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The Kinetics and Mechanism of Plutonium (IV) Reduction by Hydroxylamine

G. Scott Barney

August 1971

Atlantic Richfield Hanford Company
Richland, Washington 99352

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PREPARED FOR THE U.S. ATOMIC ENERGY
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THE KINETICS AND MECHANISM OF
PLUTONIUM(IV) REDUCTION BY HYDROXYLAMINE

By

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Research and Development
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August 1971

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ABSTRACT

The kinetics of the reduction of plutonium(IV) to plutonium(III) with hydroxylamine have been studied in 0.3 to 2.5M nitric acid at an ionic strength of 2.5. The stoichiometry of the reaction was found to vary according to reaction conditions. The moles of Pu(IV) consumed per mole of hydroxylamine ranges between 1.3 and 1.6, depending on the initial Pu(IV) concentration. The reaction is complex, involving several steps and intermediates. Effects of $[H^+]$, $[NO_3^-]$, $[NH_3OH^+]$, ionic strength, and temperature on the reaction rate were studied. Evidence was obtained which indicates substitution of a nitrate ligand with a neutral hydroxylamine molecule to form the initial activated complex. The initial rate [with no Pu(III) present] is described by the empirical equation,

$$\{-d[Pu(IV)]/dt\}_{t=0} = \frac{[Pu(IV)]_0 [NH_3OH^+]_0 (k_1 + k_2 [NH_3OH^+]_0)}{[H^+]_0^2 (1 + k_3 [NO_3^-]_0)}$$

The fact that addition of Pu(III) markedly decreases the reaction rate indicates that there is a back reaction occurring in which Pu(III) is oxidized by some hydroxylamine-derived intermediate, possibly NH_2O . Mechanisms which are consistent with the observed kinetics are presented.

THE KINETICS AND MECHANISM OF PLUTONIUM(IV) REDUCTION BY HYDROXYLAMINE

INTRODUCTION

Hydroxylamine has been utilized for many years as a reducing agent for aqueous plutonium ions in oxidation states greater than three. Most applications of these reactions have been confined to the laboratory. Recently, however, hydroxylamine has been used⁽¹⁾ as a reductant for Pu(IV) in processes which separate plutonium from uranium and nuclear reactor fission products. This reduction occurs in solvent extraction columns in which Pu(IV) [extractable by the organic phase] is reduced to Pu(III) which is not extractable and therefore remains in the aqueous phase. The rate of reduction of Pu(IV) under extraction column conditions is a critical factor in the design of this process.

The objective of this study was to develop a general rate law for the reaction which could be applied to all expected reaction conditions in the Purex solvent extraction process. Since the reaction occurs in nitric acid in this process, this medium was used for all experiments. Also of interest were the stoichiometry and mechanism of the reaction.

The kinetics of the reaction previously have received little attention and only qualitative observations have been reported. McKibben and Bercaw⁽¹⁾ have noted a sharp decrease in reduction rate with increasing acid concentrations. Qualitative observations of the effects of acid concentration, hydroxylamine concentration, and temperature on the rate of reduction in the presence of Fe^{3+} have been reported previously by this laboratory.⁽²⁾ Because of the complex nature of the rate in the presence of iron (which catalyzed the reaction), no attempt

was made previously to reduce the rate data to a generalized rate equation.

SUMMARY AND CONCLUSIONS

The kinetics and stoichiometry of the reduction of Pu(IV) by hydroxylamine were studied in nitric acid solution. Experiments in which the reaction was allowed to go to completion show that between 1.3 and 1.6 moles of Pu(IV) are reduced for each mole of hydroxylamine oxidized. The reaction therefore yields a mixture of nitrogen and nitrous oxide by the reactions

The initial reaction rate, R_0 , can be described by the empirical rate law

$$R_0 = \frac{-d[\text{Pu(IV)}]}{dt} = \frac{[\text{Pu(IV)}]_0 [\text{NH}_3\text{OH}^+]_0 (k_1 + k_2 [\text{NH}_3\text{OH}^+]_0)}{[\text{H}^+]_0^2 (1 + k_3 [\text{NO}_3^-]_0)}$$

where $k_1 = 7.04 \pm 1.14 \text{ mol l}^{-1} \text{ sec}^{-1}$, $k_2 = 48.2 \pm 9.1 \text{ sec}^{-1}$, and $k_3 = 2.14 \pm 0.49$ at 25 °C. This rate law indicates that several rapid, reversible equilibria are involved in the mechanism of the reaction. These equilibria lead to two activated complexes, $[\text{PuOH} \cdot \text{NH}_2\text{OH}^{3+}]^*$ and $[\text{Pu} \cdot 2\text{NH}_2\text{OH}^{4+}]^*$.

The reaction is strongly inhibited by Pu(III). The Pu(III) dependence of the initial rate is given by

$$R_0 = \frac{k_6}{1 + k_7 [\text{Pu(III)}]^2}$$

A back-reaction in which a Pu(III) dimer is oxidized by a hydroxylamine-derived intermediate [possibly $\text{NH}_2\text{O}\cdot$ or HNO] could explain the observed kinetic results.

The overall reaction rate can be described by the equation

$$\frac{-d[\text{Pu(IV)}]}{dt} = \frac{k_8 [\text{Pu(IV)}]}{1 + k_9 [\text{Pu(III)}]^2 / [\text{Pu(IV)}]}$$

where

$$k_8 = \frac{[\text{NH}_3\text{OH}^+](k_1 + k_2 [\text{NH}_3\text{OH}^+])}{[\text{H}^+]^2 (1 + k_3 [\text{NO}_3^-])}$$

$$\text{and } k_9 = \frac{k_{10} [\text{H}^+]^2 [\text{NO}_3^-]}{[\text{NH}_3\text{OH}^+]} \quad (k_{10} = 4.3 \pm 1.2 \times 10^2 \text{ at } 30^\circ \text{C})$$

EXPERIMENTAL

REAGENTS

All chemicals were of reagent grade except for plutonium solutions and were used without further purification. All solutions were prepared with either quartz-distilled or de-ionized water. A plutonium(IV) nitrate stock solution was prepared by loading separations plant plutonium product solution [adjusted to 6M HNO_3] onto a column of 50 to 100 mesh nitrate-form Bio-Rex 9 anion exchange resin [Bio-Rad Laboratories]. The column was washed with 6M HNO_3 and the plutonium then eluted with 1M HNO_3 . This purification procedure was repeated and the resulting solution was adjusted to 3M HNO_3 in order to prevent disproportion of Pu(IV). Spectrographic analysis showed no significant amounts of impurities present which could conceivably affect the reaction rate [e.g., iron was less than 12 parts per million parts plutonium]. Stock solutions prepared from two different sources gave identical rate constants.

A plutonium(III) perchlorate stock solution was prepared by dissolving Pu metal in 70% perchloric acid [Baker and Adamson--B&A]. This solution was diluted with water and filtered. All plutonium solutions were analyzed using standard alpha-counting techniques.

Stock solutions of hydroxylamine nitrate were prepared by converting hydroxylamine hydrochloride [B&A] by ion exchange using 20 to 50 mesh Dowex 50W-X8 cation exchange resin [Dow Chemical Company] in the acid-form. Hydroxylamine was determined by the Raschig method.⁽³⁾

Ionic strength was kept at 2.5 by addition of a stock solution of sodium perchlorate [G. F. Smith Chemical Company]. Nitrate ion concentration was varied by the addition of a stock sodium nitrate [B&A] solution.

APPARATUS

Initial reaction rates were obtained using an Aminco-Morrow stopped-flow apparatus coupled to a Beckman DU monochromator. The disappearance of the 476 nm absorbance of plutonium(IV) was followed by recording the percent transmittance versus time curve on a Tektronix 564B storage oscilloscope. The oscilloscope traces were then photographed using Polaroid film.

The reaction was followed to greater than 90% completion with a Beckman Model DK-2A recording spectrophotometer. A correction for Pu(III) absorption at 476 nm was applied to the absorbance versus time curves obtained with this instrument.

Water at constant temperature [± 0.1 °C] was circulated through cavities surrounding the driving syringes of the stopped-flow apparatus and through the thermostated cell compartment of the spectrophotometer. All solutions of reactants were pre-equilibrated to the desired temperature in a separate water bath before mixing.

PROCEDURE

Stoichiometry

The stoichiometry of the reaction was determined by two different methods. When a molar excess of Pu(IV) was used, the concentration of Pu(IV) after completion of the reaction was determined spectrophotometrically. When an excess of hydroxylamine was present after completion of the reaction, Pu(III) was removed by adding NaF to precipitate PuF_3 . The hydroxylamine in the supernatant was then determined by the Raschig method.

Kinetics

Solutions of Pu(IV) nitrate and hydroxylamine nitrate at the desired concentrations were prepared from stock solutions. These solutions were then either placed in the stopped-flow apparatus and reacted or mixed and placed in the cell compartment of the spectrophotometer. Initial concentrations of plutonium, hydroxylamine, and nitrate were calculated on the basis of stock solution concentration and the aliquots used. Hydrogen ion was determined directly by titrating samples of the solution after completion of the experiment.

The time required between mixing and the first measurement was ~ 5 milliseconds for the stopped-flow apparatus and ~ 15 seconds for the spectrophotometer.

Initial rates were calculated by plotting the percent transmittance versus time curves and drawing tangents to the curves at zero time. From the slope of these tangents, the initial rates were obtained. A minimum of three runs were made for each set of experimental conditions. Initial reaction rates, R_0 , are all given with respect to disappearance of Pu(IV) and the units are $\text{mol l.}^{-1} \text{ sec}^{-1}$.

RESULTS AND DISCUSSION

STOICHIOMETRY

The possible nitrogen-containing products obtained from the oxidation of hydroxylamine are nitrogen, nitrous oxide, nitrous acid, or nitrate ions, depending on the number of electrons transferred. With most one-equivalent metal ion oxidants (⁴⁻⁸) such as Fe^{3+} , Ag^+ , Co^{3+} , and Cu^{2+} , the reaction product is either nitrogen or nitrous oxide or mixtures of both. Since Pu^{4+} is also a one-equivalent oxidant, a similar stoichiometry was expected. Table I gives results of experiments conducted with both an excess of hydroxylamine and an excess of Pu(IV) .

TABLE I
STOICHIOMETRY OF THE REACTION^a

$[\text{Pu(IV)}], M$		$[\text{NH}_3\text{OH}^+], M$		$\frac{\Delta[\text{Pu(IV)}]}{\Delta[\text{NH}_3\text{OH}^+]}$
Initial	Final	Initial	Final	
0.0206	0.0190	0.00103	0.0	1.6
0.0206	0.0184	0.00154	0.0	1.4
0.0206	0.0176	0.00205	0.0	1.4
0.0206	0.0153	0.00410	0.0	1.3
0.0206	0.0099	0.00820	0.0	1.3
0.0206	0.0044	0.0123	0.0	1.3
0.0911	0.0	0.226	0.153	1.3
0.0786	0.0	0.260	0.204	1.4
0.0624	0.0	0.124	0.066	1.1
0.0595	0.0	0.118	0.076	1.4
0.0476	0.0	0.118	0.086	1.5
0.0476	0.0	0.236	0.199	1.3
0.0468	0.0	0.116	0.087	1.6
0.0393	0.0	0.130	0.102	1.4
0.0262	0.0	0.130	0.112	1.5
0.0262	0.0	0.260	0.244	1.6

^a Reaction medium was 1.0M HNO_3 .

The data in Table I indicate that between 1.3 and 1.6 moles of Pu(IV) are reduced for each mole of hydroxylamine oxidized. The reaction therefore yields a mixture of nitrogen and nitrous oxide by the reactions:

INITIAL REACTION

No simple rate expression could be found which described the rate. With concentrations of hydroxylamine, acid, and nitrate ion in excess, the rate was neither first order nor second order with respect to Pu(IV) concentration. Since most reactions in solution are not of higher kinetic order than second, it was felt that a back reaction was involved.

In order to avoid the complications of a back reaction, a rate expression for the initial reaction was obtained by measuring initial reaction rates. The effects of changing initial concentrations of Pu(IV), Pu(III), NH_3OH^+ , and NO_3^- on the initial rate, R_0 , were studied. As expected, the rate is first order with respect to initial plutonium(IV) concentration, $[\text{Pu(IV)}]_0$.

Figure 1 shows the effect on R_0 of increasing $[\text{NH}_3\text{OH}^+]_0$. The slope of this curve gets larger as $[\text{NH}_3\text{OH}^+]_0$ increases. The reaction order for hydroxylamine is therefore changing to a higher order with increasing $[\text{NH}_3\text{OH}^+]_0$ and indicates the formation of a Pu(IV)- NH_3OH complex at higher hydroxylamine concentrations. R_0 can be accurately expressed as a function of $[\text{NH}_3\text{OH}^+]_0$ by the equation

$$R_0 = k[\text{NH}_3\text{OH}^+]_0 + k'[\text{NH}_3\text{OH}^+]_0^2$$

The effect of initial acid concentration, $[H^+]_0$, is shown in Figure 2. An inverse second order dependence is observed.

Nitrate ion also inhibits the reduction of Pu(IV). This is because Pu(IV) tends to form stable complexes with nitrate. These complexes are less reactive than the free hydrated Pu^{4+} species.

Figure 3 shows R_0 as a function of initial nitrate concentration, $[NO_3^-]_0$. The rate can be described adequately by the equation

$$R_0 = \frac{k''}{1 + k'''[NO_3^-]_0}$$

where the slope of the line is k'''/k'' and the intercept is $1/k''$.

Combining the above equations gives the following empirical expression for the initial rate:

$$R_0 = \frac{[Pu(IV)]_0 [NH_3OH^+]_0 (k_1 + k_2 [NH_2OH^+]_0)}{[H^+]_0^2 (1 + k_3 [NO_3^-]_0)}$$

Values for the rate constants were calculated using a computer program* which performed a least-squares analysis of the data. At 25 °C and ionic strength equal to 2.5, the calculated values for k_1 , k_2 , and k_3 are, respectively, $7.04 \pm 1.14 \text{ mol l}^{-1} \text{ sec}^{-1}$, $48.2 \pm 9.1 \text{ sec}^{-1}$, and 2.14 ± 0.49 . Table II gives a comparison of observed and calculated values for the initial rate.

The form of the empirical rate law can be explained in terms of the equilibria which exist in solution. Equilibria which involve Pu(IV) species are as follows:

* GEORGE. Vinson, Barbara B., Mathematics Department, General Electric Company, Richland, Washington.

TABLE II
COMPARISON OF OBSERVED AND CALCULATED
VALUES OF THE INITIAL RATE^a

Pu(IV)_0 M	$[\text{NH}_3\text{OH}^+]_0$ M	$[\text{H}^+]_0$ M	$[\text{NO}_3^-]_0$ M	Observed ^{b, c} $R_0 \text{ (mol l}^{-1} \text{ sec}^{-1}) \times 10^3$	Calculated $R_0 \text{ (mol l}^{-1} \text{ sec}^{-1}) \times 10^3$
0.0179	0.0665	0.90	0.95	3.50	7.95
0.0119	0.0665	0.90	0.95	2.77	4.38
0.0060	0.0665	0.90	0.95	1.47	2.06
0.0030	0.0665	0.90	0.95	0.821	0.820
0.0018	0.0665	0.90	0.95	0.550	0.396
0.0052	0.273	1.00	0.96	9.04	9.04
0.0052	0.164	1.00	0.96	4.14	4.24
0.0052	0.109	1.00	0.96	2.02	2.82
0.0052	0.055	1.00	0.96	0.919	0.884
0.0052	0.027	1.00	0.96	0.425	0.299
0.0052	0.109	1.60	0.35	1.67	1.47
0.0052	0.109	1.35	0.35	2.64	1.85
0.0052	0.109	1.10	0.35	3.38	3.23
0.0052	0.109	0.85	0.35	5.76	5.33
0.0052	0.109	0.60	0.35	10.8	11.27
0.0052	0.109	0.60	0.35	12.4	11.27
0.0052	0.109	0.60	0.60	8.47	8.49
0.0052	0.109	0.60	0.85	7.39	5.92
0.0052	0.109	0.60	1.10	5.86	5.57
0.0052	0.109	0.60	1.35	4.84	5.38

^a Temperature = 25 °C, ionic strength = 2.5

^b Average of three runs.

^c The pooled standard deviation for 60 runs was 15.7%.

Free hydroxylamine is also in equilibrium with hydroxylammonium ion:

Selected values for these equilibrium constants are given in Table III.

TABLE III
SELECTED VALUES FOR EQUILIBRIUM CONSTANTS^a

<u>Constant</u>	<u>Value</u>	<u>Reference</u>
K_1	5.3	<i>b</i>
K_h	0.054	<i>c</i>
K_a	1.1×10^{-6}	<i>d</i>
^a At 25 °C.		
^b E. L. Zebroski and F. K. Neumann. quoted USAEC Report KAPL-184, May 20, 1949.		
^c S. W. Rabideau. <u>J. Am. Chem. Soc.</u> , 79, 3675(1957).		
^d R. A. Robinson and V. E. Bower, <u>A. Phys. Chem.</u> , 65, 1279(1961).		

From the listed values of the equilibrium constants, it is evident that in nitric acid solutions, Pu(IV) is present as several different complex species. Total Pu(IV) concentration can be represented as the sum of each species.

$$[\text{Pu(IV)}] = [\text{Pu}^{4+}] + [\text{PuOH}^{3+}] + [\text{PuNO}_3^{3+}]$$

In several kinetic studies⁽⁹⁻¹²⁾ of redox reactions of Pu(IV), the species PuOH^{3+} has been postulated to be the reactive Pu(IV) species. The strongly inverse dependence of the rate on acid concentration indicates that PuOH^{3+} may also be the reactive species for the present reaction. The concentration of PuOH^{3+} in terms of total Pu(IV) concentration and the above equilibrium constants is

$$[\text{PuOH}^{3+}] = \frac{K_h[\text{Pu(IV)}]}{[\text{H}^+] + K_h + K_1[\text{H}^+][\text{NO}_3^-]}$$

($K_h \ll [\text{H}^+]$ for the acid range studied and can therefore be eliminated in the denominator). Because of the partial second order dependence of the rate on hydroxylamine, there must also be a Pu(IV)- NH_2OH complex present as a reactive species in a parallel reaction.

At the acid concentrations used in these experiments (0.3 to 2.5M), hydroxylamine exists in solution largely as NH_3OH^+ . The greater reaction rate at low acid concentration suggests, however, that free hydroxylamine is the reactive species. Also, the reduction probably involves prior coordinate-bonding of free hydroxylamine to Pu^{4+} . Assuming that the free hydroxylamine is the reactive nitrogen species, the following reactions are consistent with kinetic observations:

The rate is therefore

$$\frac{-d[\text{Pu(IV)}]}{dt} = k_4[\text{PuOH}^{3+}][\text{NH}_2\text{OH}] + k_5K_d[\text{Pu}^{4+}][\text{NH}_2\text{OH}]^2$$

or in terms of measured concentrations

$$\frac{-d[\text{Pu(IV)}]}{dt} = \frac{[\text{Pu(IV)}][\text{NH}_3\text{OH}^+](k_4K_aK_h + k_5K_a^2K_d[\text{NH}_3\text{OH}^+])}{[\text{H}^+]^2(1 + K_1[\text{NO}_3^-])} \quad (9)$$

This equation is identical to the experimentally derived rate law where $k_1 = k_4K_aK_h$, $k_2 = k_5K_a^2K_d$ and $k_3 = K_1$.

The effect of temperature on the rate constants is shown in Table IV. The values obtained for k_3 are in general agreement with literature values for K_1 ,⁽¹³⁾ the formation constant for PuNO_3^{3+} . The activation energies for k_1 and k_2 are, respectively, 21.1 ± 1.3 kcal/mol and 25.5 ± 2.7 kcal/mol.

TABLE IV
EFFECT OF TEMPERATURE ON RATE CONSTANTS

Temperature, °C	k_1 , mol l. ⁻¹ sec ⁻¹	k_2 , sec ⁻¹	k_3 (K_1)
25	7.04 ± 1.14	48.2 ± 9.1	2.14 ± 0.49
35	26.6 ± 3.5	135. ± 19.	2.10 ± 0.28
40	38.1 ± 2.9	347. ± 32.	2.49 ± 0.11
45	68.6 ± 7.0	720. ± 67.	2.82 ± 0.16

The existence of a back-reaction was confirmed by observing the effect of initial Pu(III) concentration on the rate (Figure 4). The reaction slows sharply as $[\text{Pu(III)}]_0$ increases. Figure 5 shows that R_0 can be described in terms of $[\text{Pu(III)}]$ by the following equation,

$$R_0 = \frac{k_6}{1 + k_7[\text{Pu(III)}]_0^2} \quad (10)$$

where $k_6 = 5.24 \times 10^{-3}$ mol l.⁻¹ sec⁻¹ (equal to the rate with no initial Pu(III) present and at the specified conditions) and $k_7 = 2.35 \times 10^5$ l.² mole⁻² (obtained from least-squares analysis). Table V gives values for observed and calculated R_0 at various initial Pu(III) concentrations using the above equation.

TABLE V
VALUES FOR OBSERVED AND CALCULATED R_0
AT 25 °C^a

$\frac{[\text{Pu(III)}] (\times 10^3)}{M}$	$\frac{\text{Observed } R_0 (\times 10^3)}{\text{mole l.}^{-1} \text{ sec}^{-1}}$	$\frac{\text{Calculated } R_0 (\times 10^3)}{\text{mole l.}^{-1} \text{ sec}^{-1}}$
0.0	6.65	5.24
1.8	2.59	2.98
3.5	1.42	1.35
7.1	0.403	0.408
14.1	0.110	0.110
21.2	0.0425	0.0492

^a $[\text{Pu(IV)}]_0 = 0.0119M$, $[\text{NH}_3\text{OH}^+]_0 = 0.133M$, $[\text{H}^+]_0 = 0.90M$,
 $[\text{NO}_3^-]_0 = 1.07M$, and $\mu = 2.5$.

OVERALL REACTION

In order to determine the applicability of the rate law derived for the initial reaction rate to the overall reaction, experiments were conducted in which the reaction was followed to 90% completion or greater. In all of these experiments a stoichiometric excess of NH_3OH^+ , H^+ , and NO_3^- was used so that $[\text{Pu(IV)}]$, $[\text{Pu(III)}]$, and time were the only variables for a given run. According to equations 9 and 10, the rate law under these conditions reduces to

$$\frac{-d[\text{Pu(IV)}]}{dt} = \frac{k_8 [\text{Pu(IV)}]}{1 + k_7 [\text{Pu(III)}]^2} \quad (11)$$

$$\text{where } k_8 = \frac{[\text{NH}_3\text{OH}^+] (k_1 + k_2 [\text{NH}_3\text{OH}^+])}{[\text{H}^+]^2 (1 + k_3 [\text{NO}_3^-])}$$

An attempt was made to fit the experimental data to the integrated form of equation 11 using least squares. A poor fit was obtained from each of the kinetic runs. However, a greatly improved fit was obtained with the integrated form of the equation

$$\frac{-d[\text{Pu(IV)}]}{dt} = \frac{k_8[\text{Pu(IV)}]}{1 + k_9[\text{Pu(III)}]^2/[\text{Pu(IV)}]} \quad (12)$$

A plot of the integrated form of equation 12 [no initial Pu(III)],

$$\frac{t}{\ln \frac{A_0}{[\text{Pu(IV)}]}} = \left(\frac{k_9}{k_8} \right) \frac{A_0 \left\{ 2 \ln \frac{[\text{Pu(IV)}]}{A_0} + \frac{A_0}{[\text{Pu(IV)}]} \right\} - [\text{Pu(IV)}]}{\ln \frac{A_0}{[\text{Pu(IV)}]}} + \frac{1}{k_8}$$

{ A_0 = initial [Pu(IV)]} for a typical run is shown in Figure 6. Values calculated by least-squares for k_9 are given in Table VI. Because of the indeterminate intercept of the integrated equation, k_8 values were obtained from the initial rate constants at 30 °C. Values for k_9 were calculated from k_9/k_8 .

Data in Table VI show that k_9 changes with H^+ , NO_3^- , and NH_3OH^+ concentrations. Least-squares analysis gave k_9 in terms of another constant, k_{10} , as follows:

$$k_9 = k_{10} \frac{[\text{H}^+]^2 [\text{NO}_3^-]}{[\text{NH}_3\text{OH}^+]}$$

Values calculated for k_{10} are also given in Table VI. At 30 °C, k_{10} is equal to $(4.3 \pm 1.2) \times 10^2 \text{ l.}^3 \text{ mol}^{-3}$. Table VII shows the temperature dependence of k_{10} .

TABLE VII
TEMPERATURE DEPENDENCE OF k_{10}

Temperature, °C	$k_{10} (\times 10^{-2}), \text{ l.}^3 \text{ mol}^{-3}$
30	4.3
35	3.2
40	1.7
45	1.1

TABLE VI
RATE CONSTANTS FOR OVERALL REACTION AT 30 °C

$\frac{[\text{Pu(IV)}]_0}{M}$	$\frac{[\text{NH}_3\text{OH}^+]}{M}$	$\frac{[\text{H}^+]}{M}$	$\frac{[\text{NO}_3^-]}{M}$	$\frac{k_8}{\text{sec}^{-1}}$	$\frac{k_9 (\times 10^{-4})}{\text{l. mol}^{-1}}$	$\frac{k_{10} (\times 10^{-2})}{\text{l.}^3 \text{ mol}^{-3}}$
0.0126	0.0804	2.51	2.62	0.0394	8.91	4.2
0.00838					8.79	4.0
0.00419					8.25	4.0
0.00209					7.49	3.9
0.0105	0.0207	1.53	1.65	0.0301	10.46	5.2
	0.0410			0.0661	2.65	2.8
	0.0804			0.154	1.64	3.4
	0.118			0.261	1.06	3.4
	0.155			0.378	0.703	3.0
0.0105	0.0804	1.28	0.47	0.495	0.345	3.6
		1.52		0.351	0.505	3.7
		1.72		0.274	0.621	3.6
		1.88		0.230	0.853	4.1
		2.19		0.169	1.16	4.1
0.00594	0.0991	1.54	0.54	0.422	0.468	3.5
			0.79	0.339	1.29	6.7
			1.03	0.285	1.86	5.9
			1.20	0.256	2.20	7.0
			0.38	0.501	0.538	5.9

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FIGURE 2 ACID DEPENDENCE OF THE INITIAL RATE, R_0 , AT 25°C

FIGURE 3 NITRATE ION DEPENDENCE OF THE INITIAL RATE, R_0 , AT 25°C

FIGURE 4 EFFECT OF Pu(III) CONCENTRATION ON THE INITIAL RATE, R_0 , AT 25°C

FIGURE 5 TEST OF RATE EQUATION 10

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