[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Isotopic Exchange Reactions of Neptunium Ions in Solution. V. The Np(V)-Np(VI) Exchange in D_2O[1]

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From studies in mixed electrolyte systems the conclusion is drawn that the perchlorate ion does not participate in the Np(V)-Np(VI) exchange reaction. The data do indicate that there are two possible reaction paths, one acid dependent and the other acid independent. The substitution of deuterium for hydrogen decreases the rate of the acid independent path, indicating that hydrogen atoms are involved in the mechanism for the exchange process. The hydrogen ion dependent path probably involves specific hydronium ion catalysis.

Previous communications[2-4] have reported the results of investigations of various factors affecting the rate of the Np(V)–Np(VI) isotopic exchange reaction. It has been demonstrated that the rate of the reaction is negligibly affected by the variation of the macroscopic dielectric constant in perchlorate media containing ethylene glycol or sucrose.[4] Although these results demonstrate the inapplicability of the model for exchange by electron tunneling, for the present system, in the form presented by Marcus, Zwolinski and Eyring,[5,6] they do not conclusively show that the exchange proceeds by a mechanism other than direct electron transfer.

It has been suggested for the present reaction and for similar reactions[7,8] that the exchange in perchlorate solution proceeds by a mechanism involving hydrogen atom transfer. In principle this can be demonstrated by examination of the isotope effect, *e.g.*, by carrying out the reaction in a D_2O solution. Hudis and Dodson[9] have used this technique to gain support for the view that a hydrogen atom transfer mechanism is probable for the Fe(II)–Fe(III) system. Similar measurements are reported here for the Np(V)–Np(VI) system.

In addition, evidence was sought that would indicate whether or not there was a possibility that perchlorate ion might be involved as a bridging group in the activated complex. In principle, if perchlorate enters the complex one would expect to find a dependence of the rate of the reaction with perchlorate ion concentration at constant ionic strength. Anion effects of this nature were reported by Olson and Simonson[10] for a number of reactions in dilute solution. On the other hand, in perchlorate solutions at higher ionic strengths, Silverman and Dodson[11] found that the rate of the Fe(II)–Fe(III) exchange was unaffected by the anion concentration as long as the ionic strength was unchanged. Recently, Sutcliffe and Weber,[12] working at comparable ionic strengths, obtained results that led them to postulate that the perchlorate ion was involved in the oxidation–reduction reaction between Ce(III) and Co(III).

Experimental

The salt solutions were prepared as follows; sodium perchlorate solutions were made by dissolution of the carbonate in perchloric acid. Magnesium and lanthanum perchlorate solutions were prepared by addition of an excess of the respective oxides to perchloric acid. The filtered solutions had a final *p*H of approximately 5. The authors wish to thank Miss I. Fox of the Analytical Group for performing the analyses of these solutions.

Deuteroperchloric acid was prepared in the following manner: first, deuterosulfuric acid was prepared by dissolution of anhydrous SO_3 in D_2O (99.25%). The sulfate was removed from the approximately 13 *M* D_2SO_4 by addition of barium perchlorate and centrifugation of the precipitated barium sulfate. The deuteroperchloric acid (99 ± 0.3% deuterium content) was purified by vacuum distillation. Only the center fraction of the constant boiling mixture was used for preparation of the dilutions.

Stock solutions of Np(V) and Np(VI) were prepared in $DClO_4$. The exchange reactions were carried out in solutions containing a maximum of 99% deuterium. The authors are grateful to Dr. H. Crespi for the determination of the isotopic content of the deuterated solvent solutions.

The majority of the experiments were performed at a temperature of 5.00°, employing the experimental techniques and procedures previously described.[2-4] Solvent extraction separation of the Np(VI) from Np(V) was done using theonyltrifluoroacetone in toluene for the extractant in 0.1 *M* acid and tributyl phosphate for the extractant at higher acid concentrations.

Results and Discussion

The exchange reaction previously has been found to be bimolecular.[2,3] The rate of the exchange may be expressed by the equation

$$R = k[\mathrm{Np(V)}]\,[\mathrm{Np(VI)}] \qquad (1)$$

The specific rate constant, *k*, is determined from the exponential rate law for a radioactive exchange written as

$$t = \frac{\ln(1 - F)}{([\mathrm{Np(V)}] + [\mathrm{Np(VI)}])k} \qquad (2)$$

where *F* is the fraction exchanged at time, *t*. Details of the method of treatment of the data are given in an earlier communication.[2]

The Influence of Ionic Strength and Hydrogen Ion Concentration.—The effect of ionic strength is depicted graphically in Fig. 1. Table I shows the effect of varying the hydrogen ion at constant

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

[2] D. Cohen, J. C. Sullivan and J. C. Hindman, THIS JOURNAL, **76**, 352 (1954).

[3] D. Cohen, J. C. Sullivan and J. C. Hindman, *ibid.*, **77**, 4964 (1955).

[4] D. Cohen, J. C. Sullivan, E. S. Amis and J. C. Hindman *ibid.*, **78**, 1543 (1956).

[5] R. J. Marcus, B. J. Zwolinski and H. Eyring, *J. Phys. Chem.*, **53**, 432 (1954).

[6] B. J. Zwolinski, R. J. Marcus and H. Eyring, *Chem. Revs.*, **55**, 157 (1955).

[7] R. W. Dodson, *J. Phys. Chem.*, **56**, 852 (1952); R. W. Dodson and N. Davidson, *ibid.*, **56**, 866 (1952), remarks in discussion at 1952 A.C.S. Symposium at Notre Dame.

[8] J. Hudis and A. C. Wahl, THIS JOURNAL, **75**, 4153 (1953).

[9] J. Hudis and R. W. Dodson, *ibid.*, **78**, 911 (1956).

[10] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

[11] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

[12] L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, **52**, 1225 (1956).

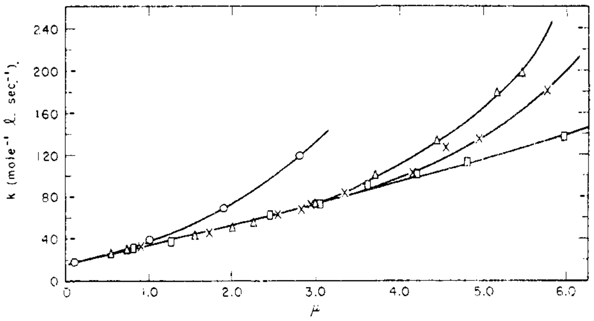


Fig. 1.—The effect of ionic strength and hydrogen ion concentration on the Np(V)–Np(VI) exchange. [Np(V)] = [Np(VI)] ≅ 2 × $10^{-5}M$; t, 5.00°: ○, [H$^+$]; [H$^+$] 0.1 M and △, $NaClO_4$, × $Mg(ClO_4)_2$, □ $La[ClO_4]_3$.

ionic strength. The following conclusions may be drawn from these data: first, the invariance of the rate at constant ionic strength in the sodium, magnesium and lanthanum perchlorate solutions, up to $\mu = 3$, indicates that the perchlorate ion participates neither in an equilibrium prior to the rate-determining step nor in the activated complex. In this respect the results are similar to those observed for the Fe(II)–Fe(III) system by Silverman and Dodson.[11] Second, the data in Fig. 1 suggest that an alternate exchange path involving hydrogen ion becomes increasingly important at high acidities. In an earlier communication observations at lower temperatures also suggested this possibility.[3] The results shown in Table I strongly support this hypothesis. The observed rates can be reproduced by a rate law of the form

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

TABLE I

THE EFFECT OF HYDROGEN ION CONCENTRATION ON THE EXCHANGE RATE AT $\mu = 3.0$, $t = 4.5°$

H$^+$ moles/l.)	k_{obsd} (l. mole^{-1} sec.$^{-1}$)	k_{calcd} (l. mole^{-1} sec.$^{-1}$)
0.1	75	75
1.0	86	88.5
1.55	90	96.5
2.17	109	106
3.00	118	118.5

where k_1 is the specific rate constant for the acid independent path and k_2 the specific rate constant for the acid dependent path. At 4.5°, $k_1 = 73.5$ and $k_2 = 15$. From the earlier data[3] at 0° we would estimate $k_1 = 50$ and $k_2 = 10$. Calculation yields a value of 12 ± 5 (95% confidence level) for the activation energy of the acid independent path and 15 ± 7 kcal. for the acid dependent path. There is the implicit assumption in these calculations that the ionic strength data given in Fig. 1 can be interpreted to mean that the activity coefficients remain essentially constant at ionic strengths up to 3.0 M with changes in the medium composition.

The Effect of Deuterium Concentration.—Table II summarizes the data on the effect of deuterium on the rate of the reaction under different conditions. Table III shows the effect of varying the deuterium content for the 0.1 M acid solutions, where the effect of replacing [H$^+$] by [D$^+$] is maximal. The uncertainties given are for the 95% confidence level. The fact that the rate of the exchange is slower by a factor of 1.4 in the 0.1 M acid solutions in the presence of deuterium we interpret as evidence for the participation of hydrogen in the exchange process for the acid independent reaction path. Various suggestions for hydrogen transfer processes involving participation of the solvent have been made.[7,8,13] All involve some kind of group transfer. The isotope factor observed for the present case is minimal for a process involving transfer of hydrogen atoms and corresponds to the situation where the bonding in the activated complex is as strong as in the reactants or to the case where a new bond is formed as the old bond is broken.[14] This suggests that we might visualize the electron transfer process through a water bridge as one which does not involve group transfer but only a stretching of bonds. One possible representation of such a process is depicted schematically as

TABLE II

SUMMARY OF RELATIVE RATES OF REACTION AND ENERGIES OF ACTIVATION FOR THE EXCHANGE IN H_2O AND D_2O SOLUTIONS

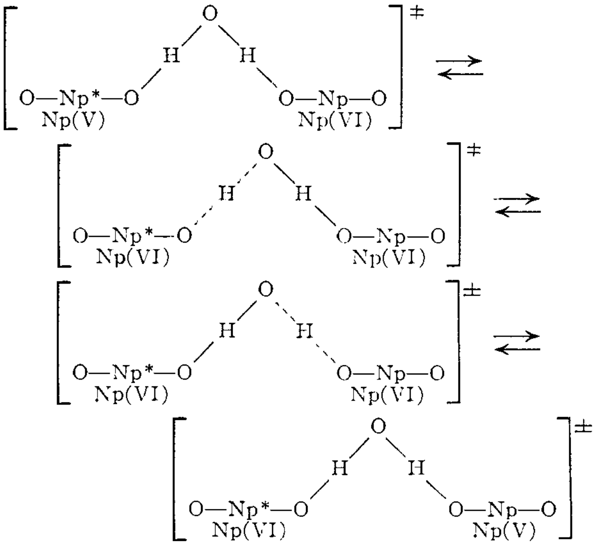
$t = 5°$, [Np(V)] = [Np(VI)] = 2 × 10^{-5} M

H$^+$ (mole/l.) (μ)	$k_{\text{H}^+}/k_{\text{D}^+}$	E_{expt} ($HClO_4$) (kcal./mole)	E_{expt} ($DClO_4$)[a] (kcal./mole)
0.1	1.4 ± 0.1	11.6 ± 0.8	12.1 ± 1.6
1.0	1.3 ± .1	10.6 ± .8	11.6 ± 1.0
3.0	1.2 ± .1	10.6 ± .8	

[a] 99 ± 0.7% deuterium content.

$$\text{Np}^*\text{O}_2^+ + \text{NpO}_2^{++} + \text{H}_2\text{O} \rightleftarrows [\text{X}^{+3}]^\ddagger \longrightarrow \text{NpO}_2^+ + \text{Np}^*\text{O}_2^{++} + \text{H}_2\text{O} \qquad (4)$$

where the electron transfer could be considered as involving the internal rearrangements in the activated complex



The dotted lines indicate stretching of bonds to conform to the transfer of an electron to a proton to approach the configuration of a hydrogen atom.

In their discussion of the interpretation of the deuterium effect on the Fe(II)–Fe(III) exchange,

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[13] W. L. Reynolds and R. W. Lumry, *J. Chem. Phys.*, **23**, 2460 (1955).

[14] K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

TABLE III

RATE OF EXCHANGE AS A FUNCTION OF VOLUME % DEUTERIUM

$[Np(V)] = [Np(VI)] = 2 \times 10^{-5}\ M$, $t = 5.0°$, $\mu = 0.1$, $[H^+] = 0.1\ M$

Vol. % D	k_{obsd}	Vol. % D	k_{obsd}
0	18.3 ± 1.2	50	15.5 ± 1.2
5	16.0	75	14.7
10	16.2	99	13.5

Hudis and Dodson[9] pointed out that the viscosity difference between D_2O and H_2O could lead to a collision frequency difference of about 20%. However, for reactions involving activation energies of the order of magnitude under consideration diffusion cannot be the rate-determining step, hence viscosity differences will be of little importance.[15] This view is supported in the present case by the experimental results in mixed solvent systems.[4] In these systems, despite much larger viscosity differences the rate was not affected.

The decrease in the k_{H^+} to k_{D^+} ratio with increasing acid concentration indicates a difference in the isotope effect between the acid independent and acid dependent reaction paths. The rate of the reaction for the acid dependent path appears to be more rapid in D_2O solution ($k_{D^+}/k_{H^+} \sim 1.1$). This result suggests that this reaction path involves specific hydronium ion catalysis.[14,16] A reasonable mechanism would involve the two step process

$$Np^*O_2^+ + H^+ \rightleftharpoons Np^*O_2H^{++} \qquad (5)$$

and

$$NpO_2^{++} + Np^*O_2H^{++} \rightleftharpoons [X^{+4}]^{\ddagger} \longrightarrow Np^*O_2^{++} + NpO_2H^{++} \qquad (6)$$

The small isotope effect could be explained as follows: first, the rate in D_2O would be enhanced by the probable shift of the pre-equilibrium (5) in favor of the acid, $Np^*O_2D^{++}$. However, since the ions, NpO_2H^{++} and NpO_2D^{++}, would be strong acids the isotope effect would be minimal.[14] In addition, it is possible that the subsequent reaction 6 has a normal isotope effect, thus decreasing the net isotope effect. This would be true if the transition state were $[O–Np–O–H–O–Np–O^{4+}]^{\ddagger}$ and the exchange process involved the transfer of a hydrogen atom.

Virtues of the mechanism as written are: (1) the transition state is symmetrical. (2) The formation of the transition state would involve the minimum of rearrangement of configuration for the reacting ions. (3) The products of the reaction are the same as the reactants. It should also be pointed out that the normal isotope effect could be small for the mechanism as written since a simultaneous making and breaking of bonds could occur. The net isotope effect would require that the normal isotope effect be small if the isotope effect on the pre-equilibrium (5) is minimal.

A different interpretation has been advanced by Duke and Pinkerton[17] to explain the isotope effect on the rate of the U(V) disproportionation, a reaction similar to that under discussion. A k_{D^+}/k_{H^+} ratio of 1.7 was found. They attribute the enhanced rate in D_2O to a shift in the equilibrium

$$UO_2^+ + H^+ \rightleftharpoons UO_2H^{++} \qquad (5a)$$

They consider, however, that the transfer of a proton is unlikely and that the reaction more probably involves a hydroxyl atom transfer

$$O–U–OH^{++} + O–U–O^+ \rightleftharpoons [X^{+3}]^{\ddagger} \longrightarrow O–U^{++} + H–O–U–O_2^+ \qquad (7)$$

If we consider the possibility of hydroxyl atom transfer for the present reaction we have

$$O–Np^*–OH^{++} + O–Np–O^{++} \rightleftharpoons [X^{+4}]^{+} \longrightarrow O–Np^*–OH^{+3} + O–Np–O^+ \qquad (8)$$

Examination of reaction 8 reveals that OH cannot be transferred in the exchange process. Basically the reaction would have to be considered as an electron transfer through a bridging hydroxyl ion. Little or no isotope effect might be expected in this step. To have a OH transfer in the present case we would have to assume the formation of the less probable species of Np(VI), $O–Np–OH^{+3}$, in the pre-equilibrium step and the reaction

$$O–Np–O–H^{+3} + O–Np^*–O^+ \rightleftharpoons [X^{+4}]^{\ddagger} \rightleftharpoons O–Np^{+3} + H–O–Np^*–O_2^+ \qquad (9)$$

This mechanism would involve the breaking of a Np–O bond. In view of the great stability of the O–Np–O structure this is considered a highly unlikely process.

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(15) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 400–401.

(16) R. P. Bell, "Acid–Base Catalysis," Oxford Press, New York, N. Y., 1941, p. 145.

(17) F. R. Duke and R. C. Pinkerton, THIS JOURNAL, **73**, 2361 (1951).