water and excess 8-quinolinol, was obtained analysis showed the composition $NbO(C_9H_6ON)_3$. The same technique by which niobium 8-quinolinolate was prepared failed to produce a compound from a pure tantalum solution. When pure tantalum and niobium were mixed however, tantalum appeared to have formed a similar compound. When tantalum pentachloride and 8-quinolinol were combined in benzene solutions, a stable addition compound containing about 5 moles of 8-quinolinol was formed. Niobium pentachloride appeared to form a compound similar to the tantalum addition compound with 8-quinolinol but which was quite unstable.

Niobium 8-quinolinolate shows a strong characteristic band at about 10.9 μ in the infrared spectra that apparently is due to the "NbO" group.[9,10]

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(9) R. G. Charles, H. Frieser, R. Friedel, L. E. Hilliard and W. D. Johnston, *Spectrochim. Acta*, **8**, 1 (1956).

(10) J. P. Phillips and J. F. Deye, *Anal. Chim. Acta*, **17**, 233 (1957).

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[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

Kinetics of the Neptunium(III)–Neptunium(V) Reaction in Perchlorate Solution[1]

BY J. C. HINDMAN, J. C. SULLIVAN AND DONALD COHEN

RECEIVED OCTOBER 10, 1957

The kinetics of the Np(III)-Np(V) reaction in perchlorate solution have been investigated. The rate law for the forward reaction can be written as $-\partial[NpO_2^+]/\partial t = k_1[Np^{+3}][NpO_2^+][H^+]$. At 25° and $\mu = 2.0$, $k_1 = 2590$ l.^{2} mole^{-2} min.$^{-1}$. The rate is slightly decreased in a deuterated medium. The experimental activation energy is 6.5 ± 0.5 kcal. in $HClO_4$ solution and 5.6 ± 0.5 kcal. in $DClO_4$ solution. Possible mechanisms for the reaction are considered.

Reactions which involve the oxidation of Np(IV) to Np(V) appear to proceed through hydrolyzed species of the lower state.[2-4] Similar behavior is noted for reactions of the analogous species of U(IV)[5] and plutonium (IV).[6] It has been suggested[4] that the mechanism of such reactions involves the formation of species which can readily be converted to the XO_2^+ or XO_2^{++} ions. It is of considerable interest to examine the mechanism for the reverse situation, *i.e.*, the reduction of an oxygenated cation to an ion of a lower unhydrolyzed oxidation state. The reaction studied in the present investigation was the reduction of Np(V) by Np(III), yielding Np(IV) quantitatively.

Two investigations have been made of the reduction of Np(V) by Fe(II).[2,7] The rate law for the reaction appeared to be given by the expression $d(NpO_2^+)/dt = k[NpO_2^+][Fe^{++}][H^+]$. A similar rate law has been indicated for the reduction of PuO_2^+ by Pu^{+3}.[6] The role of the hydrogen ion in these reactions is of particular interest. For this reason the present investigation has been carried out both in H_2O and D_2O solutions.

Experimental

The general aspects of the experimental techniques and preparation of reagents have been described in previous papers.[3,4] Two methods were employed in the preparation of the Np(III) solutions. The first method used was a reduction of the Np(V) stock solutions with hydrogen gas at a platinized platinum catalyst.

Considerable difficulty was experienced in obtaining consistent results with these solutions. More reproducible results were obtained if the Np(III) solutions were prepared by electrolytic reduction.

The instability of Np(III) with respect to air oxidation necessitated working under an inert atmosphere. Deaerated Np(V) solutions of the desired composition were transferred to five-cm. quartz absorption cells, modified by addition of an extra opening for the insertion of a gas bubbler assembly. Gas was kept flowing through the cell until temperature equilibrium was reached (*ca.* two hours) after which the Np(III) was transferred under nitrogen to the absorption cell and mixed. The course of the reaction was followed by spectrophotometric monitoring of the 7230 Å. absorption band of Np(IV). The temperature in the absorption cell compartment of the Cary spectrophotometer was maintained to ±0.1°.

Results and Discussion

Molecularity of the Reaction.—The molecularity of the reaction with respect to the metal and hydrogen ions was determined by experiments in which the concentrations of the species were varied in the reaction mixture. The reaction was found to be bimolecular with respect to the metal ions. Data for a typical experiment are summarized in Table I. The apparent rate constant, k', was calculated by the integrated equation for a bimolecular process. No correction for the back reaction is necessary since at equilibrium the concentrations of Np(III) and Np(V) are negligible. Data on the effect

TABLE I

THE RATE OF REACTION OF Np(III) WITH Np(V) AT 16.1 ± 0.1°

$\mu = 2.0$, $[H^+] = 0.31\ M$, Np(III) = Np(V) = $6.90 \times 10^{-4}\ M$

Time, min.	$D_{obs.}$ 7230 Å.	Apparent rate constant k', l. mole^{-1} min.$^{-1}$	Time, min.	$D_{obs.}$ 7230 Å.	Apparent rate constant k', l. mole^{-1} min.$^{-1}$
0.25	0.092	614.5	2.00	0.437	605.8
.50	.170	623.8	2.25	.466	607.9
.75	.233	619.7	2.50	.492	609.8
1.00	.282	603.0	2.75	.518	618.0
1.25	.331	610.0	3.00	.540	621.5
1.50	.371	609.0	∞	.960	
1.75	.405	604.7			
				Av.	612.3 ± 6.0

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. R. Huizenga and L. B. Magnusson, THIS JOURNAL, **73**, 3202 (1951).

(3) J. C. Hindman, J. C. Sullivan and D. Cohen, *ibid.*, **76**, 3278 (1954).

(4) J. C. Sullivan, D. Cohen and J. C. Hindman, *ibid.*, **79**, 4029 (1957).

(5) R. H. Betts, *Can. J. Chem.*, **33**, 1780 (1955).

(6) See R. E. Connick, Chapter 8, Vol. 14A, National Nuclear Energy Series, Div. IV, "The Actinide Elements," McGraw-Hill Book Co., New York, N. Y., 1949.

(7) L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, Paper 15.11, Vol. 14B, National Nuclear Energy Series, "The Transuranium Elements," McGraw-Hill Book Co., New York, N. Y., 1949.

of changing the metal ion concentrations are given in Table II. The data are consistent with the bimolecular dependence of the rate on the Np(III) and the Np(V) concentrations. Table III summarized the experiments at varying hydrogen ion concentration.

TABLE II

EFFECT OF METAL ION CONCENTRATION ON THE RATE OF THE Np(III)-Np(V) REACTION AT 16.1°

$\mu = 2.0$, $[H^+] = 0.31\ M$

Initial Np(III), moles/l. × 10^4	Initial Np(V), moles/l. × 10^4	Apparent rate constant k', l. mole^{-1} min.$^{-1}$
2.98	10.05	588
3.41	10.05	554
6.82	5.03	536
6.82	5.03	517
10.40	2.51	555
6.90	6.90	612
6.90	6.90	606
	Av.	567 ± 31

TABLE III

EFFECT OF $[H^+]$ ON THE RATE OF THE Np(III)-Np(V) REACTION

$t = 15.9°$, $\mu = 2.0$, $[Np(III)] = [Np(V)] \sim 6 \times 10^{-4}\ M$

$[H^+]$, moles l.$^{-1}$	Apparent rate constant k', l. mole^{-1} min.$^{-1}$	$k'/[H^+]$
0.109	226	2070
.108	209	1940
.260	509	1960
.275	572	2080
.523	980	1880
.523	1020	1950
1.019	1645	1610
1.018	1780	1750
1.91	3720	1930
1.91	3290	1720
	Mean	1870 ± 115

Analyses of the data by least squares yields a hydrogen order of $[H^+]^{1.05 \pm 0.02}$. The rate law for the forward reaction can therefore be written as

$$-\frac{\partial[NpO_2^+]}{\partial t} = k_1[Np^{+3}][NpO_2^+][H^+] \qquad (1)$$

The value of k_1 is computed from the observed bimolecular rate constants by the relation

$$k_1 = k'/[H^+] \qquad (2)$$

The k_1 value computed from the hydrogen ion data in Table III is 1870 ± 115 l.^{2} mole^{-2} min.$^{-1}$. This is in satisfactory agreement with the mean value of 1830 ± 180 l.^{2} mole^{-2} min.$^{-1}$ obtained from the metal ion order data in Table II.

The Effect of Deuterium on the Rate—As shown in Table IV, the rate is decreased slightly in the presence of deuterium.

The Effect of Temperature.—Least squares analysis of the data on the temperature coefficient of this reaction rate on H_2O and D_2O yields activation energies of 6.52 ± 0.53 and 5.62 ± 0.54 kcal., respectively (95% confidence level). The apparent activation energies are the lowest thus far found for any neptunium oxidation–reduction system.

Mechanism of the Reaction.—The direct dependence of the reaction rate on hydrogen ion concentration indicates that hydrolysis products of Np(III) are not involved. The general correspondence of the stoichiometry suggests that the fundamental mechanism is probably the same for the Np(III)–Np(V), Fe(II)–Np(V) and Pu(V)–Pu(III) reactions.

TABLE IV

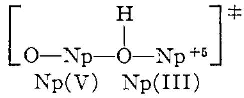
THE EFFECT OF DEUTERIUM AND TEMPERATURE ON THE RATE OF THE Np(III)-Np(V) REACTION

$\mu = 2.0$, $[H^+]_i = 0.25\ M$, $Np(III) = Np(V) \sim 6 \times 10^{-4}\ M$

Temp., °C.	k_1(H) (mean), l.^{2} mol^{-2} min.$^{-1}$	k_1(D)[a] (mean), l.^{2} mole^{-2} min.$^{-1}$	kH/kD
5.53	1190	1060	1.13
16.10	1870	1560	1.20
25.00	2590	2060	1.25

[a] A 95% deuterium content.

The role of the hydrogen ion is not clear. A reasonable assumption would appear to be that the hydrogen ion is involved in a pre-equilibrium reaction with the NpO_2^+ ion to give $NpOOH^{++}$. In view of the positive charge on the Np(III) ion it would not appear likely that the activated complex is bridged through hydrogen. The relatively slight effect of deuterium on the reaction is supporting evidence that the hydrogen is not directly involved in the reaction. The low activation energy for the reaction suggests that extensive rearrangements are unlikely in the formation of the activated complex. Two configurations that would be consistent with the data are



$$\left[O{-}Np{-}\overset{\overset{\displaystyle H}{|}}{O}{-}Np^{+5}\right]^{\ddagger}$$

A

and $[HO{-}Np{-}O{-}Np^{+5}]^{\ddagger}$

Np(V) Np(III)

B

For configuration B, one of the two possibilities, *i.e.*, an oxygen atom transfer mechanism, would appear unlikely since a single electron reaction step should be favored. There are three remaining possibilities: electron transfer across an oxygen or hydroxyl bridge and a hydroxyl atom transfer. If the mechanism is by electron transfer *via* an oxygen bridge there would not appear to be any reason for the involvement of hydrogen ions in the reaction. Indeed, the increase in net charge for the activated complex due to the hydrogen would be expected to decrease the probability for reaction. On the other hand, a mechanism which involves the formation of a hydroxyl bridged intermediate would provide an explanation for the appearance of hydrogen ion in the stoichiometry of the reaction. The data cannot distinguish between a process in which an electron transfer is considered to occur by a radiationless transition between the metal ions which are bridged by a hydroxyl ion and a process in which the electron transfer occurs by way of an intermediate state in which the hydroxyl bridge approaches the configuration of a hydroxyl atom. The small isotope effect could be attributed to the stretching of the O–H bond in the formation of the activated complex. "Solvent effects" have also been used to explain isotope effects of this order of magnitude.[8] The Np^{+4} (aq.) ion presumably is formed by further reaction of the dismutation products of the activated complex with hydrogen ions.

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[8] *Cf.* V. Gold and D. P. N. Satchell, *Quart. Rev.*, **9**, 51 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Polarographic Study of Mercuric Cyanide and the Stability of Cyanomercuriate Ions[1]

BY LEONARD NEWMAN, JOAO DE O. CABRAL AND DAVID N. HUME

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The reduction of mercury cyanide and the oxidation of mercury in hydrogen cyanide were shown to be polarographically irreversible in acid solutions, becoming reversible in basic solutions. In basic solutions the cyanide released by the reduction can complex mercuric cyanide at or around the surface of the drop. The species being reduced are $Hg(CN)_2$, $Hg(CN)_3^-$ and $Hg(CN)_4^{--}$. The logarithms of the over-all formation constants of these species are 33.9, 38.1 and 40.6, at an ionic strength of 2.0 and a temperature of 30°.

Introduction

The reduction of mercuric cyanide at the dropping mercury electrode was first extensively studied by Tomeš[2] who found in the range *p*H 6.0 to 9.5 a reversible wave corresponding to the over-all electrode reaction

$$Hg(CN)_2 + 2H^+ + 2e^- \longrightarrow Hg + 2HCN$$

In basic media the reaction became

$$Hg(CN)_2 + 2e^- \longrightarrow Hg + 2CN^-$$

The half-wave potentials in the *p*H range above 9.5 were observed to deviate from predicted values, and this was attributed to complexation of mercuric cyanide by cyanide ions liberated in the electrode reaction. Tomeš offered no experimental evidence for the formation of higher complexes, and the deviations were in the opposite direction from that expected to be caused by such an effect. It has been the purpose of the present investigation to study the polarographic behavior of mercuric cyanide over a much wider range of *p*H values and determine the nature and effect of possible complex formation.

Since the completion of this study,[1] Tanaka and Murayama[3] have reported an extensive study of the anodic wave of mercury in cyanide medium which corroborates our findings regarding the formation of higher cyanide complexes of mercury at the drop and leads to values for the formation constants which are in substantial agreement with those determined from our cathodic waves of mercuric cyanide. About the same time, Anderegg[4] published the results of a potentiometric determination of mercuric cyanide stability constants.

Theory

Tomeš derived for the equation of the wave, the expression

$$E_{de} = E_{1/2} + 0.030 \log \frac{i_d}{2} + 0.03 \log \frac{(i_d - i)}{i^2} \quad (1)$$

and pointed out that $E_{1/2}$ was not independent of concentration. In place of $E_{1/2}$ it is more convenient to use the concentration-independent potential on the wave, which we shall call E_f and which leads to

$$E_{de} = E_f + 0.030 \log \left(\frac{i_d - i}{i^2}\right) \quad (2)$$

for the equation of the wave. It is shown readily that

$$E_f = E' + 0.060 \log \frac{K_A + C^0_H + f_H + f_{CN^-}}{K_A} \quad (3)$$

in which

$$E' = E_0 + 0.030 \log \frac{d_1{}^2}{d_n K_2 f^2_{CN^-}} \quad (4)$$

where K_A is the ionization constant of hydrogen cyanide, $C^0_{H^+}$ is the concentration of hydrogen ion at the electrode surface, f_{H^+} and f_{CN^-} are the activity coefficients of hydrogen and cyanide ions, E_0 is the standard potential of the mercury–mercuric ion couple, d_1 and d_n are the diffusion coefficients of cyanide and mercuric cyanide, respectively, and K_2 the formation constant of mercuric cyanide. It is seen that E_{de} is equal to E_f when $(i_d - i)/i^2$ is equal to unity and that E_f is independent of mercuric cyanide concentration. It should be noted, however, that the relative position of E_f on the wave shifts with concentration. If all measurements are done at a fixed, high ionic strength, activity coefficients may be assumed to be constant. The equation of the wave predicts a plot of E_f *vs.* *p*H to be linear with a slope of 60 mv. per *p*H as long as $C^0_{H^+} f_{H^+} f_{CN^-} >> K_A$. For values of $C^0_{H^+} f_{H^+} f_{CN^-} << K_A$, E_f should be independent of *p*H.

Experimental

Reagents. Mercuric Cyanide.—C.P. Baker Analyzed was used without further purification. A 0.1 *M* stock solution was made. Airco Prepurified Nitrogen was further purified by successively scrubbing with chromous chloride, sodium hydroxide and water. For all other chemicals, analytical grade reagents were used.

Apparatus.—The polarographic cell consisted of a 100-ml. beaker fitted with a rubber stopper which was bored for nitrogen inlet and outlet tubes, the dropping mercury electrode (D.M.E.), a fritted-glass-disc salt bridge and an inlet for covering the solution with a blanket of nitrogen. The D.M.E. was constructed from marine barometer tubing with an adjustable leveling bulb to maintain a constant head of pressure on the capillary.

The capillary characteristics were determined using a 0.1 *M* potassium chloride solution in the cell with dropping

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[1] Taken in part from the Doctoral Dissertation of Leonard Newman, Massachusetts Institute of Technology, 1956.

[2] J. Tomeš, *Collection Czech. Chem. Commun.*, **9**, 81 (1937).

[3] N. Tanaka and T. Murayama, *Z. physik. Chem. N. F.*, **11**, 366 (1957).

[4] G. Anderegg, *Helv. Chim. Acta*, **40**, 1022 (1957).