$N(R_2)_0$ for various values of y and N_0 are tabulated in Table V. $N(R_2)/N(R_2)_0$ is not strongly dependent on N_0 as can be seen from Table V. However, in order to calculate the variation in the actual R_2 yield, a spur size distribution is needed, along with the amount of R_2 produced in a spur of a given size. This information is given by Samuels and Magee to a reasonable approximation. $G_{R_2}/G°_{R_2}$, the ratio of the observed R_2 yield to the R_2 yield at zero concentration of the solute, is given in the last column of Table V. This model predicts what is found experimentally, that the $G_{R_2}/G°_{R_2}$ is dependent mainly on the concentration of solute and independent of the nature of R_2. Actually, the values would be different for H_2 and H_2O_2 since the number of molecules produced per spur is different in each case. However, in view of the small dependence on N_0, this effect is neglected.

TABLE V

CALCULATED VALUES OF $N(R_2)/N(R_2)_0$

y	N_0 2	4	6	10	20	$G_{R_2}/G^0_{R_2}$
10^{-4}	0.9604	0.9568	0.9534	0.9467	0.9339	0.955
10^{-3}	.8822	.8720	.8617	.8412	.8093	.864
10^{-2}	.6845	.6571	.6356	.5976	.5372	.642
10^{-1}	.3258	.3040	.2794	.2415	.1872	.288
2×10^{-1}	.2227	.2080	.1873	.1558	.1156	.192

In order to compare these kinetics with the experimental results, it is necessary to fix $B\tau'$. If $B\tau'$ is taken as 8×10^{-2} for NO_2^- solutions, the curve in Fig. 1 is obtained.

The agreement of the curve with the experimental data is quite good considering the approximations that were made. At high solute concentrations, most of the radicals do react with the solute, and the effect of the approximations on G_{R_2} is small. However the assumption that N does not vary as radicals combine makes $G°_{R_2}$ too large. Hence the calculated $G_{R_2}/G°_{R_2}$ should be too small.

At low solute concentration, the R_2 yield is still high, and both G_{R_2} and $G°_{R_2}$ will be affected to about the same degree by this assumption. However, the assumption that combination of radicals does not affect the distribution will overemphasize the amount of combinations in the early stages and make the calculated G_{R_2} too large.

It remains to determine whether the magnitude found for the parameter $B\tau'$ is reasonable. The diffusion coefficient may be found in terms of the number of jumps a radical makes per second, n, and the mean square root path length of a jump λ.

$$D = 1/6n\lambda^2$$

From equation 7

$$D = \pi(\bar{r}_0')^2/16\tau'$$

If reaction occurs on every encounter in the solution, B will be given by the product of the number of jumps a radical makes per sec. and the amount of new "reaction volume" the radical sees per jump. The latter quantity will be given by the product of the cross section for reaction, σ, and the mean free path, l. Hence

$$B = n\sigma l$$

Combining the above quantities and equating l and λ as a first approximation

$$B_{\tau}' = \frac{3\pi\sigma(\bar{r}_0')^2}{8l} \times \frac{N}{1000}$$

where N is Avogadro's number, and $N/1000$ is included to convert the constant to liters per mole per second. If σ is taken as $4\pi \times 10^{-6}$ cm.², $\bar{r}_0'$ as 6×10^{-8} cm. and l as 10^{-8} cm., then $B\tau' \cong 0.3$.

Values of $B\tau'$ for the various solutions in Fig. 1 are found by multiplying the normalization constant of the solute by 8×10^{-2}, the value of $B\tau'$ for NO_2^- solutions. They range from 6×10^{-4} to 0.74 and thus are all of the order of magnitude expected from a radical diffusion model.

Acknowledgment.—The author wishes to thank Dr. A. O. Allen for helpful discussions and criticism of this work.

UPTON, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Isotopic Exchange Reactions of Neptunium Ions in Solution. III. The Effect of Chloride and Nitrate Ions on the Rate of the Np(V)–Np(VI) Exchange[1]

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

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Possible catalytic effects of nitrate and chloride ions on the rate of the isotopic exchange reactions between Np(V) and Np(VI) have been investigated. Nitrate ion has little influence on the exchange rate. A marked catalysis is found in chloride solution. The results have been analyzed in terms of the formation of the complexes NpO_2Cl^+ and NpO_2Cl_2. Data are given on the energetics of the various exchange paths and for the formation of the complex species. Mechanisms for the exchange reaction are discussed.

A number of anionic complexing agents have been found to markedly affect the rate of isotopic exchange reactions between simple cations.[2] Determination of the exact role of the anion is of considerable interest. In certain cases where the ligand on the complex exchanges only slowly, it has been possible to demonstrate that a bridged activated complex is formed and that the ligand is transferred in the exchange process.[3-5] Net transfer of the ligand is not, however, a necessary feature of the electron transfer process.[5]

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] See, for example, J. Hudis and A. C. Wahl, THIS JOURNAL, **75**, 4153 (1953), and the systems cited therein.

[3] H. Taube and E. L. King, *ibid.*, **76**, 4053 (1954).

[4] H. Taube, H. Meyers and R. L. Rich, *ibid.*, **75**, 4118 (1953).

[5] H. Taube and H. Meyers, *ibid.*, **76**, 2103 (1954).

For the large number of cation complexes with readily exchangeable ligands indirect means are necessarily employed in deducing probable mechanism for the electron transfer reaction. In many cases arguments as to probable mechanisms have been based on the observed energetics of the reactions. Hudis and Wahl[2] have suggested that the relatively slight effect of the anions on the heat and entropy of the Fe(II)–Fe(III) exchange is due to the reaction proceeding in all cases by a hydrogen atom transfer mechanism.

Direct electron transfer by the penetration of a potential barrier has been proposed by Libby,[6] by Marcus, Zwolinski and Eyring[7] and by Weiss.[8] In the hypothesis as developed by Marcus, Zwolinski and Eyring, the free energy of activation is determined essentially by three terms, a probability factor for the electronic transmission through the barrier, a repulsion term and a rearrangement term (Franck-Condon). In this model, the ligand is considered to affect primarily the shape and height of the potential barrier. The negative entropies of activation are considered to represent a low probability for the electron penetration of the potential barrier. These authors consider that the Fe(II)–Fe(III) exchanges proceed by this mechanism.

In an earlier communication,[9] it was pointed out that due to the structure and symmetry of the ions, Franck-Condon restrictions on the exchange should be minimal for NpO_2^+ and NpO_2^{++}. Nevertheless, the heat and entropy of activation for the exchange reaction obtained were very similar to those found for the Fe(II)–Fe(III) exchange. Therefore, to provide a broader experimental basis for discussion of the probable mechanisms of the exchange reactions, experiments were undertaken in chloride and nitrate media. Additional data have also been obtained on the effect of hydrogen ion concentration and ionic strength on the rate of the exchange reaction.

Experimental

The experimental procedures have been described fully in a previous communication.[9] The hydrochloric and nitric acids used were triple distilled from reagent grade chemicals and standardized against sodium hydroxide. All concentrations are given in units of moles per liter.

Treatment of the Data

Since we were dealing with small differences in measured rates it was considered desirable to develop a method for treating the experimental data which would obviate the necessity for the subjective step of drawing a "best straight line" through the given experimental points and then graphically correcting for the zero-time exchange. Accordingly the following procedure was used. The exponential rate law for radioactive exchange is written in the form

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

where F is the fraction exchanged defined as the specific activity in Np(VI) at time t compared to the specific activity in the Np(VI) at complete exchange. k is the specific rate constant since

$$R = k[\mathrm{Np(V)}][\mathrm{Np(VI)}] \qquad (2)$$

The apparent zero-time exchange can be formally compensated for by addition of a pseudo time, t_0, to the left-hand side of equation 1 which becomes

$$t + t_0 = \frac{\ln(1 - F)}{([\mathrm{Np(V)}] + [\mathrm{Np(VI)}])k} \qquad (3)$$

The apparent zero-time exchange is considered to be constant for a given experiment. A value of t_0 determined by the method of least squares is substituted back into equation 3 and a value of k computed for each run of a given experiment. For each experiment the fraction exchanged was measured for at least six time intervals. The values of k are then averaged for each experiment. Constant values for k calculated in this manner serve as a valuable confirmation of the assumption explicit in equation 3. While this procedure does not have the physical significance of the one developed by Prestwood and Wahl,[10] it provides a highly expedient, objective method of treating the data.

Results

Heterogeneous Catalytic Effects.—Table I summarizes the data for experiments in which the effect of metals and other surfaces on the rate of exchange were investigated. Within experimental error, no effect was found in going from an inert surface such as Teflon to a glass system. The addition of platinum or gold metal increased the exchange rate. This behavior is different from that observed for the Np(IV)–Np(V) exchange mechanism in high acid where both inert and conducting surfaces catalyze the reaction.[11] The fact that a conductor may increase the exchange rate has been previously noted by Prestwood and Wahl[10] in their studies on the Tl(I)–Tl(III) exchange. The effect found in the present experiments is, however, much less than observed by these authors.

TABLE I

EFFECT OF SURFACE ON THE RATE OF THE Np(V)–Np(VI) EXCHANGE

$t = 0°$ C., $[\mathrm{Np(V)}] = [\mathrm{Np(VI)}] \cong 2 \times 10^{-5} M$

Surface	μ	k, mole^{-1} l. sec.$^{-1}$
Teflon	0.99	29.8
Pyrex	0.99	30.6
Pyrex	3.00	89
Platinum	3.00	107
Gold	3.00	97

Effect of Tracer Activity Level.—No effect on the exchange rate was found when the activity level of the Np^{239} tracer varied between 1 mr. and 2r. At activity levels as high as 10 r. erratic results were obtained. This may have been due to radiation decomposition of the water producing interfering reactants.

The Influence of Ionic Strength and Hydrogen Ion Concentration.—The hydrogen ion and ionic strength effects are summarized in Table II. Qualitatively, the increase in rate with increasing

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(6) W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

(7) (a) R. J. Marcus, B. J. Zwolinski and H. Eyring, *ibid.*, **58**, 432 (1954); (b) *Chem. Revs.*, **55**, 157 (1955).

(8) J. Weiss, *Proc. Roy. Soc. (London)*, **A222**, 128 (1954).

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

(10) R. J. Prestwood and A. C. Wahl, *ibid.*, **71**, 3137 (1949).

(11) J. C. Sullivan, Donald Cohen and J. C. Hindman, *ibid.*, **76**, 4275 (1954).

ionic strength is in the direction expected theoretically for a reaction involving two ions of like sign.

TABLE II

EFFECT OF IONIC STRENGTH AND HYDROGEN ION CONCENTRATION ON THE RATE OF THE Np(V)-Np(VI) EXCHANGE

$t = 0°$, $[Np(V)] = [Np(VI)] \cong 2 \times 10^{-5}$ *M*

Ionic strength, μ	$[H^+]$, moles l.$^{-1}$	k, mole^{-1} l. sec.$^{-1}$	Ionic strength, μ	$[H^+]$, moles l.$^{-1}$	k, mole^{-1} l. sec.$^{-1}$
0.99	0.99	30.6	4.18	0.99	120.6
1.63	.99	36.1	3.00	.50	76
2.26	.99	45.5	3.00	1.00	74[a]
2.90	.99	69.7	3.00	2.00	76
3.54	.99	94.9	3.00	3.00	88.8

[a] Interpolated value.

In an earlier investigation, the hydrogen ion concentration was found not to affect the rate of the reaction when varied from 0.32 to 0.99 *M* at a total ionic strength of unity. Since the studies of the anion effects were carried out at an ionic strength of three, the data on hydrogen ion dependence were extended to 3.0 *M*. Perusal of Table II shows that the rate is independent of hydrogen ion concentration at $\mu = 3.0$ from 0.5 to 2.0 *M* hydrogen ion. There appears to be a small but definite increase in rate on raising the acid concentration further to 3.0 *M*. The limited extent of the data make an interpretation of the effect uncertain. One possible explanation is that a proton is added to one of the oxygenated ions at high acidity, furnishing an additional exchange path through an activated complex of the type $[O-Np-O-H-O-Np-O]^{+4}$.

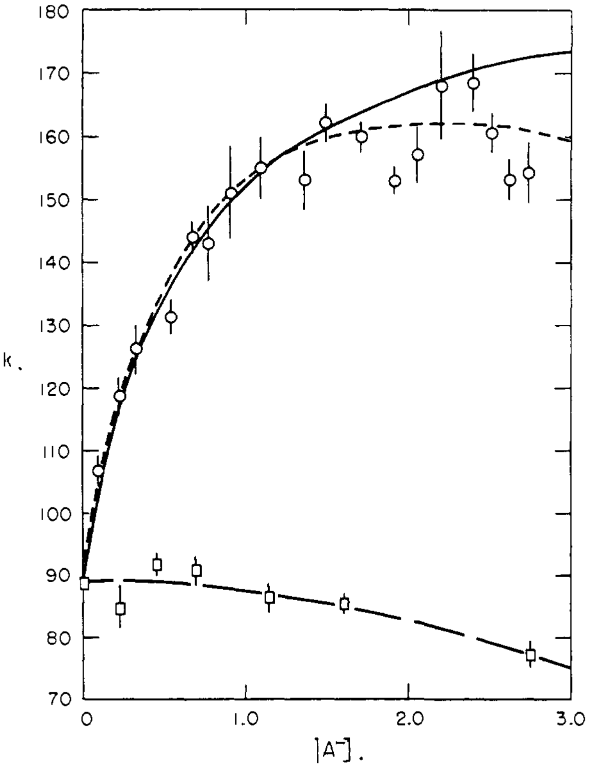

Fig. 1.—The effect of anions on the exchange rate, $t = 0°$, $\mu = 3.0$, $[H^+] = 3.0$: ——, single chloride complex NpO_2Cl^+; --------, two chloride complexes, NpO_2Cl^+ and NpO_2Cl_2; — —, nitrate solutions.

The Effect of Nitrate Ion.—Varying the nitrate concentration between 0 and 2.7 *M* has little effect on the exchange rate. The data are graphically shown in Fig. 1. If the slight decrease in the exchange rate at higher nitrate concentration is attributed to the incipient formation of a nitrate complex of Np(VI) then the exchange rate through this path must be low. Although no systematic studies on nitrate complexes of either Np(V) or Np(VI) have been made, it is known from spectral observations that there is no evidence of complex formation in molar nitric acid for either ion. The possibility that a weak complex of Np(VI) is formed can be deduced from data on U(VI) and Pu(VI). Ahrland[12] and Day and Powers[13] have reported values for the first association constant of

TABLE III

THE EFFECT OF CHLORIDE IONS ON THE Np(V)-Np(VI) EXCHANGE

$\mu = 3.00$, $[H^+] = 3.00$ *M*

$[Cl^-]$, (moles l.$^{-1}$)	$[Np(V)]$ ($\times 10^{-5}$ *M*)	$[Np(VI)]$ ($\times 10^{-5}$ *M*)	k, mole^{-1} l. sec.$^{-1}$
	0.0°		
0	1.13	2.02	88.8
0.10	1.90	2.03	107.0
.23	1.90	2.03	118.7
.34	1.13	2.02	126.2
.55	1.13	2.11	131.7
.55	0.77	3.38	129.0
.55	1.93	2.11	127.0
.55	3.09	0.84	138.2
.69	1.13	2.02	144.4
.78	1.13	2.02	143.0
.92	1.13	2.02	151.0
1.10	1.13	2.02	155.0
1.37	1.13	2.02	153.2
1.37	1.93	2.11	148.6
1.37	0.77	3.38	154.9
1.37	3.09	0.84	150.6
1.50	1.13	2.02	162.2
1.72	1.13	2.02	160.0
1.92	1.13	2.02	153.2
2.06	1.13	2.02	157.1
2.20	1.13	2.02	168.2
2.40	1.13	2.11	168.8
2.52	1.13	2.11	160.8
2.62	1.13	2.11	153.2
2.74	1.13	2.02	154.4
	4.78°		
0	1.64	2.18	127.7
0.21	1.92	2.22	174.7
0.55	1.64	2.21	191.7
1.10	1.92	2.22	220.2
1.37	1.64	2.18	241.0
	9.84°		
0	1.93	2.11	174.8
0.21	1.92	2.22	241.9
0.55	1.61	2.21	292.2
1.10	1.92	2.22	343.0
1.37	1.61	2.21	396.7

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(12) S. Ahrland, *Acta Chem. Scand.*, **5**, 1271 (1951).

(13) R. A. Day, Jr., and R. M. Powers, THIS JOURNAL, **76**, 3895 (1954).

uranyl and nitrate at $\mu = 1$ and 25° of 0.5 and 0.3, respectively. In the case of Pu(VI) there is no evidence for the formation of nitrate complexes until the nitrate concentration exceeds 3 molar.[14]

The Effect of Chloride Ion.—The data in Table III and Fig. 1 summarize the effect of chloride on the exchange rate. The exchange rate is markedly increased in the presence of chloride ions. Included in Table III are data showing that the metal ion order is unchanged by changing chloride concentration. Analysis of the data shows that two or more paths exist for the exchange in chloride media. No evidence has been obtained for complex formation between Np(V) and chloride. The data are analyzed therefore only in terms of possible Np(VI) chloro complexes. Assuming a reaction path involving a single Np(VI) chloride complex, *e.g.*, NpO_2Cl^+, equation 2 becomes

$$R = k_0(NpO_2{}^+)(NpO_2{}^{++}) + k_1(NpO_2{}^+)(NpO_2Cl^+) \quad (4)$$

where R is the measured rate and k and k_1 are the respective specific rate constants for the two paths. The association constant for the formation of the chloride complex, K_1, is

$$K_1 = \frac{(NpO_2Cl^+)}{(NpO_2{}^{++})(Cl^-)} \quad (5)$$

Substituting the apparent rate constant

$$k = \frac{R}{[Np(V)][Np(VI)]}$$

and K_1 into equation 4 we obtain

$$k = \frac{k_0 + k_1K_1(Cl^-)}{1 + K_1(Cl^-)} \quad (6)$$

In these equations the parentheses represent actual concentrations and the brackets total concentrations. The apparent rate constant, k, for the data at 0° is plotted in Fig. 1 as the solid line. The values of the constants used are given in Table IV.

TABLE IV

KINETIC AND EQUILIBRIUM CONSTANTS FOR THE EXCHANGE REACTIONS

$\mu = 3.0$, $[H^+] = 3.0\ M$

Temp., °C.	k_0, l. mole^{-1} sec.$^{-1}$	k_1, l. mole^{-1} sec.$^{-1}$	k_2, l. mole^{-1} sec.$^{-1}$	K_1	K_2
0.0	88.8	191[a]	..	1.62	..
0.0	88.8	215	86	1.26	0.16
4.78	127.7	308[a]	..	1.15	..
4.78	127.7	330	158	1.00	0.18
9.84	174.8	554[a]	..	0.87	..
9.84	174.8	573	229	0.81	0.20

[a] Assuming a single path through Cl^-.

The experimental points appear to deviate from the theoretical curve in a manner that suggests an additional path may contribute significantly to the reaction at high chloride concentration. Assuming a second chloride complex of Np(VI) is formed with an association constant, K_2, equal to

$$K_2 = \frac{(NpO_2Cl_2)}{K_1(NpO_2{}^{++})(Cl^-)^2} \quad (7)$$

and combining with the rate expression

$$R = k_0(NpO_2{}^+)(NpO_2{}^{++}) + k_1(NpO_2{}^+)(NpO_2Cl^+) + k_2(NpO_2{}^+)(NpO_2Cl_2) \quad (8)$$

we obtain

$$k = \frac{k_0 + k_1K_1(Cl^-) + k_2K_1K_2(Cl^-)^2}{1 + K_1(Cl^-) + K_1K_2(Cl^-)^2} \quad (9)$$

k for the 0° data as computed from equation 9 is plotted in Fig. 1 using the constants summarized in Table IV.

The data are fit equally well up to a concentration of 1.5 molar chloride by the assumption of either one or two complexes. Despite the large experimental uncertainties at high chloride concentrations, the data are best represented in this region by the mechanism involving two chloride paths. There is an alternative possibility that should be considered. The slow falling off of the rate in the mixed nitrate perchlorate solutions could be interpreted in terms of an activity coefficient change. A similar change in the mixed chloride–perchlorate solutions could lead to the apparent leveling off or decrease in the rate at very high chloride concentrations.

The Temperature Dependence.—Tables III and IV contain the data from which the energies of activation for the various exchange paths have been calculated. These are summarized in Table V. Also given in Table V are free energy and entropy of activation values calculated from the usual equations.[15]

The uncertainties assigned to the values of the free energy of activation are based on the experimental deviation for the respective values of k_0. The uncertainties that have been assigned to the derived k's are based on the maximum allowable variation that can be assigned and still adequately reproduce the experimental results. The uncertainty in the activation energy was calculated by a least squares determination for the path not involving chloride. For the halide dependent paths, the errors are assigned from a consideration of the uncertainties in the derived k's since a statistical treatment of the data indicated precision equivalent to that attained in the case of the path involving hydrated neptunium ions.

TABLE V

ENERGY, ENTROPY AND FREE ENERGY OF ACTIVATION FOR THE DIFFERENT EXCHANGE PATHS

$t = 0°C.$, $\mu = 3.0$

Path	E_{exp}, kcal. mole^{-1}	ΔS^*, cal. deg.$^{-1}$ mole^{-1}	ΔF^*, kcal. mole$^-$
$NpO_2{}^+–NpO_2{}^{++}$	10.6 ± 0.4	−12.6 ± 1.5	13.48 ± 0.02
$NpO_2{}^+–NpO_2Cl^+$	16.6 ± 0.9[a]	10.9 ± 3.3	13.06 ± .04
$NpO_2{}^+–NpO_2Cl^+$	15.4 ± 1.2	6.7 ± 4.7	13.02 ± .04
$NpO_2{}^+–NpO_2Cl_2$	15.3 ± 2.3	5 ± 5	13.52 ± .08

[a] Assuming a single path through Cl^-.

A change in the activation energy of the halide independent path with change in ionic strength is noted. At $\mu = 3.0$, the energy of activation is 10.6 kcal. mole^{-1} and the entropy of activation is −12.6 cal. deg.$^{-1}$ mole^{-1} as compared with $E_{exp} = 8.3$ kcal. mole^{-1}, $\Delta S^* = -24$ cal. deg.$^{-1}$ mole^{-1} at ionic strength unity. Although the values have changed in the direction that would be predicted theoretically,[16] the ionic strength is too high to make

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(14) J. C. Hindman, Paper 4.4, "The Transuranium Elements," Vol. 14B of the National Nuclear Energy Series, McGraw-Hill Book Co., New York, N. Y., 1949.

(15) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 197–199.

(16) Reference 15, pp. 433–438.

quantitative computation possible. There is in addition the possibility that a contribution from an alternate chloride independent path is included (*vide infra*).

Analysis of the data also yields values for the change in heat content and entropy in the formation of the chloro complexes. If a single exchange path involving chloride is assumed then $\Delta H_{273} = -8.7$ kcal. mole^{-1} and $\Delta S_{273} = -32.2$ cal. deg.$^{-1}$ mole^{-1} for the reaction

$$NpO_2^{++} + Cl^- \rightleftharpoons NpO_2Cl^+ \quad (10)$$

The large negative quantities for the heat and entropy change in the formation of the complex are unexpected. Although the assumption of two chloride complexes leads to more positive values the difference is not marked. The computed values of the heat and entropy change are $\Delta H_{273} = -6.9$ kcal. mole^{-1} and $\Delta S_{273} = -21$ cal. deg.$^{-1}$ mole^{-1} for reaction (10) and $\Delta H_{273} = 3.5$ kcal. mole^{-1} and $\Delta S_{273} = 16$ cal. deg.$^{-1}$ mole^{-1} for the reaction

$$NpO_2Cl^+ + Cl^- \rightleftharpoons NpO_2Cl_2 \quad (11)$$

In magnitude, the association constant for the first Np(VI) chloride complex is very similar to that reported for U(VI).[12,13] At 10°, K_1 for the U(VI) chloride complex has been given as 0.58.[13] The two systems differ, however, in that the U(VI) complex is stabilized by increasing temperature, $\Delta H_{298} = 3.8$ kcal. mole^{-1} and $\Delta S_{298} = 12$ cal. deg.$^{-1}$ mole^{-1}. The underlying cause for this difference in behavior is not obvious. Measurements of the complexity of the systems by different methods should be made.

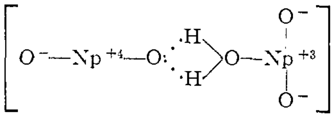
Mechanisms of the Reactions.—One of the most interesting results of the present study is the fact that the activation energy and entropy for the paths involving chloride are appreciably more positive than for the path through the hydrated ions. The effect of the halide complexing on these quantities is markedly greater than observed in the Fe(II)–Fe(III) exchange studies.[2] If the similarity in the activation energy, free energy and entropy in the case of the iron exchange systems are considered to indicate a single operative mechanism, then a change in mechanism between the chloride independent and chloride dependent paths appears likely for the Np(V)–Np(VI) system.

For example, if the NpO_2^+–NpO_2^{++} exchange proceeds by a hydrogen atom transfer, as suggested by Hudis and Wahl[2] to explain the Fe(II)–Fe(III) data, then the NpO_2^+–NpO_2Cl^+ exchange probably proceeds by a chlorine atom transfer. If more than a single path through chloride is involved, the data suggest that the mechanism is the same in both cases.

Similarly, if the NpO_2^+–NpO_2^{++} exchange proceeds by a direct electron transfer *via* the tunneling mechanism of Marcus, Zwolinski and Eyring,[7] then the NpO_2^+–NpO_2Cl^+ exchange presumably proceeds by an atom transfer mechanism. Although it is possible to fit the NpO_2^+–NpO_2^{++} data to the direct electron transfer process[7b] by adjustment of the empirical parameters in the equations, the positive entropy of activation precludes this mechanism for the halide dependent path if the electronic transmission coefficient, κ_e, is defined by the relation[7a] $\Delta S^* = R \ln \kappa_e$. The simplest explanation is that the halide dependent path involves a chlorine atom transfer

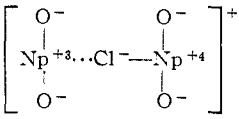
$$NpO_2Cl^+ + Np^*O_2^+ = [O_2NpCl\text{–}Np^*O_2]^{++} = NpO_2^+ + Np^*O_2Cl^+ \quad (12)$$

It should be pointed out that any calculation will depend on the model assumed for the activated complex. For example, the Np(V) and Np(VI) ions can be considered as linear species with the following charge distribution: O^-–Np^{+3}–O^- and O^-–Np^{+4}–O^-.[17] The six water molecules of the primary hydration sphere are arranged in a puckered ring in a plane at right angles to the O–M–O axis. One possible form for the activated complex involving the uncomplexed ions is then



(A)

For the activated complex involving chloride, or where exchange is through shared water molecules, the activated complex could be



(B)

Obviously, both the free energy and entropy terms will differ for the two models. In model (A) no rearrangement in the hydration spheres is involved in the formation of the activated complex. Because of the charge distribution there will be a significant difference in the repulsion energy for the two models where the bridging is through water molecules. In the formation of the activated complex of model (B) water must be unfrozen in the formation of the intermediate. Direct electron transfer in both cases could presumably occur. There would, however, be a marked difference in both energy and entropy values. A similar argument can be made if direct electron transfer occurs, and the activated complex formed for the uncomplexed species is (A) and for the halide complexed species is (B). It would, therefore, appear naive to attempt to argue about probable mechanisms in the present case from energetics alone.

LEMONT, ILLINOIS

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[17] J. C. Hindman, "The Actinide Elements," McGraw-Hill Book Co., Inc., New York, N. Y., 1954, Chapter 9.