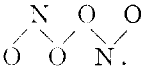
The observed bimolecular rate constants are greater by a factor of eight than extrapolated values for the bimolecular "Bodenstein" mechanism, for which the transition state is believed to be . It seems unlikely, but not entirely excluded, that this is due to an error in extrapolation. Possibly a simple extension of the Ashmore and Levitt NO_3 mechanism, including reaction 21, can account for the additional reaction path. However, the data now available indicate that this should increase the extrapolated rate only by a factor of two. Possibly there is some other as yet unrecognized reaction path. Possibly the discrepancy is in the present work. This question requires further work, but the present investigagation has fairly definitely established the occurrence of both unimolecular and bimolecular reaction paths.

Acknowledgments.—This work has been supported by the O.N.R. One of us has received fellowships from the Corning Glass Works Foundation and the General Education Board. An initial investigation of the shock pyrolysis of NO_2 was carried out in these Laboratories several years ago by Dr. W. R. Gilkerson. Our work has been developed on the basis of the foundation which he laid.

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[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

The Effect of Deuterium on the Kinetics of Reactions Involving Neptunium(IV), (V) and (VI) Ions[1]

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

RECEIVED DECEMBER 5, 1958

The rate of neptunium(IV)-neptunium(VI) reaction is markedly decreased in both sulfate and perchlorate solutions by the addition of deuterium. The ratio of the observed rate constants for perchlorate solutions at 25° is $k_H/k_D = 5.0$. The similarity of the effect in both sulfate and perchlorate solutions lends support to the previous suggestions that the mechanism is the same in both media. The disproportionation rate of neptunium(V) in sulfate solution is increased by deuterium. The interpretation of the isotope effect in terms of possible pre-equilibria and reaction intermediates is discussed.

Introduction

As a result of studies on the kinetics of the reactions involving Np(IV), Np(V) and Np(VI) in both perchlorate[2] and sulfate[3] media, it has been suggested that the mechanism of the reaction is governed by the tendency of the reacting ions to attain and maintain a configuration close to the O–M–O structure. With this basic assumption, strong arguments can be made against mechanisms which involve either oxygen or hydroxyl atom transfer. Either an electron transfer or a hydrogen atom transfer process would be possible mechanisms.

To shed further light on this problem we have undertaken an investigation of the reactions of the Np(IV), (V) and (VI) ions in deuterium solutions. A large isotope effect has been observed. The magnitude of the isotope effect is essentially the same in either perchlorate or sulfate media. This lends support to the suggestion that the mechanism of reaction is probably the same in the two media.[3]

Experimental

The preparation of stock solution of neptunium and the general experimental techniques have been described in previous publications.[2,3] The deuterio-sulfuric acid used in the present investigation was obtained through the courtesy of Dr. J. J. Katz of this Laboratory. The deuterioperchloric acid was prepared as previously described.[4]

Results

I. The Np(IV) + Np(VI) → 2Np(V) Reaction.—The order of the reaction with respect to each of the metal ions has been determined previously.[2,3] The reaction is bimolecular both in perchlorate and sulfate media. The rate constant, k_{obsd}, in the present work therefore was calculated by means of the integrated equation for a bimolecular reaction.

The Effect of Acid Concentrations.—Table I summarizes the data on the effect of acid concentration on the rate of the reaction. Least squares analysis yields a value for n in the equation

$$k_{obsd} = k[H^+]^n \qquad (1)$$

of -2.140 ± 0.022 (99% confidence level) for the hydrogen containing solutions and of -2.154 ± 0.022 (99% confidence level) for the 95% deuterium solutions. Within experimental error there is no significant effect of deuterium on the acid dependence of the reaction. The data in perchlorate solution may be analyzed in terms of more than a single reaction path. Least squares treatment of the data yields values of the rate constants for the equation

$$k_{obsd} = k_1[H^+]^{-2} + k_2[H^+]^{-3} \qquad (2)$$

in the hydrogen medium, $k_1 = 4.27 \times 10^{-2}$ mole liter^{-1} sec.$^{-1}$ and $k_2 = 5.04 \times 10^{-3}$ mole^2 liter^{-2} sec.$^{-1}$. In the deuterium solutions, $k_1 = 8.56 \times 10^{-3}$ mole liter^{-1} sec.$^{-1}$ and $k_2 = 1.02 \times 10^{-3}$ mole^2 liter^{-2} sec.$^{-1}$.

The Effect of Deuterium Concentration.—Examination of Table I shows that there is a significant effect of deuterium on the reaction rate. Table II illustrates this in more detail. A plot of the observed rate against the percentage of deute-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. C. Hindman, J. C. Sullivan and D. Cohen, THIS JOURNAL, **76**, 3278 (1954).

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

[4] J. C. Sullivan, D. Cohen and J. C. Hindman, *ibid.*, **79**, 3672 (1957).

rium in the solution was used to obtain the rate constant for a 100% deuterium solution. It is found that at 25° the ratio k_H/k_D is 5.0.

TABLE I

THE EFFECT OF HYDROGEN AND DEUTERIUM ION CONCENTRATIONS ON THE RATE OF THE Np(IV)-Np(VI) REACTIONS IN PERCHLORATE SOLUTION

$\mu = 2.2$, $t = 24.9°$

$[H^+]$, moles/l.	$[D^+]$,[a] moles/l.	[(Np(IV)], moles/l. $\times 10^3$	[Np(VI)], moles/l. $\times 10^3$	Obsd. rate constant, k l. mole^{-1} min.$^{-1}$
0.271		2.61	2.77	47.2
		2.61	2.77	46.3
		2.60	4.12	47.1
0.634		2.60	4.12	8.07
		2.60	4.12	7.87
1.24		2.60	4.12	1.84
		2.60	4.12	1.76
1.95		2.60	4.12	0.736
		2.60	4.12	0.693
	0.273	2.61	2.77	9.30
		2.61	2.77	10.1
		2.60	4.12	10.3
	0.500	2.60	4.12	2.53
		2.60	4.12	2.61
	0.996	2.60	4.06	0.574
		2.60	4.06	.530
	1.97	2.60	4.12	.138
		2.60	4.12	.145

[a] Total deuterium content 95%.

TABLE II

THE RATE OF THE Np(IV)-Np(VI) REACTION AS A FUNCTION OF DEUTERIUM CONCENTRATION

$\mu = 2.2$, $t = 24.9°$

Acid $[H^+, D^+]$, moles/l.	D content, %	Obsd. rate constant, k l. mole^{-1} min.$^{-1}$	k_{obsd}/k_H
0.273	95	9.90	0.211
.270	79.2	12.8	.273
.270	47.5	23.6	.502
.271	0	46.9 (av.)	1.00

Temperature Effect in Perchlorate Solution.—Table III gives the data on the effect of temperature on the rate. The ratio of k_H to k_D increases with decreasing temperature. This is reflected in the slightly higher activation energy for the reaction in D_2O solution. The least squares values of the energies of activation are 26.85 ± 0.27 kcal. for D_2O solutions and 25.32 ± 0.28 kcal. for H_2O solutions. The activation energy found in the present investigation for H_2O solution is in satisfactory agreement with that previously reported, 25.2 ± 1.6 kcal.[2]

TABLE III

THE EFFECT OF TEMPERATURE ON THE RATE OF THE Np(IV)-Np(VI) REACTION IN PERCHLORATE SOLUTION

$[H^+] = [D^+] = 0.271\ M$, $\mu = 2.2$, $[Np(IV)] = 2.60 \times 10^{-3}\ M$, $[Np(VI)] = 4.06 \times 10^{-3}\ M$

Temp., °C.	Obsd. rate constant, k_H l. mole^{-1} min.$^{-1}$	Obsd. rate[a] constant, k_D l. mole^{-1} min.$^{-1}$	k_H/k_D
5.0	2.08	0.370	5.65
14.9	10.1	1.92	5.26
24.9	46.9	9.90	4.74
35.1	174.9	40.4	4.33

[a] 95% total deuterium content.

The Isotope Effect in Sulfate Solution.—Figure 1 is a plot of the observed rate constant k_{obsd} for various initial concentrations of sulfuric and deuteriosulfuric acid. As shown in the figure the general shape of the curve resembles that determined in the hydrogen-containing media.[3] Multiplication of the rate constants for the deuteriosulfuric acid solutions by a factor of 4.6 gives a curve that lies close to that obtained in sulfuric acid. The magnitude of the isotope effect supports the previous suggestions that the reaction mechanism is the same as in perchlorate solution. The deviation of the curves for the two media at high sulfate concentrations may be a reflection of accumulating effects of dissociation and hydrolysis constant differences.

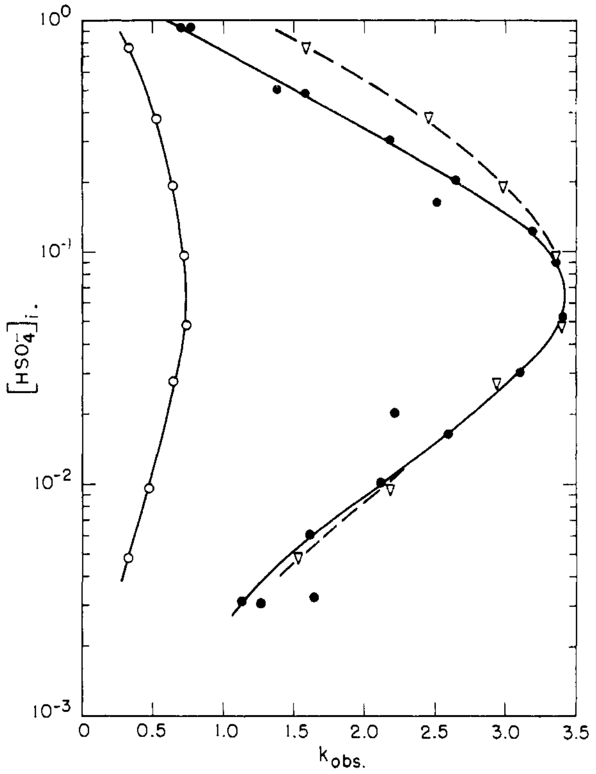

Fig. 1.—The effect of deuterium on the rate of the Np(IV)-Np(VI) reaction in sulfate solution; $t = 25°$, $\mu = 2.2$, $[H^+] = 2.2$: ○, rate observed in $D_2O-D_2SO_4$ solution (95% total D); ●, rate observed in $H_2O-H_2SO_4$ solution; △, rate observed in $D_2O-D_2SO_4$ solution × 4.6.

II. The 2Np(V) → Np(IV) + Np(VI) Reaction.—This reaction previously has been shown to have a second-power dependence on the concentration of Np(V).[3] The observed rate constant, $k_{obsd.}$, was therefore calculated in the same manner as for the Np(IV)-Np(VI) reaction. Table IV summarizes the rate data. For this reaction it is found that the rate is faster in deuterium solution. It is possible to express the results in an equation of the form previously used.[3] The resulting values of k'_5 and k'_6 are for deuteriosulfuric acid solution,

$$k_{obsd} = k'_5\,[HSO_4^-] + k'_6\,[HSO_4^-]^2 \qquad (3)$$

$k'_5 = 1.17 \times 10^{-2}$ liter^2 sec.$^{-1}$ and $k'_6 = 0.58 \times 10^{-2}$ mole^{-3} liter^3 sec.$^{-1}$. These compare with

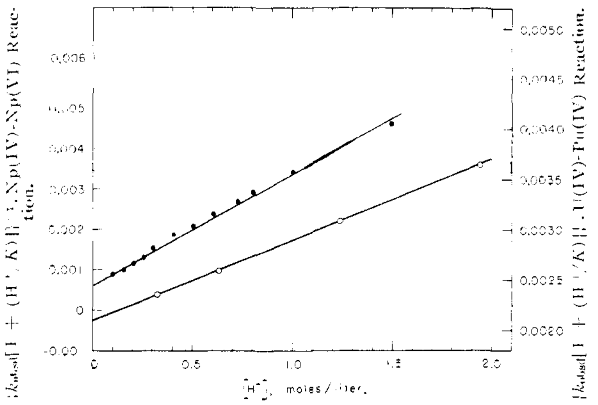

Fig. 2.—Plot of $\{k_{obsd.}[1 + (H^+/K)]\}^{-1}$ for Np(IV)–Np(VI) and U(IV)–Pu(VI) reactions: ●, U(IV)-Pu(VI) reaction; O, Np(IV)–Np(VI) reaction.

the values of $k'_5 = 0.43 \times 10^{-2}$ liter^2 sec.$^{-1}$ and $k'_6 = 0.23 \times 10^{-2}$ mole^{-3} liter^3 sec.$^{-1}$ found for sulfuric acid solution. The specific rate constants for the reaction are higher by a factor of 2.5 to 2.7 in deuterium solutions.

TABLE IV

RATE DATA FOR THE DISPROPORTIONATION REACTION IN D_2O SOLUTION

$[Np(V)]_1 = 7.50 \times 10^{-3}$ M, $t = 25°$, $\mu = 2.0$, total D = 95%, $[D^+] = 2.0$ M

Initial concn. $[D_2SO_4]$, moles l.$^{-1}$	Obsd. rate constant, k_D, l. mole^{-1} min.$^{-1}$	Obsd. rate constant, k_H, l. mole^{-1} min.$^{-1}$
0.500	0.31	0.15
	0.31	
1.00	1.21	0.38
	1.14	
2.00	3.43	1.00
	3.42	

Discussion

In a recent investigation of the kinetics of the U(IV)–Pu(VI) reaction, Newton[5] has postulated a mechanism involving an inhibiting back reaction favored by hydrogen ion. It was further suggested that this type of mechanism may be general and would include the Np(IV)–Np(VI) reaction. This suggestion is of considerable interest and we have re-examined the data on the neptunium system using the more extensive rate measurements reported in the present paper.

For the M(IV)–M(VI) reactions to be considered, a general mechanism involving consecutive steps can be written as

$$M^{+n} + MO_2^{++} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [x_1]^{\pm} + wH^+ \qquad (4)$$

$$[x_1]^{\pm} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [x_2]^{=} + pH^+ \qquad (5)$$

$$[x_2]^+ \xrightarrow{k_3} \text{products} \qquad (6)$$

for which the rate equation is

$$-\frac{\partial[M_{IV}]}{\partial t} = k_{obsd}[M_{IV}][MO_2H] = \frac{k_1[M^{+n}][MO_2^{++}]}{1 + \frac{k_{-1}}{k_2}[H^+]^w + \frac{k_{-1}k_{-2}}{k_2k_3}[H^+]^{w+p}} \qquad (7)$$

where $[M^+]^n$ is the concentration of the reacting species of oxidation state +4 and $[M_{IV}]$ is the total metal ion concentration of this oxidation state. The final form of the rate equation will depend on the number of transition states and on the M_{IV} species assumed to be involved in the initial reaction. Newton took cognizance of the two simplest possibilities, *i.e.*, U^{4+} and two reaction intermediates and $U(OH)^{3+}$ with the concomitant single transition state,[6] in his examination of the U–Pu system. We have tested our data with similar assumptions. For the case where $NpOH^{+3}$ is considered to be the initial reaction species, the rate equation 7 is put in the form

$$\left\{k_{obsd}\left(1 + \frac{H^+}{K}\right)\right\}^{-1} = k_1^{-1} + k_1^{-1}k_2^{-1}k_{-1}[H^+]^w + k_1^{-1}k_2^{-1}k_3^{-1}k_{-1}k_{-2}[H^+]^{w+p} \qquad (8)$$

where K is the hydrolysis constant of the +4 ion.

$$M^{+4}(aq.) \overset{K}{\rightleftarrows} MOH^{+3}(aq.) + H^+ \qquad (9)$$

A plot of the left side of equation 8 is made against hydrogen ion. The intercept will be $1/k_1$ and the slope will depend on the number of transition states and the number of hydrogen ions evolved (*i.e.*, the values of w, p, etc.). For the U^{+4}–PuO_2^{+2} data, the expected straight line with a positive intercept is found, confirming that the proposed mechanism is consistent with the data (see Fig. 2). Similar treatment of the neptunium data[7] also yields a reasonable straight line. However, in this case the intercept is negative, indicating that the proposed mechanism does not hold for this reaction.

A similar plot of our data for the case where Np^{+4} is considered as the initial reactant gives a curved line with the intercept again negative or so close to zero that we cannot deduce support for the mechanism. It might be pointed out that if the intercept is zero or close to zero (large $1/k_1$), then the equations for the successive reactions reduce to the same form as for parallel reactions. In other words, if k_1 is sufficiently large it becomes difficult to distinguish between parallel and consecutive reactions.

Turning to the deuterium isotope effect on the rates, one can make the following comments. Since the empirically observed rate laws for both the Np(IV)–Np(VI) and the Np(V) disproportionation reaction in deuterium solution can be expressed in the same form as in hydrogen solution, the mechanism is probably the same in both media. The problem is then to consider the probable effect of deuterium on the different stages of the reactions.

The observed inverse hydrogen ion dependence of the reproportionation reaction may be formally

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(5) T. W. Newton, *J. Phys. Chem.*, **62**, 916 (1958).

(6) S. W. Rabideau, L. B. Asprey, T. K. Keenan and T. W. Newton, paper presented before the 2nd International Meeting on the Peaceful Uses of Atomic Energy, Geneva, September, 1958.

(7) A value of k_H for Np^{+4} of 0.039 has been estimated from the constants for uranium(IV) and plutonium(IV).[5] Since the interpretation of the isotope effect on the neptunium reaction required a knowledge of K_H in both H_2O and D_2O, the constant has been determined in both media by a combination of spectrophotometric and pH measurements. Surprisingly, the behavior of neptunium(IV) appears to be markedly different from both uranium and plutonium. In H_2O, K_H is found to be $5 \pm 0.3 \times 10^{-3}$ and in D_2O to be $3.2 \pm 0.5 \times 10^{-3}$ ($\mu = 2.00$, ClO_4^-). Further reaction results in polymerization. Details of these experiments will be given in a subsequent publication.

depicted by a number of kinetically indistinguishable postulates. The assumption previously made of a rapid and reversible hydrolytic pre-equilibrium is not overly attractive in the light of the equilibrium experiments. Although it is possible to formulate an entity such as $Np(OH)_2^{++}$ and attribute the observed isotope effect to the hydrolytic equilibrium, it is equally plausible to assume that if hydrogen is split off in the activated complex a deuterium effect of similar magnitude would be obtained. It is not readily apparent that the isotope effect can distinguish between these two possibilities.

In contrast to the Np(IV)-Np(VI) reaction, the rate of the Np(V) disproportionation is increased by D_2O. It has been suggested that for the Np(V) reaction, as well as for the kinetically similar U(V) and Pu(V) disproportionation, the first step in a reasonable mechanism would be an equilibrium

$$MO_2^+ + H^+ \overset{K}{\rightleftarrows} MO_2H^{+2} \qquad (10)$$

This would be followed by one or more steps

$$MO_2^+ + MO_2H^{++} \xrightarrow{k_2} \text{products} \qquad (11)$$

$$MO_2H^{++} + MO_2H^{++} \xrightarrow{k_3} \text{products} \qquad (12)$$

Since the species MO_2H^{++} would be a strong acid, no isotope effect would be expected for the pre-equilibrium. Logically then one would interpret the observed isotope effect as arising from a tighter bonding of hydrogen in the activated complex than in reactant species such as MO_2H^{+2} or MO_2HSO_4. It does not appear feasible to define further the condition of the hydrogen in the activated complex or draw any conclusion as to detailed mechanism of a hydrogen atom transfer from the isotope data.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

Kinetics of the Exchange of Deuterium between Diborane and Tetraborane[1]

BY J. E. TODD AND W. S. KOSKI

RECEIVED NOVEMBER 1, 1958

The kinetics of the exchange of deuterium between diborane and tetraborane have been found to be complex. The results indicate that the exchange proceeds by two different paths—one involves two hydrogen positions in tetraborane and the other involves the remaining eight or all ten hydrogen positions. The major reaction is interpreted in terms of a rate-determining reaction of BD_3 from diborane with B_4H_{10} while the minor reaction is envisaged as a rate-determining activation of two sites in tetraborane followed by rapid deuterium exchange with B_2D_6. Boron atoms also exchange in this system although detailed kinetics studies have not been made.

Introduction

The equilibria which are the bases for understanding interconversion reactions of the boron hydrides have been investigated by two types of chemical or quasi-chemical investigations. The purely chemical method consists of studies of product formation whereas the quasi-chemical method involves kinetic studies of isotope exchange. In either case the equilibria involved are deduced by proposing mechanisms compatible with the observed change of the system.

The advantage of directness inherent in the chemical method is frequently offset by complications introduced by product interference so that, in many systems, only initial-rate studies are feasible. Frequently, isotope exchange experiments may be performed under such conditions that any chemical change is either negligible or corrigible. Moreover, the elementary steps contributing to the mechanisms of both types of reactions are often the same so that the equilibria involved may be elucidated more directly by the isotope exchange method. An example of this is the B_2H_6–BH_3 equilibrium which has been postulated in both chemical and isotope exchange reactions involving diborane.[2,3]

In less ideal situations the exchange results may yield information about the lability of atoms of the exchanging isotope which is chemically significant. The B_2D_6–B_4H_{10} exchange reaction, reported in the following paragraphs, appears to fall in this category as well as the former. In addition, it appears to be the first gas-phase exchange reaction in which atoms of the same element in one compound exchange at two measurably different rates.

Experimental

A. **Preparation of Materials.**—Diborane (B_2H_6, B_2D_6 and $B^{10}{}_2H_6$) was prepared by treating lithium aluminum hydride or deuteride with boron trifluoride in ether. The details of the preparation and purification have been described previously.[4] Deuterium resulting from the thermal decomposition of the diborane ranged from 95-98% pure, and the diluent is hydrogen.

Tetraborane was prepared by the B_5H_{11}–H_2 reaction. The apparatus and procedure for this preparation are described by Burg and Stone.[5] The tetraborane was purified by distillation from a trap at about −78° (Dry Ice-acetone) to one at −119° (melting ethyl bromide) with continuous pumping to remove diborane. Tetraborane purified in this manner was free from impurities as indicated by its infrared spectrum. The purification procedures used for both B_4H_{10} and B_2D_6 were spot-checked by vapor-phase chromatography and found to be free of detectable amounts of impurities.

B. **Isotopic Analysis.**—Two methods were used in analyzing the boron hydrides for their specific deuterium content. (The term specific deuterium content is herein defined as the total number of deuterium atoms in a sample of compound divided by the total number of atoms of hydrogen and deuterium in the sample.) In the more fundamental

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600)-1526. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) R. P. Clarke and R. N. Pease, THIS JOURNAL, **73**, 2132 (1951).

(3) P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).

(4) W. S. Koski, P. C. Maybury and J. J. Kaufman, *Anal. Chem.*, **26**, 1992 (1954).

(5) A. B. Burg and F. G. A. Stone, THIS JOURNAL, **75**, 228 (1953).