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Kinetics of Reduction of Neptunium(VI) with Oxalic Acid in Aqueous Perchloric Acid

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The kinetics for the reduction of neptunium(VI) with oxalic acid has been studied in aqueous perchlorate media. The rate law for the reaction was found to be

$$\frac{d[\mathrm{Np(V)}]}{dt} = k\frac{[\mathrm{Np(VI)}]\,[\text{total oxalate}]}{[\mathrm{H^+}]}$$

Specific velocity constants and activation energy have been determined. A possible mechanism has been suggested which explains the observed kinetics and the stoichiometry of the reaction.

Introduction

Potassium oxalalte has been found to reduce neptunium(VI) to neptunium(V). Further reduction is pH dependent; however, at the acidity used in these experiments reduction did not proceed beyond the Np(V) stage within the observed time limit. Complex formation between neptunium(V) and oxalate ions is reported.[1] This complex formation is also a function of pH. This work was undertaken to investigate the kinetics and mechanism of the reduction of neptunium(VI) with potassium oxalate in the range of hydrogen ion concentration in which no complex formation takes place between the oxalate and neptunium(V). Yellow color was observed on mixing the reactants in perchloric acid solution. This color was attributed to complex formation between neptunium(VI) and oxalate.

Experimental Section

Stock solution of neptunium(VI) was prepared by electrolytic oxidation of a pure neptunium(V) solution in standard aqueous perchloric acid.[2] The course of oxidation was followed spectrophotometrically. Complete oxidation was ascertained by observing the neptunium(VI) peaks at 1230, 557, and 476 mμ to the exclusion of others on a Beckman DK-1 recording spectrophotometer.[2,3] The neptunium concentration was determined by α-particle counting on the basis of 790 α counts min^{-1} μg^{-1} specific counting yield on a Nuclear Chicago gas flow counter.

All solutions were prepared with deionized distilled water. A standard stock solution of potassium oxalate was prepared by weight. Stock solution of perchloric acid was prepared by diluting the concentrated acid obtained from the Mallinckrodt Chemical Works. This solution was standardized against standard sodium hydroxide using phenolphthalein as an indicator. Stock solution of sodium perchlorate used to adjust the ionic strength was prepared by direct weighing.

Appropriate amounts of all solutions except neptunium(VI) were mixed and placed in a thermostated bath. Neptunium(VI) solution was also placed separately in the bath and the two solutions were allowed to attain thermal equilibrium. The temperature of the bath was maintained within ±0.1°. The thermometer used was calibrated against an NBS thermometer. The reaction was started by adding neptunium(VI) solution and the start of the reaction was timed when half of the solution drained out of the pipet. A thorough mixing of the reactants was ensured before the sample was transferred to a stoppered silica spectrophotometric cell. The cell was placed in the thermostated cell compartment of a Beckman DU spectrophotometer maintained within ±0.1°. The reaction was followed by making absorption measurements at the 983-mμ absorption band of neptunium(V) at constant slit width. In all runs the reference used was a mixture of perchloric acid and potassium oxalate of the same concentration and ionic strength as the sample. All reactions were carried to over 50% completion and yielded consistent results over the entire range in each case.

Results

Neptunium(VI) in aqueous perchloric acid has a pink color. Upon the addition of oxalate it changed to yellow. One mole of potassium oxalate was found to react with 4 mol of neptunium(VI). The stoichiometry was determined by making triplicate runs with an excess of Np(VI) and taking the final spectrophotometric reading of the Np(V) peak after the completion of the reaction. The results of the three runs presented in Table I are in good agreement. Data for a typical run are given in Table II.

At constant ionic strength, the kinetics were found to be consistently of second order (first order with respect to neptunium(VI) and first order with respect to

TABLE I
INITIAL CONCENTRATIONS OF NEPTUNIUM(VI) AND POTASSIUM OXALATE AND THE RATIO OF NEPTUNIUM(V) PRODUCED TO TOTAL OXALATE

10^3[Np(IV)], *M*	10^3[$K_2C_2O_4$], *M*	$\frac{[\text{Np(V) produced}]}{[\text{total oxalate}]}$
2.72	0.2	3.9
2.72	0.4	3.8
2.72	0.6	3.8

TABLE II
THE CONCENTRATION OF Np(V) AS A FUNCTION OF TIME FOR THE REDUCTION OF Np(VI) WITH POTASSIUM OXALATE AT 25°[a]

Time, min	10^3[Np(V)], *M*	Time, min	10^3[Np(V)], *M*
7	0.21	180	0.51
30	0.27	390	0.67
60	0.33	∞	0.79
120	0.43		

[a] $[\mathrm{Np(VI)}] = 2.72 \times 10^{-3}$ *M*; $[\mathrm{K_2C_2O_4}] = 0.2 \times 10^{-3}$ *M*; $[\mathrm{H^+}] = 402 \times 10^{-3}$ *M*.

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[1] D. M. Gruen and J. J. Katz, *J. Am. Chem. Soc.*, **75**, 3772 (1953).
[2] A. Sjoblom and J. C. Hindman, *ibid.*, **73**, 1744 (1951).
[3] W. E. Keder, *J. Inorg. Nucl. Chem.*, **16**, 138 (1960).

postassium oxalate). In most cases runs were made in a large excess of potassium oxalate such that the change in its concentration during the reduction was negligible and the rate data were treated as a pseudounimolecular reaction. In other cases the apparent second-order rate constants, k', were determined by the rate expression

$$k't = \frac{2.303 \times 4}{(a - 4b)} \log \frac{4b(a - x)}{a(4b - x)}$$

where a and b are the initial concentrations of neptunium(VI) and potassium oxalate, respectively, and x is the amount of neptunium(V) produced at time t. Data for typical runs are given in Tables II and III. Data in Table II are for a run in which potassium oxalate is not in excess of neptunium(VI) and the apparent second-order rate equation is applicable. Data in Table III are for the case where potassium oxalate is in large excess of neptunium(VI) and the rate data were treated as a pseudounimolecular reaction.

TABLE III[a]

THE CONCENTRATION OF Np(V) AS A FUNCTION OF TIME AT 25° WITH POTASSIUM OXALATE IN EXCESS

Time, min	10^3[Np(V)], M	Time, min	10^3[Np(V)], M
2	0.33	25	1.65
5	0.58	30	1.81
10	0.94	40	2.03
15	1.22	50	2.20
21	1.50		

[a] $[\mathrm{Np(VI)}] = 2.72 \times 10^{-3}\ M$; $[\mathrm{K_2C_2O_4}] = 20 \times 10^{-3}\ M$; $[\mathrm{H^+}] = 402 \times 10^{-3}\ M$.

In the runs made at constant neptunium(VI) and potassium oxalate concentrations but varying hydrogen ion concentration at the same ionic strength, the apparent rate constant, k', was found to vary inversely with the acid concentration. A plot of log k' against log $[\mathrm{H^+}]$ gives a straight line with a negative slope of 1. The data at 25° and $\mu = 1$ are summarized in Table IV and Figure 1. The range of hydrogen ion concentration within which this reaction can be studied is limited between 0.3 and 0.9 M. Any decrease in the acidity leads to a complex formation between the neptunium(V) formed and potassium oxalate. Any increase beyond 0.9 M results in precipitation. The precipitate conformed to a test for oxalate and in view of the high concentration of perchloric acid the precipitate was assumed to be oxalic acid.

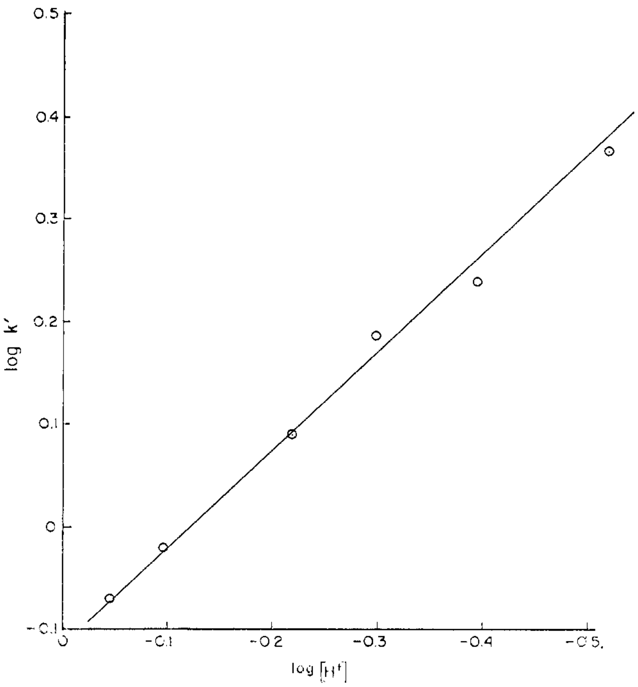

Figure 1.—Effect of hydrogen ion concentration on the apparent rate constant k' at 25° and $\mu = 1$, in the reduction of neptunium(VI) with oxalic acid.

TABLE IV

SPECIFIC VELOCITY CONSTANTS AT 25° AND $\mu = 1$ IN THE REDUCTION OF NEPTUNIUM(VI) WITH POTASSIUM OXALATE IN PERCHLORIC ACID

10^3[Np(VI)], M	10^3[$\mathrm{K_2C_2O_4}$], M	10^3[$\mathrm{H^+}$], M	k', M^{-1} sec^{-1}		k, sec^{-1}
2.72	20	402	0.029		0.12
1.36	20	402	0.028		0.011
10.96	20	402	0.032		0.013
5.44	20	402	0.028		0.011
2.72	20	402	0.028		0.011
2.72	15	402	0.028		0.011
2.72	10	402	0.030		0.012
2.72	5	402	0.027		0.011
2.72	0.2	402	0.024		0.011
2.72	20	900	0.014		0.013
2.72	20	800	0.016		0.013
2.72	20	600	0.020		0.013
2.72	20	500	0.026		0.013
2.72	20	300	0.038		0.012
				Av	0.012 ± 0.001

No perceptible effect on the rate was observed when the ionic strength was varied with the addition of sodium perchlorate. The k values obtained were 0.012 and 0.011 sec^{-1} for ionic strengths 0.5 and 1.0, respectively.

Energy of Activation

The energy of activation was determined by carrying out the reaction at four temperatures. From the data summarized in Table V and Figure 2, the energy of activation is calculated to be 15.5 kcal mol^{-1}.

TABLE V[a]

EFFECT OF TEMPERATURE UPON THE SPECIFIC VELOCITY CONSTANTS IN THE REDUCTION OF NEPTUNIUM(VI) WITH POTASSIUM OXALATE

Temp, °C	k, sec^{-1}	Temp, °C	k, sec^{-1}
25	0.012	35	0.026
30	0.016	40	0.033

[a] $[\mathrm{Np(VI)}] = 2.72 \times 10^{-3}\ M$; $[\mathrm{K_2C_2O_4}] = 20 \times 10^{-3}\ M$; $[\mathrm{H^+}] = 402 \times 10^{-3}\ M$.

Discussion and Mechanism

The rate law for the reaction was found to be

$$\frac{d[\mathrm{Np(V)}]}{dt} = \frac{k[\mathrm{Np(VI)}][\text{total oxalate}]}{[\mathrm{H^+}]}$$

Reduction of neptunium(VI) by potassium oxalate in acid solutions can be explained if the rate-controlling

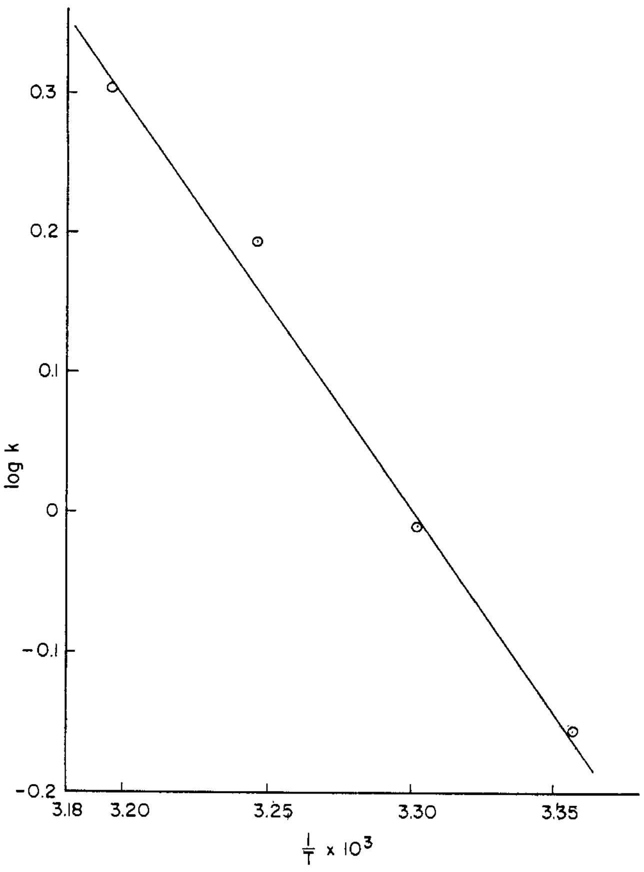

Figure 2.—Plot of log k against $(1/T) \times 10^3$ to determine the energy of activation in the reduction of neptunium(VI) with oxalic acid.

step is the formation of a hydrolyzed neptunium(VI)–oxalic acid complex followed by the oxidation of the complex by additional NpO_2^{2+} ions. The assumptions are reasonable for at the acidity used in the runs the oxalate would have reacted as oxalic acid. That a complex is formed when oxalic acid is added to NpO_2^{2+} solution is supported by the color change, from the pink of Np(VI) to a marked yellow. For 4 equiv of NpO_2^{2+} ion to be reduced per mole of oxalate oxidized it would be necessary for oxygen to be oxidized to the element which probably occurs through the intermediate formation of a percarbonate. The following equations explain the stoichiometry and the orders observed with respect to reactants

$$NpO_2^{2+} + H_2C_2O_4 + H_2O \xrightarrow{\text{slow}} NpO_2(OH)H_2C_2O_4^+ + H^+ \quad (1)$$

$$3NpO_2^{2+} + NpO_2(OH)H_2C_2O_4^+ \xrightarrow{\text{fast}} 4NpO_2^+ + 2CO_2 + 3H^+ + 0.5O_2 \quad (2)$$

$$4NpO_2^{2+} + H_2C_2O_4 + H_2O \longrightarrow 4NpO_2^+ + 2CO_2 + 4H^+ + 0.5O_2 \quad (3)$$

Carbon dioxide was detected as a product of the reaction, but oxygen, while not detected, was included as a product in order to account for the stoichiometry and mechanism of the reaction. The oxygen produced was at such low concentration, of the order of 10^{-3} M for complete reaction, that it would have been difficult to distinguish it from atmospheric oxygen although no runs free of atmospheric oxygen were attempted. Of course the product Np(V) was used in the analysis.

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The Chloryl Cation, ClO_2^+

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The 1:1 adducts $ClO_2F \cdot AsF_5$ and $ClO_2F \cdot BF_3$ have been investigated. Whereas $ClO_2F \cdot AsF_5$ is stable at ambient temperature, the $ClO_2F \cdot BF_3$ adduct shows a dissociation pressure of 225 mm at 25°. A pressure–temperature curve gives a heat of reaction of 24.0 kcal mol^{-1}, for the dissociation process: $ClO_2F \cdot BF_3(s) = ClO_2F(g) + BF_3(g)$. The X-ray powder patterns of $ClO_2F \cdot AsF_6$ and $ClF_3 \cdot AsF_5$ were recorded and indexed. Infrared and Raman measurements show that $ClO_2F \cdot AsF_5$ and $ClO_2F \cdot BF_3$ have the ionic structures $ClO_2^+AsF_6^-$ and $ClO_2^+BF_4^-$, respectively, in the solid state. All fundamental vibrations were observed and a valence force field was calculated for ClO_2^+.

Introduction

The existence of adducts between ClO_2F and Lewis acids such as SbF_5, AsF_5, BF_3, PF_5, VF_5, SnF_4, etc., is well known and has been discussed in a review article.[1a] Ionic structures involving the ClO_2^+ cation are generally assumed for these complexes.[1a,b] However, no experimental data have been reported to support this assumption. Since ClO_2F is the preferred product formed by the reaction of water,[2] oxides, or hydroxides with chlorine fluorides (independent of their oxidation state), it is the most common impurity in reactions involving any chlorine fluoride. Poorly passivated sections of metal vacuum lines or contact with glass is often sufficient to produce substantial amounts of ClO_2F. Thus, in reactions between chlorine fluorides and Lewis acids, ClO_2F is extremely difficult to remove from the

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(1) (a) M. Schmeisser and K. Brändle, *Advan. Inorg. Chem. Radiochem.*, **5**, 41 (1963). (b) After submitting this paper for publication, we have learned about a paper by G. A. Carter, A. M. Qureshi, and F. Aubke, *Chem. Commun.*, 1461 (1968), dealing with the existence of the ClO_2^+ cation in solution.

(2) R. Bougon, M. Carles, and J. Aubert, *Compt. Rend.*, **265**, 179 (1967).