TABLE III

RELATIVE VALUES OF THE MOLAR EXTINCTION COEFFICIENT
OF $C_6H_6 \cdot I$ AT 4200 AND 4900 Å.

$(k/\epsilon_c) \times 10^{-6}$ (cm./sec.)

Cell	4200	4900	$\epsilon_{c_{4200}}/\epsilon_{c_{4900}}$
E	7.3	3.7	0.51
F	7.6	3.9	.51
G	7.1	3.5	.50
A-3	5.9	3.1	.53

A very small deflection was also measured at 6000 Å. indicating slight absorption by the complex at this wave length but was too small to permit the accurate calculation of k/ϵ_{c6000} after the deflections were corrected for stray light of other wave lengths transmitted by the filter.

Discussion

The calculated extinction coefficients in Table II, although large, are to be expected from Mulliken's theory of intermolecular charge-transfer interaction.[8] The several simplifications of the theory[22,23] used to explain certain regularities between the ionization potential of the donor molecules and the observed maximum of the charge-transfer spectrum involving molecular iodine should not hold with this system because the constants involved are considerably different for different acceptors.[24] Qualitatively, though, the complex involving I atoms might be expected to be more stable than the corresponding I_2 complex because of the larger electron affinity of the I atom, so that ϵ_{max} should shift toward longer wave lengths. The data of Table III and the observed very slight absorption at 6000 Å., admittedly very scanty, suggest that a maximum exists between 4000 and 5000 Å. This shift is quite large compared to that of only 200 Å. for quite different acceptor molecules.[22]

(22) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

(23) S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, THIS JOURNAL, **75**, 2901 (1953).

(24) R. S. Mulliken, *Rec. trav. chim.*, **75**, 845 (1956).

Increased stability of the complex theoretically should also lead to an increase in the intensity of the charge-transfer spectrum, although the results of Benesi and Hildebrand[7] indicate that ϵ_{max} decreases with increasing complex stability in the methylated benzene series. (Orgel and Mulliken,[25] however, have suggested that the observed intensities are composed of both "contact" and "complex" charge-transfer spectra. When an appropriate division is made between the two possibilities, an increase in ϵ_c with increasing complex stability can be calculated.) Thus the values given in Table II for ϵ_c are reasonable, especially at the larger values of ϕ, even though 4200 Å. is obviously not the wave length of maximum absorption.

Even the smallest possible value for the rate of complex combination (*i.e.*, 1.02×10^{11} l. mole^{-1} sec.$^{-1}$, when $\phi = 1$) is about 18 times larger than the recombination of iodine atoms in carbon tetrachloride.[3] This is surprising, for if the rate of combination is diffusion-controlled as presumed[6] then k should be *smaller* for the complexed atom (with its larger diffusion diameter) than for the free atom. The fact that both ϵ_c and k are large at $\phi = 1$, and increase markedly to unreasonable values with decreasing ϕ, supports the view that the formation of the complex stabilizes the I atoms so that most of them escape recombination into the parent molecule in contrast to the caging effect and low degree of dissociation of I_2 in inert solvents.

(25) L. E. Orgel and R. S. Mulliken, THIS JOURNAL, **79**, 4839 (1957).

TROY, NEW YORK

Kinetics and Mechanisms for the Oxidation of Trivalent Plutonium by Nitrous Acid[1]

BY E. K. DUKES

The rate of oxidation of plutonium(III) by nitrous acid was investigated in nitric, hydrochloric and perchloric acids. The rate expressions obtained were in HCl or $HClO_4$, $- d[Pu(III)]/dt = K_1[Pu(III)][H^+][HNO_2]$; in HNO_3, $- d[Pu(III)]/dt = K_2[Pu(III)][H^+][NO_3^-][HNO_2]$ where $K_1 = 18 \pm 3.5$ moles^{-2} min.$^{-1}$ and $K_2 = 90 \pm 20$ moles^{-3} min.$^{-1}$. The proposed mechanisms for the oxidation of Pu(III) by nitrous acid involve N_2O_4 as an intermediate in HNO_3 and NO^+ as an intermediate in HCl or $HClO_4$. Activation energies of 14.0 ± 0.5 and 6.0 ± 0.3 kcal./mole were found for K_1 and K_2. Studies were made with solutions 10^{-5} to 10^{-6} molar in plutonium and the change in distribution coefficient of plutonium into 30 vol. % tributyl phosphate (TBP) was used to follow the reaction.

Introduction

Nitrous acid oxidizes trivalent plutonium to tetravalent plutonium in acid solutions by the

reaction

$$Pu(III) + H^+ + HNO_2 \longrightarrow Pu(IV) + NO + H_2O$$
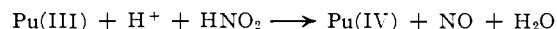
The rate of this reaction is measurable at tracer concentrations of Pu but no data have been published. This paper reports the results of a study of the
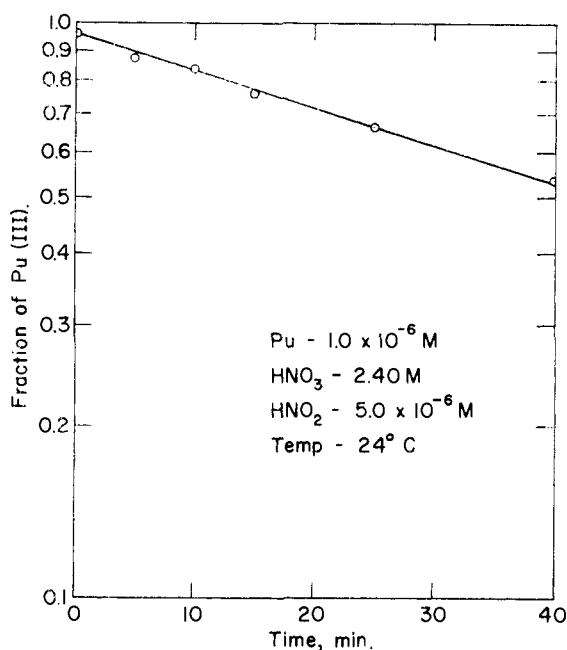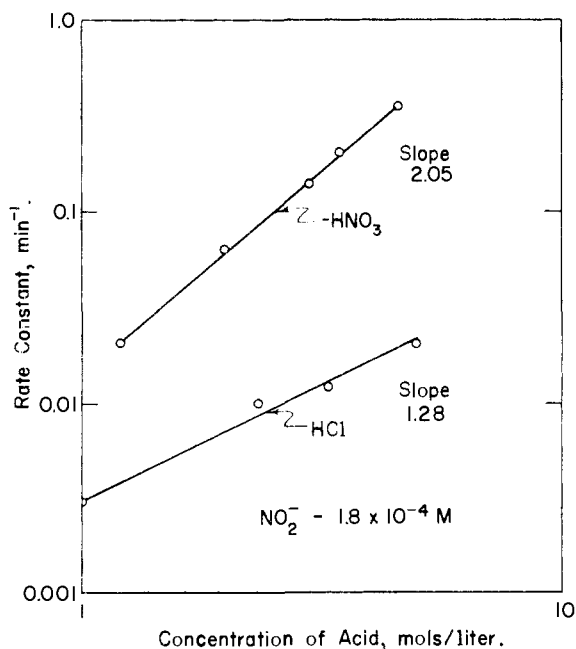
Fig. 1.—Typical curve.

Fig. 2.—Effect of HCl and HNO_3.

kinetics of the $Pu(III)-HNO_2$ reaction in HNO_3, HCl and $HClO_4$.

Preparation of Reagents

Tetravalent Plutonium.—Solvent extraction or ion exchange was used to purify solutions of Pu(IV). In the solvent extraction method, plutonium(IV) was extracted from 4 M nitric acid into a solution of 30 vol. % tributyl phosphate (TBP) in n-dodecane. The extract was scrubbed three times with 4 M nitric acid and the plutonium(IV) was back-extracted into 0.5 M nitric acid. In the anion-exchange method, plutonium(IV) was absorbed from 8 M nitric acid on "Dowex" 21-K resin and was eluted with 0.5 M nitric acid. The ion-exchange procedure also was used to prepare solutions of plutonium(IV) in hydrochloric acid.
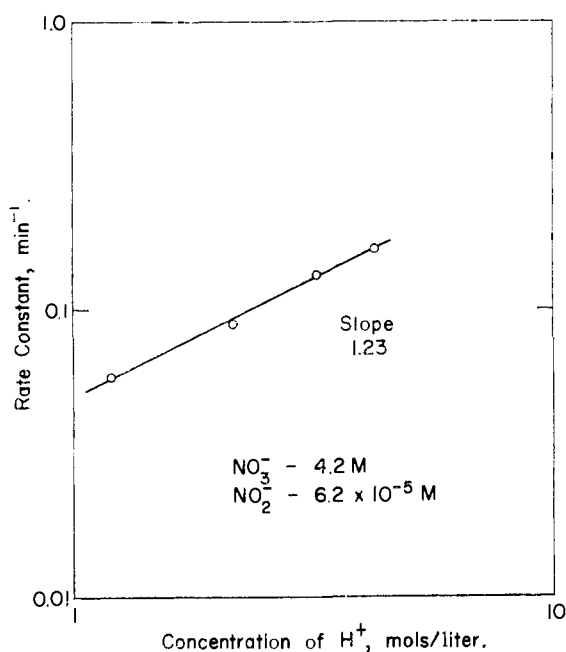

Fig. 3.—Effect of hydrogen ion concentration.

Trivalent Plutonium.—Solutions of trivalent plutonium were prepared from solutions of Pu(IV) in HNO_3 or HCl by the hydrogen reduction of plutonium(IV) with a strip of platinized platinum as a catalyst.[2] Analyses of these solutions by solvent extraction showed that the plutonium(III) content averaged 94%. The low concentration of plutonium(IV) in these solutions was not important because each solution was analyzed immediately before use.

Tributyl Phosphate and n-Dodecane.—TBP was purified by crystallization of its uranyl nitrate addition compound from n-hexane.[3] Thirty volume per cent. (1.09 M) solutions of TBP in n-dodecane were used throughout the study. The n-dodecane, olefin free grade, was obtained from the Humphrey-Wilkinson Co. and was used without further treatment.

Other Chemicals.—All other solutions were prepared from reagent grade chemicals and were used without further purification.

Experimental Procedure

These studies were made at Pu concentrations of 10^{-5} to 10^{-6} M to minimize interferences from peroxide produced by α-particles and from disproportionation reactions that might occur at high concentrations of Pu. An excess of nitrous acid was used in all experiments to diminish the importance of an autocatalytic effect that arises from the production of 1.5 moles of HNO_2 for each mole of HNO_2 consumed by the reaction.

Measurements of the reaction rate were made by determination of the Pu(III) in acidic solutions by solvent extraction with 30 vol. % TBP. Under the experimental conditions, only Pu(III) and Pu(IV) were present; the fraction of

$$Pu(III) = \frac{Pu(III)_{aq} + Pu(III)_{org}}{Pu(III)_{aq} + Pu(III)_{org} + Pu(IV)_{aq} + Pu(IV)_{org}}$$

The distribution coefficient (E_S) of a mixture of Pu(III) and Pu(IV) is

$$E_S = \frac{Pu(IV)_{org} + Pu(III)_{org}}{Pu(IV)_{aq} + Pu(III)_{aq}}$$

The distribution coefficients of pure Pu(III) and pure Pu(IV) are

(2) G. T. Seaborg, J. J. Katz and W. M. Manning, "The Transuranium Elements," (National Nuclear Energy Series IV-14B), McGraw-Hill Book Co., New York, N. Y., 1949.

(3) E. K. Dukes, "The Formation and Effects of Dibutyl Phosphate in Solvent Extraction," E. I. du Pont de Nemours & Co., Savannah River Laboratory, DP-250, November, 1957.
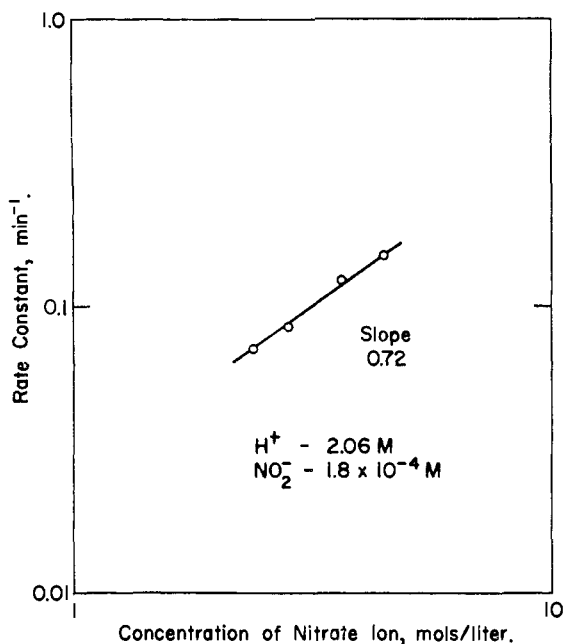
Fig. 4.—Effect of nitrate ion concentration.

$$E_{(III)} = \frac{Pu(III)_{org}}{Pu(III)_{aq}} \qquad E_{(IV)} = \frac{Pu(IV)_{org}}{Pu(IV)_{aq}}$$

Simultaneous solution and algebraic manipulation yield an expression for the fraction, $F(III)$, of Pu(III) in a mixture of Pu(III) and Pu(IV)

$$F_{(III)} = \frac{(E_{IV} - E_8)(E_{III} + 1)}{(E_8 + 1)(E_{IV} - E_{III})}$$

This expression is valid when the volumes of the aqueous and organic phases are equal. With this equation, the determination of Pu(III) in a mixture of Pu(III) and Pu(IV) requires determination of the distribution coefficient of the mixed Pu(III) and Pu(IV), and knowledge of the distribution coefficient of pure Pu(III) and pure Pu(IV) under the same conditions of acidity, temperature, etc.

Distribution coefficients were determined in the following manner: A solution of Pu (10^{-5} to 10^{-6} M) and an equal volume of 30% TBP in n-dodecane were mixed thoroughly. Equilibrium was reached in less than 20 seconds of mixing. The phases were separated by centrifugation, and the plutonium content of each phase was determined by α-count of an aliquot. This distribution coefficient was the ratio of the α-activity in the organic phase to the α-activity in the aqueous phase. All distribution coefficients were determined at $0°$. Tables I and II contain distribution coefficients for pure Pu(III) and pure Pu(IV) in solutions with

TABLE I

DISTRIBUTION OF PLUTONIUM(III) AT $0°$

HNO₃ (M) concn.					
(aq.)	1.05	1.57	2.70	3.60	4.60
Distribution coefficient (org./aq.)	0.042	0.052	0.058	0.055	0.049

TABLE II

DISTRIBUTION OF PLUTONIUM(IV) AT $0°$

HNO₃ (M) concn. (aq.)	1.03	1.40	2.16	3.10	3.80	5.30
Distribution coefficient (org./aq.)	2.20	3.90	6.60	11.00	15.50	25.00

compositions of interest to the rate determination. The proper valence was ensured by adding ferrous sulfamate for Pu(III) or NaNO₂ for Pu(IV).

In the determination of reaction rates, an aliquot of a stock solution of Pu(III) was added to the acid solution of

the desired composition, and the solution was analyzed by solvent extraction to determine the initial fraction of Pu-(III). A measured amount of sodium nitrite was added to start the reaction. Aliquots of the solution were withdrawn at timed intervals, chilled at $0°$ to decrease the rate of the reaction, and the fraction of Pu(III) determined by solvent extraction.
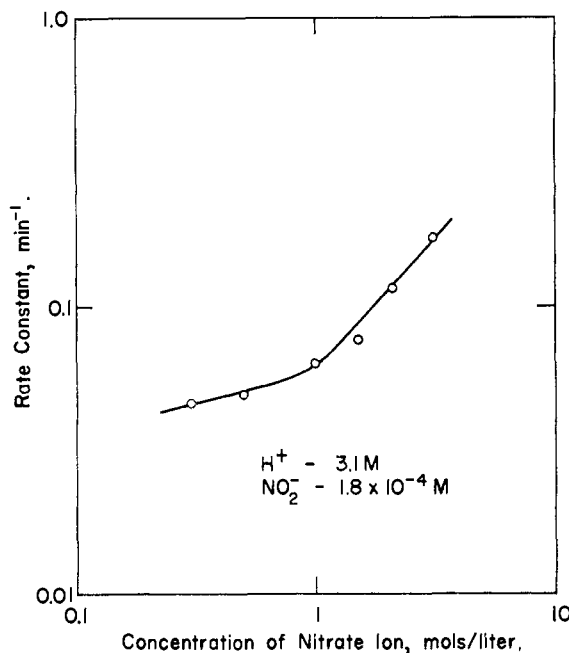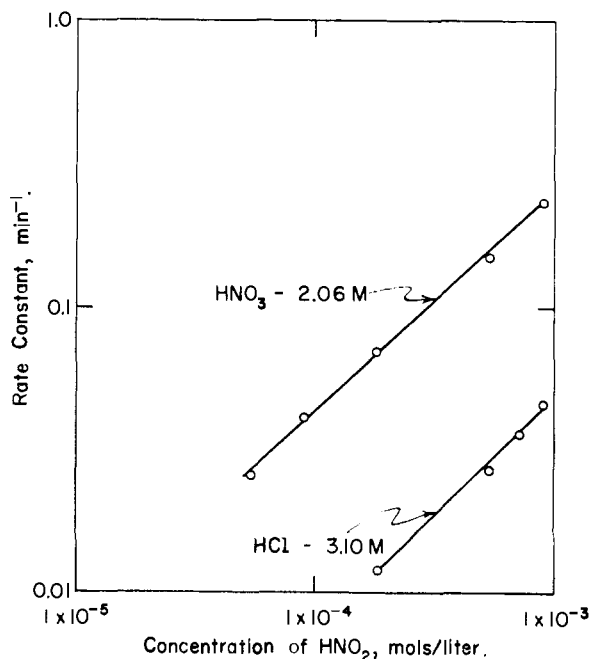

Fig. 5.—Effect of nitrate ion in HCl.

Fig. 6.—Effect of HNO₂.

The distribution data obtained with Pu in HNO₃ also were used to analyze for Pu(III) in HCl or HClO₄. Aliquots of the samples were diluted in nitric acid before the equilibration with TBP. Low concentrations of HCl or HClO₄ in nitric acid did not cause significant changes in the distribution coefficients for pure nitric acid. The remainder of the procedure was the same as the procedure in nitric acid.
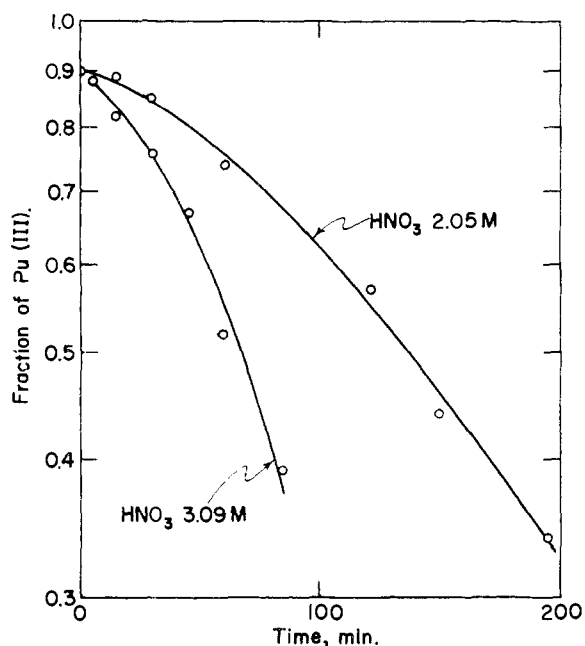
Fig. 7.—Oxidation of Pu(III) in HNO_3.

Fig. 8.—Effect of temperature on oxidation of Pu(III) to Pu(IV).

Results

Effect of Concentration of Plutonium.—The oxidation of trivalent plutonium by nitrous acid was first order with respect to plutonium. Rate constants were the same at 1.0×10^{-6} M as at 5.0×10^{-5} M Pu. Typical data are shown in Fig. 1.

Dependence on HNO_3, HCl and $HClO_4$.—The rates of oxidation of Pu(III) depended on the second power of the concentration of HNO_3 and the first power of the concentration of HCl (Fig. 2). Rates were slower in HCl than in comparable concentrations of HNO_3.

The dependence on the concentration of HNO_3 was due to the combined effects of the hydrogen and nitrate ions. Variations of the hydrogen ion concentration, with $NaNO_3$ added to maintain a constant nitrate concentration, showed that the hydrogen ion dependence of the reaction was approximately first power (Fig. 3). Rate determinations in solutions of constant acidity, with varied sodium nitrate concentrations, showed an approximate first power dependence on the nitrate ion (Fig. 4). Determination of the rates in mixtures of HCl—HNO_3, at constant ionic strength, showed an exact first power dependence of the rate on nitrate concentrations above 1 M in nitrate. At lower nitrate concentrations the reaction apparently was less dependent on nitrate concentration (Fig. 5). These data suggested that at least two mechanisms were involved in the oxidation of Pu(III).

The rates of oxidation were identical in HCl and $HClO_4$ (Table III); therefore, either the chloride ion and the perchlorate ion had the same effect on the reaction rate, or neither affected the reaction rate. It was assumed in this study that neither the chloride ion nor the perchlorate ion affected the reaction rate.

Dependence on Nitrous Acid.—Rates of oxidation depended on the first power of the concentration
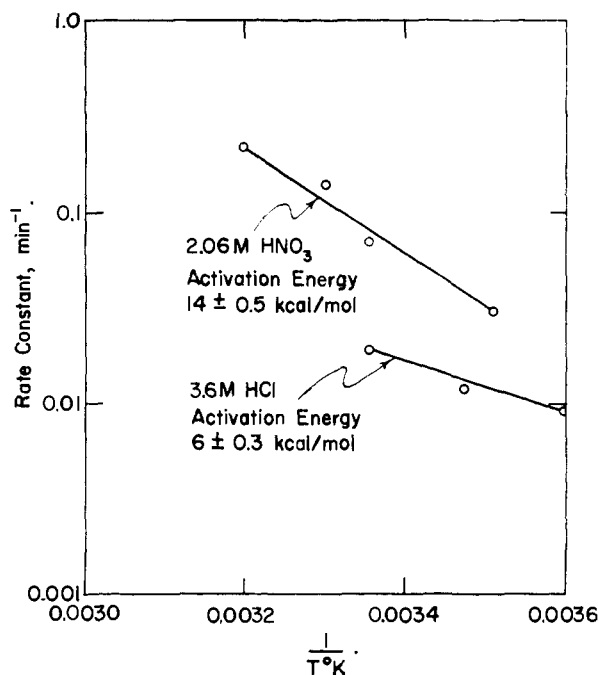
of HNO_2 in HNO_3 and HCl (Fig. 6). Oxidation of Pu(III) was autocatalytic in solutions of nitric acid if the concentration of HNO_2 was less than or equal to the concentration of plutonium (Fig. 7). Uniform rates of oxidation were obtained by main-

TABLE III

COMPARISON OF RATES OF OXIDATION IN HCl AND $HClO_4$

Acid	Concn., M	HNO_2, M	Rate, min.$^{-1}$
HCl	3.60	5.4×10^{-4}	0.034
$HClO_4$	3.60	5.4×10^{-4}	.031
HCl	3.06	1.8×10^{-4}	.012
$HClO_4$	3.06	1.8×10^{-4}	.013
HCl	1.60	5.4×10^{-4}	.013
$HClO_4$	1.60	5.4×10^{-4}	.019

taining an excess of HNO_2. In some experiments nitrous acid was lost during the reaction; however, the loss of nitrous acid was slow enough to allow the determination of rate constants from initial rates of oxidation.

Discussion

The oxidation of Pu(III) by nitrous acid fits the rate expressions

in HCl or $HClO_4$

$$-\frac{d[Pu(III)]}{dt} = K_1[Pu(III)][H^+][HNO_2] \quad (1)$$

in HNO_3

$$-\frac{d[Pu(III)]}{dt} = K_2[Pu(III)][H^+][NO_3^-][HNO_2] \quad (2)$$

The contribution of expression 1 to the rate of oxidation is small at concentrations of nitrate ion greater than 1.0 M but expressions 1 and 2 must be combined at lower concentrations of nitrate.

Observed rates were used in (1) and (2) to calculate an average value of 18 ± 3.5 moles^{-2} min.$^{-1}$ for K_1 and 90 ± 20 moles^{-3} min.$^{-1}$ for K_2.

From the data in Fig. 8 the activation energy was calculated to be 6.0 ± 0.3 kcal./mole for (1) and 14.0 ± 0.5 kcal./mole for (2).

Different rate constants and activation energies for the different acids suggest at least two mechanisms for the oxidation of Pu(III) by nitrous acid. More complicated mechanisms may be involved but two possible mechanisms that are in accord with the results are

$HNO_2 + H^+ \rightleftarrows NO^+ + H_2O$; rapid reversible (3)

$NO^+ + Pu(III) \longrightarrow NO + Pu(IV)$; rate controlling

$HNO_2 + HNO_3 \rightleftarrows N_2O_4 + H_2O$; rapid, reversible (4)

$N_2O_4 + Pu(III) \longrightarrow NO_2^- + NO_2 + Pu(IV)$; rate controlling
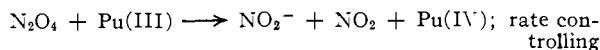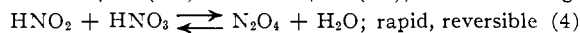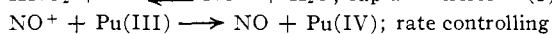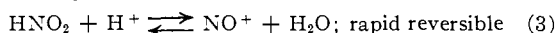
In (3) the oxidation of Pu(III) by NO^+ is analogous to the mechanism proposed by Abel[4] for the oxidation of Fe(II) by HNO_2 in acid media. It is proposed that in solutions of nitric acid oxidation occurs through both mechanisms. Studies in HCl showed that (3) becomes important only at low concentration of the nitrate ion.

(4) E. Abel, *Monatsh.*, **80**, 379 (1949).

AIKEN, SOUTH CAROLINA

[CONTRIBUTION FROM GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

The Oxidation of Captive Oxalate

BY PATRICIA SAFFIR AND HENRY TAUBE

The oxidation of $(NH_3)_5CoC_2O_4^+$ by Ce(IV) takes place with almost perfect stoichiometry, one Ce(IV) being consumed for each mole of the Co(III) complex, and one Co^{++} being formed. Co^{+++} aq. and $S_2O_8^=$ with Ag^+ as catalyst behave similarly. However, H_2O_2 catalyzed by Mo(VI), and Cl_2 act to preserve the oxidation state of Co(III) and $(NH_3)_5CoOH_2^{+++}$ is formed. The difference in behavior of the two classes of oxidizing agents is ascribed to this: Ce(IV), Co(III) and some intermediate in the $S_2O_8^= + Ag^+$ system act by extracting one electron at a time, while the other two act in a manner which is equivalent to extracting two electrons simultaneously.

In many systems it has been observed that metal ions though present in small amounts may alter the kinetics and even the course of oxidation-reduction reaction. Usually the studies have been done with metal ions which are substitution-labile and the interpretation of the results is made difficult because the way the metal ion is combined in the various stages of the reaction in which it is active is not known. The experiments reported in this paper, on the reaction of oxidizing agents with a reducing agent bound to a substitution-inert metal ion center, are relevant to this subject. The reducing agent–metal ion complex we chose for study is $(NH_3)_5CoC_2O_4^+$, and the feature of particular interest was to learn whether and when the Co(III) takes part in the oxidation of the bound oxalate brought about by external oxidizing agents.

Materials.—The $(NH_3)_5CoC_2O_4H(ClO_4)_2$ was prepared by warming a solution of $(NH_3)_5CoH_2O(ClO_4)_3$ with a slight excess of oxalic acid. The solid which separated on cooling was recrystallized and submitted for analysis (analysis reported at 16.02% N and 16.35% Cl to be compared with the theoretical values of 16.21 and 16.41%, respectively). The solution containing Co^{+++} aq. was prepared by the method of Weiser.[1] The carbonato complex is prepared in saturated $NaHCO_3$ using H_2O_2 as oxidant on a cobaltous salt. The solution is added slowly to a cooled solution of $HClO_4$ aq.

All other reagents were standard C.P. or A.R. chemicals.

Results

Reaction with Ce(IV) Perchlorate.—In a typical experiment, a solution was used which was 0.025 M in $(NH_3)_5$-$CoC_2O_4H(ClO_4)_2$, 0.047 M in Ce(IV) and 1 M in $HClO_4$. The progress of the reaction was followed by titrating Ce(IV) with Fe^{++} (the cobalti complex does not react rapidly with this reducing agent). The reaction of Ce(IV) with the cobalti complex is very much slower than it is with uncomplexed oxalate, and a period of *ca*. 20 hr. is required to ensure complete reaction at room temperature at the concentrations obtaining in our present experiments; for the uncomplexed oxalate, a few minutes would suffice.

(1) D. W. Weiser, Ph.D. Dissertation, University of Chicago, 1956.

There is apparently a slow loss of Ce(IV) even after the oxalato complex has disappeared; this loss is perhaps attributable to the oxidation of water by Ce(IV), catalyzed by Co^{++}. The effect is much reduced at 10°, and at this temperature clear-cut results on the stoichiometry are obtained. After 73 hr., the oxalato complex has disappeared and the ratio of Ce(IV) consumed to total oxalato complex is 1.01, after 146 hr. the ratio is 1.02 and after 250 hr., 1.04. Correcting for the continued slow loss of Ce(IV), the conclusion follows that the reaction of Ce(IV) with the oxalato complex takes place with almost perfect stoichiometry, *one* Ce(IV) being required for each oxalate. The cobalt product is not $(NH_3)_5CoOH_2^{+++}$ as would be expected if the cobalt oxidation state were preserved, but Co^{++}. The net change can be represented by the equation

$$(NH_3)_5CoC_2O_4H^{++} + Ce(IV) + 4H^+ = Co^{++} +$$
$$Ce^{+++} + 2CO_2 + 5NH_4^+$$
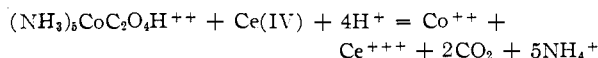
Reaction with Co^{+++}.—The observations with Co^{+++} aq. as oxidizing agent are complicated by the reaction of Co^{+++} aq. to liberate O_2 from water but the intrinsic stoichiometry in the reaction of interest can nevertheless be fairly well established. In an experiment with $(NH_3)_5CoC_2O_4H(ClO_4)_2$ at 0.0021 M, Co^{+++} initially at 0.0041 M and $HClO_4$ at 2 M, at 10° and in the dark, after 144 hr. the total amount of Co^{+++} aq. consumed (as determined by titration) compared to the initial amount of the oxalato complex was 1.28. After this time, the extinctions of the solution at λ's = 4020 and 6020 Å. could be accounted for quantitatively by the residual Co^{+++} shown by titration and the Co^{++} resulting from the reduction of Co^{+++} and the Co(III) complex. If $(NH_3)_5Co(OH_2)^{+++}$ or $(NH_3)_5CoC_2O_4H^{++}$ were present, it would contribute appreciably to the extinction at 4020 Å.; at most 5% of an ammino complex remains. We conclude that in this reaction also, the oxidation of the bound oxalate by the external oxidizing agent brings about the reduction of Co(III) in the complex. The consumption of Co^{+++} aq. in excess of that prescribed by this stoichiometry is attributable to the spontaneous oxidation of H_2O by Co^{+++} aq., rather than to the $2e^-$ oxidation of the oxalato complex by the Co^{+++} aq.

The Ag^+ Catalyzed Reaction with $S_2O_8^=$.—The reaction of $S_2O_8^=$ with $(NH_3)_5CoC_2O_4^+$ is very slow, but when Ag^+ is present (~ 0.1 M $AgClO_4$ was used), reaction takes place immediately and Co^{++} is formed. A blank experiment with $(NH_3)_5CoOH_2^{+++}$ in place of the oxalato complex shows that the aquo ion survives this treatment. We can conclude