissolved in hydrochloric acid. The plutonium solution in hydrochloric acid was subjected to electrolytic reduction.

Specific reaction rates (k') obtained with each of these solutions adjusted to varying hydrochloric acid concentrations are shown in Fig. 1 (curve I). The higher k' values obtained in the earlier work (curve II, Fig. 1) might have been due to the presence of a minute quantity of some unknown impurity which was not getting eliminated by either of the two purification procedures adopted.

- ⁽²⁾ G. T. SEABORG and A. C. WAHL, *The Transuranium Elements*, NNES Paper 1.6, McGraw-Hill, New York (1949); B. B. Cunningham and L. B. Werner, *Ibid Paper* 1.8.
- ⁽⁸⁾ J. W. HAMAKER and C. W. KOCH, *The Transuranium Elements*, NNES Paper 6.02, McGraw-Hill, New York (1949); J. A. LEARY, A. N. MORGAN and W. J. MARAMAN, *Industr. Engng. Chem.* 51, 27 (1959).

Investigation regarding catalysis of this reaction by certain materials is, therefore, considered interesting and is in progress. The few preliminary results obtained so far revealed positive catalysis by copper ions. However, work with 2×10^{-4} M cupric ions showed that they got separated by deposition on the cathode, during the electrolytic reduction of plutonium(IV) to (III).

As the experimental points pertaining to method (b) were much scattered around the curve 1 of Fig. 1, this method was not adopted any further in this work. Reaction rates were measured at room temperature (conditioned to $26 \pm 1^{\circ}$ C) as well as at higher temperatures. For rate measurements at higher temperatures, the reactants before mixing were kept in two different cells in a specially made chamber lined with insulating materials and having an arrangement for circulation of hot water. The cell compartment of the Beckman DU Spectrophotometer was also fitted with "thermospacers" supplied along with the instrument. Water maintained at a given temperature within $\pm 0.1^{\circ}$ C in a thermostatic bath was circulated through the thermospacers as well as through the especially made chamber. When their temperature attained a constant value, the reactants were mixed by pipetting chlorine solution into the absorption cell compartment and then commenced measurements of optical density as a function of time.

RESULTS

It was confirmed that the oxidation of plutonium(III) to (IV) by chlorine according to the reaction $Pu(III) + \frac{1}{2}Cl_2 \rightarrow Pu(IV) + Cl^-$ followed an apparently first order rate law with respect to both reactants since the plots of log plutonium(III) concentration vs time were linear. The apparent specific reaction rate (k') at room temperature was found, as previously, not to depend significantly upon acidity when total chloride ion

HCl concen- tration (M)	k' (× 10 ² min ⁻¹)					Experimental activation	Thermodynamic quantities of activation at 26°C		
	45°C	42°C	35°C	26°C	17·5°C	energy (kcal/mole)	ΔF^* (kcal/mole)	ΔH^* (kcal/mole)	ΔS^* (cal/°mole)
3·2 6·8	0·25 3·40	0·23 2·95	0·11 1·65	0•06 0∙80	0.32	$ \begin{array}{c} 15 \cdot 3 & - & 1 \cdot 8 \\ 15 \cdot 9 & - & 1 \cdot 3 \end{array} $	24·4 22·9	14·7 15·4	-32.5 5.9 -25.2 4.4

Table 1.—Experimental activation energy and thermodynamic quantities of activation (initial plutonium(III) = 0.01 M, initial chlorine = 0.025 M)

concentration was constant, but was markedly dependent on the latter, other conditions remaining fixed. The variation of k' with hydrochloric acid concentration between 1 and 8 M at 0.01 M plutonium and about 0.02 M chlorine concentration is shown in Fig. 1, which also includes the previously reported values for comparison. It would be seen that the trends of the variation are exactly similar, though the present k' values are significantly lower.

The effects of initial chlorine concentration and of initial plutonium(III) concentration on k' are again similar to those reported previously. Fresh data in 7 M hydrochloric acid solutions are shown in Fig. 2.

Rate in perchloric acid and in perchloric-hydrochloric acid mixtures

In chloride-free perchloric acid solutions, the rate of oxidation was relatively very slow at room temperature $(0.01-0.02 \times 10^{-2} \text{ min}^{-1} \text{ in } 3-7 \text{ M} \text{ perchloric acid, the rate of any self-oxidation due to radiolysis by plutonium π-rays or otherwise having been found to be negligible). Data on k' values in acid mixtures of different total molarity and at varying chloride ion concentration are shown in Fig. 3. A few of the experimental points are no doubt somewhat scattered; nevertheless, the data seem to show clearly that for a given total anion concentration, k' increases with chloride ion concentration, rather steeply at first (up to around 2-3 M), and then gradually towards$



FIG. 2.—Variation of k' values with initial concentration of chlorine at different initial concentrations of Pu(III); HCl concentration = 7.0 M. • initial Pu(III) concentration 0.02 M. × initial Pu(III) concentration 0.01 M. \bigcirc initial Pu(III) concentration 0.05 M.



FIG. 3.—Dependence of k' values on chloride ion concentration at different total anion concentrations. Initial Pu(III) concentration = 0.01 M; initial chlorine concentration = 0.02 M (approx.). × Total anion concentration, 7.5–7.6 M; total anion concentration, 6.4–6.6 M; ○ total anion concentration, 2.4–2.9 M.

a maximum. Moreover, in addition to the foregoing specific effect of chloride ions there exists an effect of the total anion concentration and therefore of the ionic strength. The latter effect was, however, not detected in the earlier work.

Temperature coefficient of reaction rate and activation energy

The effect of the variation of temperature upon k' was studied in 3.2 and 6.8 M hydrochloric acid solutions. The results are given in the table, which also includes experimental activation energies calculated from a linear plot of log k' vs 1/T; and thermodynamic quantities of activation, calculated from the equations of the absolute reaction rate theory.⁽⁴⁾

MECHANISM

As suggested in the previous paper, plutonium(III) is probably oxidized by Cl_3^- ions which are known to form rapidly from chlorine and chloride ions.⁽⁵⁾ The following mechanism which may not be unique is proposed to explain the observations made:

$$\operatorname{Cl}_2 + \operatorname{Cl}^- \rightleftharpoons \operatorname{Cl}_3^-, \quad K_1 = \frac{[\operatorname{Cl}_3^-]}{[\operatorname{Cl}_2][\operatorname{Cl}^-]}$$
(1)

$$\mathbf{Pu^{3+} + Cl_3^{-} \xrightarrow{k_2} (Pu \dots Cl_3)^{2+}}$$
(2)

$$(\operatorname{Pu}\ldots\operatorname{Cl}_3)^{2+} \xrightarrow{k_3} \operatorname{Pu}^{3+} + \operatorname{Cl}_3^{-}$$
(3)

$$(\operatorname{Pu}\ldots\operatorname{Cl}_3)^{2+}+\operatorname{Cl}_3\xrightarrow{k_4}\operatorname{Pu}^{3+}+2\operatorname{Cl}_3\xrightarrow{k_4},(\operatorname{Pu}\ldots\operatorname{Cl}_6)^{1+} \text{ etc.}$$
(4)

$$(\operatorname{Pu} \ldots \operatorname{Cl}_3)^{2+} + \operatorname{Pu}^{3+} \xrightarrow{k_5} 2\operatorname{Pu}^{3+} + \operatorname{Cl}_3^{-}$$
(5)

$$(Pu \dots Cl_3)^{2+} + Pu^{3+} \xrightarrow{k_6} 2PuCl^{3+} + Cl^- \text{ (rate determining step)}$$
(6)

(Pu... Cl_3)²⁺ assumed to be formed from the oppositely charged ions according to the reaction (2) above is a transient species, and is possibly not a compound of plutonium in its pentapositive oxidation state, since plutonium(V) is known to disproportionate easily to plutonium(IV) and plutonium(VI) in solutions of pH lower than 1.⁽⁶⁾ Moreover, we did not get any spectrophotometric evidence of Pu(VI) at 830–840 m μ , nor of Pu(V) at 565–575 m μ . Reactions (3), (4) and (5) above, are representative processes which lead to disappearance of the transient species without producing oxidation, the first through processes independent of the concentration of reactants, and the second through all collision processes with Cl_3^- ions. The fraction of collisions with Pu³⁺ ions, which produce the oxidation reaction is given by $k_6/(k_5 + k_6)$. According to the proposed mechanism, Equation (6) which is supposed to be the rate determining step, yields directly a complexed form of Pu(IV), which is in keeping with the property of Pu(IV) in chloride solutions.⁽⁷⁾

⁽⁷⁾ S. W. RABIDEAU and H. D. COWAN, J. Amer. Chem. Soc. 77, 6145 (1955).

⁽⁴⁾ S. GLASSTONE, K. J. LAIDLER and H. EYRING, *The Theory of Rate Processes*, pp. 197–199, McGraw-Hill, New York (1941).

⁽⁵⁾ F. A. LONG and A. R. OLSON, J. Amer. Chem. Soc. 58, 2214 (1936); N. V. SIDGWICK, The Chemical Elements and their Compounds Vol. 2, p. 1192. Oxford (1932).

⁽⁶⁾ R. E. CONNICK, *The Transuranium Elements*, NNES IV, Vol. 14-B, p. 268 (1949); *J. Amer. Chem. Soc.* 71, 1528 (1949); S. W. RABIDEAU, *Ibid.* 79, 6350 (1957).

It may be quite possible that complexed ions of plutonium(III) formed in chloride solutions according to equilibrium reactions like

$$\mathbf{Pu^{3+}} + \mathbf{Cl^{-}} \rightleftharpoons \mathbf{PuCl^{2+}},\tag{7}$$

(8)

take part in the reaction mechanism rather than or along with uncomplexed Pu³⁺ ions. In that case the positively charged chloride complexes would form with Cl_3^{-1} ions the corresponding transient species, and the above reactions mutatis mutandis would then be applicable. The data presented here, however, do not enable us to choose between these possibilities.

Applying steady state conditions, the concentration of the transient species [Pu . . . Cl_3^{2+} would be given by the following relationship:

$$k_{2}[Pu^{3+}][Cl_{3}^{-}] = k_{3}[Pu \dots Cl_{3}^{2+}] + k_{4}[Pu \dots Cl_{3}^{2+}][Cl_{3}^{-}] + (k_{5} + k_{6})[Pu \dots Cl_{3}^{2+}][Pu^{3+}]$$

$$Pu \dots Cl_{3}^{2+}] = \frac{k_{2}[Pu^{3+}][Cl_{3}^{-}]}{k_{3} + k_{4}[Cl_{3}^{-}] + (k_{5} + k_{6})[Pu^{3+}]}$$
(8)

or,

An apparent first order rate law would be expected provided the above mentioned steady state conditions are assumed since

$$\frac{-d(\operatorname{PuIII})}{dt} = 0.5 \times k_6[\operatorname{Pu} \dots \operatorname{Cl}_3^{2+}][\operatorname{Pu}^{3+}] = k'[\operatorname{Pu}^{3+}]$$

The reacting ions of the reaction (6) are both similarly charged. Hence, k_6 and thus k' are expected to increase with the ionic strength of the solution,⁽⁸⁾ and therefore with the molarity of the supporting electrolyte, as we have observed.

The concentration of the transient species is assumed to remain constant at a particular steady state value in course of any particular kinetic run. But it might change from one run to another depending upon the relative concentrations of the reacting species at the beginning of the reaction. This may be seen from the following relationship (9), derived from Equations (1) and (8).

$$[\operatorname{Pu} \dots \operatorname{Cl}_{3}^{2+}] = \frac{K_{1}k_{2}[\operatorname{Pu}^{3+}]_{0}[\operatorname{Cl}_{2}]_{0}[\operatorname{Cl}^{-}]}{k_{3} + K_{1}k_{4}[\operatorname{Cl}_{2}]_{0}[\operatorname{Cl}^{-}] + (k_{5} + k_{6})[\operatorname{Pu}^{3+}]_{0}}$$
(9)

where the quantities within the square brackets with zero subscript represent initial concentrations. In solutions having fixed chloride ion and total anion concentrations, if the initial plutonium concentration be high and the initial chlorine concentration be low, so that $k_3 + K_1 k_4 [Cl_2]_0 [Cl^-]$ becomes rather small as compared to $(k_5 + k_6) [Pu^{3+}]_0$ then

[Pu...Cl₃²⁺] tends to be equal to
$$\frac{k_2K_1[Cl_2]_0[Cl^-]}{k_5+k_6}$$

that is to say k' should be nearly proportional to $[Cl_2]_0$; whereas in solutions having low plutonium concentration and high chlorine concentration, k' would be similarly independent of initial chlorine concentration but would be roughly proportional to

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⁽⁸⁾ V. K. LA MER, Chem. Rev. 10, 179 (1932); R. LIVINGSTON, J. Chem. Educ. (Canada) 7, 2287 (1930); A. R. OLSON and T. R. SIMONSON, J. Chem. Phys. 17, 1167 (1949); R. L. MOORE, J. Amer. Chem. Soc. 77, 1504 (1955).

the initial plutonium(III) concentration, since $[Pu \dots Cl_3^{2^+}]$ tends to be equal to $\frac{k_2[Pu^{3+}]_0}{k_4}$. The data of Fig. 2 seem to be in conformity to these expectations, the maximum k' values being nearly 0.6, 1.2 and more than $2.2 \times 10^{-2} \text{ min}^{-1}$ with 0.005, 0.01 and 0.02 M respectively of plutonium concentration.

Finally, it can be shown from Equation (1) that for a given ionic strength

$$[\mathbf{Cl}_{3}^{-}]_{0} = [\text{Total } \mathbf{Cl}_{2}]_{0} \left\{ \frac{K_{1}[\mathbf{Cl}^{-}]}{1 + K_{1}[\mathbf{Cl}^{-}]} \right\}$$
(10)

remembering that total chlorine = chlorine combined in the form of $Cl_3^- +$ uncombined chlorine. Therefore with a given concentration of total chlorine, $[Cl_3^-]_0$ tends to increase rapidly at first with $[Cl^-]$ but then very slowly in high concentration of the latter as $1 + K_1[Cl^-]$ tends to equalize with $K[Cl^-]$. Thus the data of Fig. 3 would be interpreted at least qualitatively considering that the concentrations of Cl_3^- ions determine the reaction rate. This type of chloride ion dependence in solutions having fixed ionic strength would further be expected if a chloride complex of Pu(III) in lieu of Pu³⁺ be assumed to take part in the reaction mechanism, since the relationship between the concentrations of a chloride complex of Pu(III) and of total Pu(III) would be similar in form to that shown in Equation (10).

The mechanism discussed above seems to be applicable only in chloride solutions, as preliminary work in sulphate solutions has revealed a different rate law.

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