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

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Abstract—Oxidation of plutonium(III) to (IV) by chlorine has been shown to follow an apparently first order rate law, with respect to both the reactants, when other conditions are constant. The rate was independent of acidity, but markedly dependent on the chloride ion concentration, and this dependence has been shown to be due to a specific effect of chloride ions rather than to a general effect of anions or ionic strength.

THE oxidation of plutonium(III) to (IV) by chlorine is reported to be slow in 0·5 M hydrochloric acid, being only about 10 per cent in 5 hr.(1) The kinetics of this oxidation, which were observed to be markedly dependent upon the chloride ion concentration of the medium, have been studied, since apart from the interest concerning the mechanism of the reaction, data were required for some current work on the radiolytic oxidation of plutonium(III) in which chlorine is a possible intermediate.

Stoicheiometry of the oxidation

Excess chlorine was found to oxidize plutonium(III) at first to plutonium(IV) in hydrochloric acid. When the acid concentration was less than 3·5 M, the plutonium(IV), thus formed in a few hours, was then oxidized slowly to plutonium(VI); but no plutonium(VI) was formed in higher acidities (e.g. at 5·4 M) even when the reaction was allowed to proceed overnight. In the higher acid solutions the decrease in plutonium(III) concentration was found to be practically quantitative according to the reaction, $\mathrm{Pu(III)} + \frac{1}{2}\mathrm{Cl_2} \rightarrow \mathrm{Pu(IV)} + \mathrm{Cl^-}$ when the chlorine added varied between 0·012 to 0·12 mole/mole of plutonium.

Order of the reaction

The rate of reaction was measured at several hydrochloric acid concentrations. The linearity of the graphs of log plutonium(III) concentration against time (Fig. 1) indicates that at a given hydrochloric acid concentration, oxidation followed an apparently first order rate law with respect to both reactants. This was confirmed by calculating rate constant values to orders of 1·5 and 2. Although these graphs were linear the slopes of the lines were markedly dependent upon the hydrochloric acid concentration.

Effect of hydrogen ion concentration

Separate series of experiments were carried out in which the chloride concentration was maintained constant by addition of lithium or potassium chlorides to varying hydrochloric acid concentrations. The apparent specific reaction rate (k') was found

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(1) R. E. CONNICK and W. H. McVEY, *The Transuranium Elements*, paper 3.10, NNES, McGraw-Hill, New York (1949)

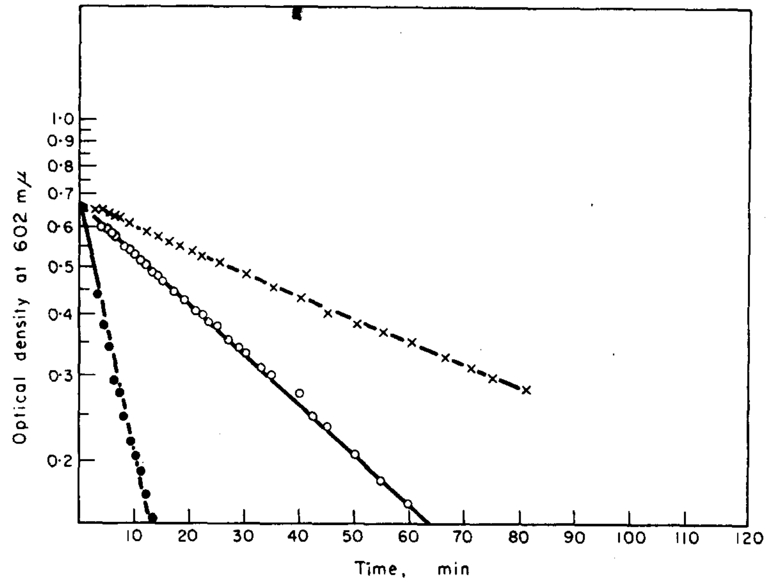

FIG. 1.—Rate of oxidation of Pu(III) by chlorine. Concentration of Pu(III): 1·67 × 10^{-2} M; concentration of chlorine: 2·8 × 10^{-2} N; concentration of HCl: × 3·0 M, ○ 4·5 M, ● 6·0 M.

not to depend significantly upon acidity when total chloride ion concentration was constant. Some typical data are shown below:

Total chloride ion (LiCl + HCl) conc. (M)	Range of varying HCl conc. (M)	Initial conc. of Pu(III) (M × 10^2)	Initial conc. of chlorine (M × 10^2)	k'(× 10^2 min^{-1})
6·0	3·02 and 6·00	1·38	3·43	5·1
4·5	2·95 and 4·50	1·28	3·55	1·1

Effect of initial chlorine and of total plutonium concentration

Despite the first order rate dependence, k' increased gradually with the initial chlorine concentration and finally tended towards a constant value for a given plutonium concentration. This constant value was found to increase with increase in plutonium concentration in the range 0·002–0·02 M. k' values obtained in 3·04 M hydrochloric acid are shown in Fig. 2. At other hydrochloric acid concentrations also similar effect of initial chlorine concentration was observed.

Effect of chloride ion concentration

The rate of reaction was found to increase with increased concentrations of chloride ion. The variation of k' with chloride ion concentration at 0·01 M plutonium and about 0·02 M chlorine concentrations is shown in Fig. 3. k' increased from 0·5 to 0·9 10^{-2} min^{-1} and then rapidly to 27 × 10^{-2} min^{-1}, as the chloride ion concentration was increased from 1 to 4 M and then to 8 M respectively.

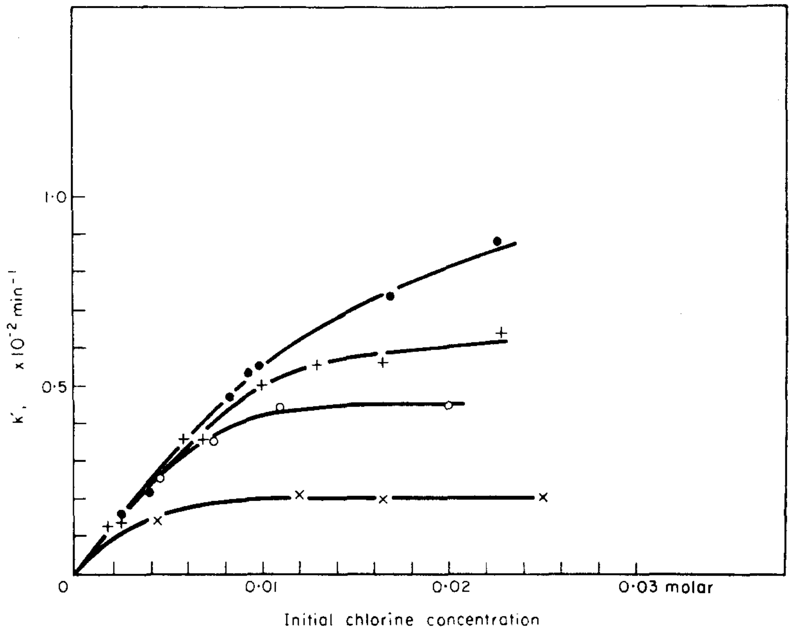

Fig. 2.—Variation of k' with initial concentration of chlorine at different initial concentrations of Pu(III); HCl concentration = 3·04 M; ● initial Pu(III) concentration 0·02 M; + initial Pu(III) concentration 0·01 M; ○ initial Pu(III) concentration 0·005 M; × initial Pu(III) concentration 0·002 M.

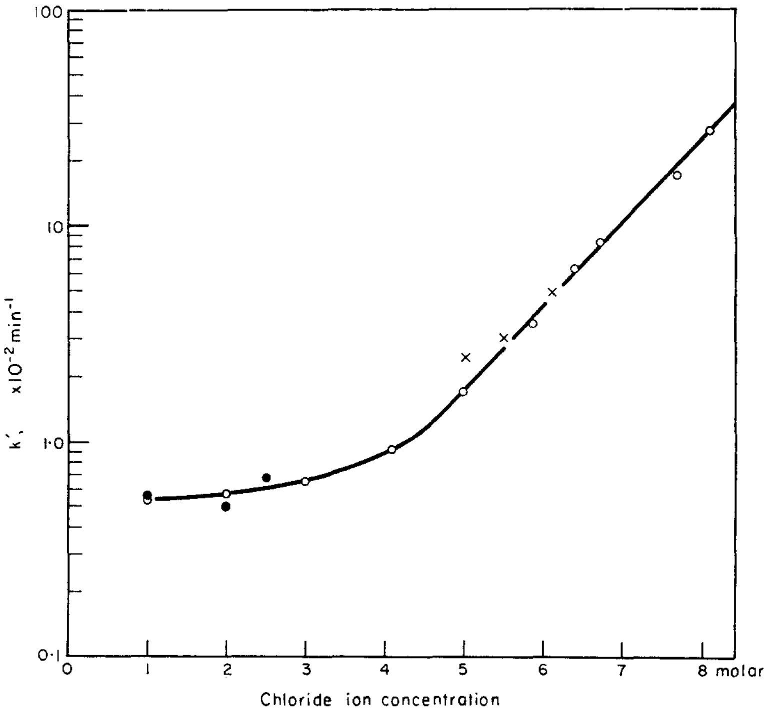

Fig. 3.—Variation of k' values with chloride ion concentration. ○ in hydrochloric acid; ● in hydrochloric–perchloric acid mixture, total anion concentration 3·0 M; × in hydrochloric–perchloric acid mixture, total anion concentration 6·5 M.

Rate in perchloric acid and in perchloric–hydrochloric acid mixtures

In perchloric acid alone, varying from 3·0 to 7·5 M, k' remained almost constant at $0{\cdot}1 \times 10^{-2}$ min.$^{-1}$. In acid mixtures, when the chloride ion concentration was varied at constant total anion concentration, variation of k' was of the same order of magnitude as in perchlorate-free medium (Fig. 3). Lastly, the variation in k' with total anion concentration and at a fixed chloride ion concentration was very slight as shown below:–

Range of total anion conc. (M)	Chloride ion conc. (M)	Observed variation in k' ($\times 10^2$ min^{-1})
3·05 and 7·35	0·2	Almost constant at 0·2
4·0 and 6·1	4·0	0·8–1·1
5·1 and 6·1	5·1	1·3–1·5

Therefore, the observed rapid rise in k' with chloride ion concentration is mainly due to a specific effect of chloride ions rather than to any ionic strength influence or a general anion effect, contributed by these ions, on reaction rates.(2)

Halide ions facilitate kinetically many oxidation reduction reactions, electrochemical(3) as well as thermal.(4) Complexing could establish a new reaction path to accelerate the overall process of electron transfer since both plutonium(III) and (IV) ions are known to form chloride complexes.(5,6) The plutonium is probably oxidized by Cl_3^- ions which are known to form rapidly from chlorine and chloride ions,(7) thus qualitatively explaining the independence of the rate on acidity. Further work is proceeding.

EXPERIMENTAL

For the purification of plutonium, two procedures were followed. In one, anion exchange resin Dowex 1 × 4 was used. In the other, which excludes the possibility of any trace contamination with organic matter, fluoride precipitation method was adopted, following an oxidation reduction cycle.(8) The plutonium fluoride thus obtained was repeatedly heated with nitric acid to convert it to the nitrate form. In both cases, from the solution obtained, plutonium was precipitated twice as hydroxide and finally dissolved in hydrochloric acid. Trivalent plutonium was obtained by cathodic reduction, and was estimated by microtitration with ceric sulphate(9). Acidity was measured by micro-alkalimetry. For iodometric assay of dissolved chlorine in solutions, the gas was swept out with nitrogen into a series of potassium iodide solutions.

Laboratory reagent grade lithium chloride was purified by recrystallization. All other reagents used were of G.R. or AnalaR quality.

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Reaction rates were measured in the stoppered absorption cells of a Beckman DU Spectrophotometer. In a typical experiment, a measured volume of a solution of chlorine in hydrochloric acid was added by means of a pipette below the surface of a solution containing a known amount of plutonium (III) in an absorption cell, which was then stoppered and shaken to mix the reactants. No evolution of gas bubbles was noticed in these experiments which were performed at the laboratory temperature, conditioned to 25° ± 2°C. The time of start of the reaction was reckoned from the middle of the operation of adding chlorine and the progress of oxidation was followed by measuring the absorption due to plutonium(III) at 602 mμ.

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