polymer of the form $CeOCe^{+6}$ or a similar type structure.[8,9] Cerium(III) complexes in perchloric acid are not well-known and in general are assumed not to exist.

The above considerations lead to the general rate expression

$$R = k_4[\mathrm{Ce(III)}]\,[\mathrm{Ce(OH)_3}^+] + k_6[\mathrm{Ce(III)}]\,[\mathrm{HOCeOCe}^{+5}] \tag{6}$$

including only those pairs of reactants which, according to the data, are pertinent to the data. Inclusion of other terms does not improve the fit of the data. This leads to

$$R = \frac{k_4K_1K_2K_3[\mathrm{Ce(IV)}]}{[\mathrm{H}^+]^2[(\mathrm{H}^+) + K_1]} + \frac{k_6K_1{}^2K_5[\mathrm{Ce(IV)}]^2}{(\mathrm{H}^+)[(\mathrm{H}^+) + K_1]^2} \tag{7}$$

in which [Ce(III)] and Ce(IV) are the over-all concentrations of cerium(III) and cerium(IV), small *k*'s are specific rate constants, large *K*'s are the equilibrium constants for the reactions involving the various hydrolyzed species listed in equation 6.

Equation 7 including more terms was analyzed termwise in order to determine which, if any, of the possible unhydrolyzed or hydrolyzed forms of cerium(IV) were involved as the rate-determining exchange reactions. The specific rate constant or pseduo-rate constant for first-order cerium(IV) dependence as the case may be, was individually evaluated from the intercept of curve A, Fig. 3, neglecting all other first-order cerium(IV) dependency terms. Similarly, the pseudo-rate constant for each term representing second-order cerium(IV) dependence was individually evaluated from slope of the same curve, neglecting all the other second-order dependency terms.

Extrapolating the data of Hardwick and Robertson[9] to 0.1°, the value of K_1 involving the species $CeOH^{+3}$, was found to be 0.52. Similar values for the slopes and intercepts were calculated for the case where the hydrogen ion concentration is 5.04 *f*, using the above values. The intercept values increase progressively as the degree of hydrolysis of the monomer increases. These values are plotted as X's on the ordinate of Fig. 3. The ordinate value of 8.88 corresponds to the hydrolyzed form $Ce(OH)_3{}^+$ and can be concluded to best agree with experimental data which are plotted as solid dots on Fig. 3. The calculated slopes yield curves B, C and D of Fig. 3 which correspond to the dimers, $CeOCe^{+6}$, $HOCeOCe^{+5}$ and $HOCeOCeOH^{+4}$, respectively. As can be seen, the experimental results might fit any of the calculated curves. Assuming that the best fit is to curve C, corresponding to dimer $HOCeOCe^{+5}$, equation 7 above is the fitted rate expression.

As the hydrogen ion concentration is decreased (Table II), the equilibria favor formation of hydrolyzed and polymerized forms of cerium(IV). Qualitatively the data in Table II indicate that at lower acidities the exchange rate is relatively fast due to the comparatively large total concentration of hydrolyzed species and the possible existence of different hydrolyzed or polymerized forms of cerium(IV).

At the higher hydrogen ion concentrations the total concentration of hydrolyzed species becomes relatively small and the curve indicates that the exchange rate approaches zero or a very low value at high acid concentration. On the basis of this the exchange rate between cerium(III) and the unhydrolyzed cerium(IV) species must be slow compared to the exchange rate involving hydrolyzed and polymerized forms of cerium(IV).

The participation of the hydrolyzed and polymerized species of cerium(IV) in the exchange mechanisms aids in explaining the comparatively high experimental activation energies obtained by Gryder and Dodson. That is, if one takes an activation energy of about 10 kcal. for the electron exchange reaction, the ΔH of hydrolysis would have to be 15 kcal., a reasonable value, in order to get the *ca.* 25 kcal. observed by Gryder and Dodson.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Isotopic Exchange Reactions of Neptunium Ions in Solution. IV. The Effect of Variation of Dielectric Constant on the Rate of the Np(V)–Np(VI) Exchange[1]

BY DONALD COHEN, J. C. SULLIVAN, E. S. AMIS[2] AND J. C. HINDMAN

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The isotopic exchange reaction between Np(V) and Np(VI) ions has been studied at zero degrees C, in a medium of aqueous perchloric acid containing varying weight percentages of ethylene glycol or sucrose. The data show that the reaction rate for the isotopic exchange is negligibly affected by the variation of the macroscopic dielectric constant in these solvents. This result is discussed in terms of the current theories of the mechanism of electron exchange reactions.

Although arguments have been presented in favor of the interpretation that the Np(V)–Np(VI) exchange proceeds *via* an atom transfer process in chloride media,[3] the mechanism of the exchange in a non-complexing system is subject to considerably more uncertainty. In an attempt to differentiate further between possible mechanisms, experiments have been carried out in media of varying dielectric constant.

From simple electrostatic considerations it is expected that the rate will decrease with a decrease in dielectric constant[4] if the actual reaction is between two ions of like charge. For more sophisti-

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

[2] Resident Research Associate from the University of Arkansas.

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

[4] G. Scatchard, *Chem. Revs.*, **10**, 229 (1932).

cated arguments involving the concept of barrier penetration,[5,6] the relation between the rate and dielectric constant, though of the same general nature, will be more complex. In particular, studies in media of varying dielectric constant furnish a crucial test for the electron tunneling hypothesis in the form presented by Marcus, Zwolinski and Eyring.[5]

Experimental

The principal features of the experimental procedure have been described elsewhere.[7] Two different solvent extraction methods were used to separate the ionic species. In addition to the tributyl phosphate extraction previously employed, separations involving the use of thenoyltrifluoroacetone in toluene were used. Faster phase separation was obtained when the latter procedure was used for extractions from the solvent mixtures low in sucrose or glycol.

Eastman Kodak ethylene glycol was purified as described by Äkerlöf.[8] Reagent grade (Merck) sucrose was used without further purification. A 63.54 weight % sucrose solution was used in preparing the dilutions.

The dielectric constants of the solutions were calculated[8] by use of the measured densities and weight compositions of the reaction mixtures. Corrections to the calculated values due to the presence of the 0.1 M $HClO_4$ have been neglected.

In view of other experiments[9] it was considered desirable to check the stability of Np(V) and Np(VI) with respect to possible oxidation or reduction in the perchloric acid–ethylene glycol solutions. Spectrophotometric observation of a 90 volume % ethylene glycol solution approximately 0.01 M in Np(VI) showed that no reduction could be detected in a period of 48 hours at 25°. The reproducible zero time exchange in a given kinetic run has been interpreted to indicate that the Np(V) is equally stable in the presence of ethylene glycol. As evidenced by the kinetic data, the Np(V) and Np(VI) were also stable in the sucrose solutions.

Results

The experimental data are plotted in Fig. 1. Each value of log k' recorded is made up of the least-squares value of five or six individual kinetic measurements. Examination of the data in the figure shows that the rate is independent of dielectric constant in both the solvent systems studied. The calculated dielectric constant varied from 68 to 88.3 in the ethylene glycol–water solutions and from 67.7 to 88.3 in the sucrose–water solutions. The average value of k' obtained for the ethylene glycol–water solutions was 20.4 ± 3.7 and for the sucrose–water solutions 22.2 ± 3.0. Experiments with varying metal ion concentrations showed the reaction to be bimolecular[7] in the two systems.

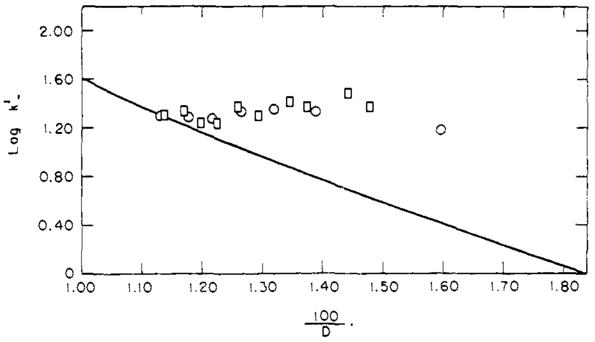

Fig. 1.—Effect of dielectric constant on the rate of the Np(V)–Np(VI) exchange; t = 0°, $[HClO_4]$ = 0.106 M: ——, theoretical curve; ⊙, water–ethylene glycol, Np(V) = Np(VI) ~ 1.41 × 10^{-5} M; ⊡, water–sucrose, Np(V) = Np(VI) ~ 1.87 × 10^{-5} M.

Discussion

If electrostatic interaction between the ions were the predominant factor affecting the reaction velocity, the simple coulombic relation[4] predicts that the observed rate, k' will vary with the dielectric constant, D, according to the equation

$$\frac{\partial \ln k'}{\partial (1/D)} = -\frac{n_a n_b e^2}{kT}\frac{1}{r} \qquad (1)$$

where n_a and n_b are the charges on the ions, r is the radius of the activated complex, e the electronic charge, k the Boltzmann constant and T the absolute temperature. Equation 1 predicts that the slope of the k' *versus* $1/D$ plot will be negative if the reaction is between the two ions, NpO_2^+ and NpO_2^{++}. If, however, alternate configurations are considered[3] for the activated complex then the sign and slope of the plot will depend on the charge distribution in the ions and the configuration of the activated complex.

Because of the structural factors no attempt has been made to apply equation 1. Rather, the electrostatic calculations have been made according to the equations of Marcus, Zwolinski and Eyring.[5] In the model proposed by these authors, the apparent free energy of activation is considered to be made up of three terms, *i.e.*

$$\Delta F^*_{\text{app}} = -RT \ln \kappa_e + \Delta F^*_{\text{rep}} + \Delta F^*_{\text{r}} \qquad (2)$$

where ΔF^*_{rep} is the coulombic interaction term, ΔF^*_{r} is the rearrangement free energy required to satisfy the Franck–Condon restrictions, and $-RT \ln \kappa_e$ is the probability factor for the penetration of the barrier. If the rearrangement free energy term is fixed, then the equations may be solved by appropriate adjustment of the various parameters to reproduce the experimental results for the aqueous solution at 0°. In this way it is possible to obtain values for the effective charges on the ions, n_a and n_b, and hence for the tunneling distance, r_{ab} (*i.e.*, roughly the diameter of the activated complex) and the related free energy terms. The results of such calculations are given in Table I. The 8.1 kcal. value for the free energy of rearrangement was

TABLE I

VALUES OF n_a, n_b, r_{ab} AND k' CALCULATED FOR D = 88.3 Z^* = 5 AND ΔF_r^* = 8.1 KCAL.

t = 0°, k'_{exp}(0.1 M $HClO_4$) = 19.5 l. mole^{-1} sec.^{-1}

n_a	n_b	r_{ab} (Å.)	k' (calcd.) (l. mole^{-1} sec.^{-1})
1	2	3.51	795
1.5	2.6	4.90	34.9
1.59	2.69	5.04	20.8
2	3	6.07	2.45
3	4	8.59	0.00794
3	4	8.59	15.1[a]

[a] ΔF_r^* = 4 kcal.

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

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

(8) G. Äkerlöf, *ibid.*, **54**, 4152 (1932).

(9) J. C. Sullivan, D. Cohen and J. C. Hindman, *ibid.*, **77**, 6203 1955).

that value selected by Marcus, Zwolinski and Eyring[5a] to reconcile the experimental data on the Fe(II)–Fe(III) exchange with their theoretical calculations. The 4 kcal. value represents our estimate based on the fact that a lower rearrangement energy should be required in the present case because of the symmetry of the ions.[7]

The following comments can be made about the results of these calculations. First, the lower rearrangement energy leads to a reasonable value of the tunneling distance if the electron transfer process occurs without interference of the primary hydration shells of the two ions. We would estimate that the radius of the activated complex must exceed 7.5 Å. if the water shells on the NpO_2^+ and NpO_2^{++} ions are to remain undisturbed. This is equivalent to assigning a radius of 1 Å. to both the Np(V) and Np(VI) ions plus two water molecule diameters. On the other hand the effective charges of +3 and +4, respectively, are probably too large since the Np–O bonds are presumably somewhere between single and double bonds.[7,10,11]

The most serious difficulties become apparent when calculations of the effect of variation of D on the rate are made. This is clearly shown in Fig. 1. The solid line represents the calculated values using $n_a = 1.59$, $n_b = 2.69$ and $r_{ab} = 5.04$ Å. The slope of the theoretical curve in the region of the dielectric constants used experimentally is -2.0. The experimental data shown in the figure can be represented by a least squares straight line with a slope of $+0.08 \pm 0.13$ standard deviation. For our experimental conditions the rate of the exchange is independent of the value of the gross dielectric constant of the solutions. The deviation of the experimental from the theoretical results is enhanced if larger n_a, n_b and r_{ab} values are used. An increase in magnitude of the numbers assigned to these parameters leads to an increase in the slope of the log k' *versus* $100/D$ plot.

It is obvious that the purported agreement between the calculated free energy of activation obtained from the equations for the electron tunneling hypothesis[5b] and the results of our experimental investigations[7] on the exchange in aqueous solution is fortuitous and occurs only because of the latitude possible in adjusting the parameters in the relevant equations.

The obvious explanation for the results of the present experiments is that non-electrostatic forces dominate the energetics. This suggests that the exchange may proceed by an atom transfer mechanism. The fact that the equations of Marcus, Zwolinski and Eyring do not apply is not, however, proof that direct electron transfer does not occur. As Platzman and Franck[12] have correctly pointed out, the Christiansen–Scatchard treatment is valid only for large distances. Polarization phenomena markedly alter the dielectric properties of the medium and at the distances involved in the formation of an activated complex the concept of the dielectric constant of the medium loses significance.[12,13] Weiss,[6] in his treatment of the electron transfer process has attempted to take this factor into account. If we accept his view that only the interaction energy in the final state (*i.e.*, in the activated complex) enters into the activation energy, then we are concerned with the optical dielectric constant of the medium and not the macroscopic value. Lack of detailed knowledge of the dielectric properties of the medium in high potential fields, however, makes calculations along these lines highly speculative at the present time.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MASSACHUSETTS AND THE DEPARTMENT OF CHEMISTRY OF OREGON STATE COLLEGE]

Solvent Extraction of Zirconium with Tributyl Phosphate[1]

BY ARNOLD E. LEVITT[2] AND HARRY FREUND

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A study of the effect of certain variables on the extraction of zirconium from hydrochloric acid solutions by tributyl phosphate (TBP) has been made. The variation in the zirconium distribution ratio D with TBP concentration in TBP–benzene solutions gives evidence of a 2:1 molar ratio of TBP to zirconium in the species extracted. Studies were made of the Cl:Zr molar ratio in the organic phase. An investigation of the variation of D with aqueous chloride concentration at constant acidity and constant ionic strength was made. The effect of aqueous acidity on D at constant chloride concentration and constant ionic strength was also investigated. The results of these studies offer evidence for $ZrCl_4(TBP)_2$ as the species present in the organic phase. A decrease in D with increasing initial zirconium concentration at constant aqueous hydrochloric acid concentration and constant organic TBP concentration indicates greater extent of zirconium polymerization in the aqueous phase than in the organic phase.

Introduction

In recent years tributyl phosphate (TBP) has come into prominence as an extracting agent. It was first used to extract various organic acids from aqueous media.[3–5] Recently it has been found to be a useful solvent for extracting metal thio-

[1] Presented before the Division of Physical and Inorganic Chemistry at the Minneapolis Meeting of the American Chemical Society, September, 1955.

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