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Equilibrium and Kinetic Studies of the Reactions between Neptunium(III) and the Complexes $(\text{NH}_3)_5\text{RuOH}_2^{3+}$ and $(\text{NH}_3)_6\text{Ru}^{3+}$ in Aqueous Trifluoromethanesulfonate Solutions¹

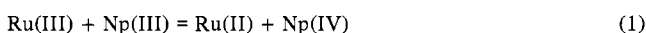
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The second-order approach to equilibrium of the reaction $\text{Np(III)} + \text{Ru(III)} = \text{Np(IV)} + \text{Ru(II)}$ has been studied for $(\text{NH}_3)_6\text{Ru}^{3+}$ and $(\text{NH}_3)_5\text{RuOH}_2^{3+}$ in trifluoromethanesulfonate media. Neither the kinetic nor equilibrium parameters which govern these reactions exhibit a discernible acid dependence. For aquopentaammineruthenium(III) + Np(III) (25° , $I = 1.00 F$), $Q = 0.062 \pm 0.008$, $k_f = 0.270 \pm 0.019 F^{-1} \text{ sec}^{-1}$, $\Delta H^\circ = -8.7 \pm 0.2$ and $\Delta H_f^\circ = 4.24 \pm 0.25$ kcal/mol, and $\Delta S^\circ = -34.8 \pm 0.8$ and $\Delta S_f^\circ = -46.9 \pm 0.9$ eu. For hexaammineruthenium(III) + Np(III) (25° , $I = 0.50 F$), $Q = 0.031 \pm 0.003$, $k_f = 0.305 \pm 0.036 F^{-1} \text{ sec}^{-1}$, $\Delta H^\circ = -11.5 \pm 0.7$ and $\Delta H_f^\circ = 3.9 \pm 1.0$ kcal/mol, and $\Delta S^\circ = -45.4 \pm 1.7$ and $\Delta S_f^\circ = -48.1 \pm 3.5$ eu. The reverse reaction of Np(IV) with aquopentaammineruthenium(II) has also been followed directly, yielding an independent determination of k_r (25° , $I = 1.00 F$) of $4.37 \pm 0.21 F^{-1} \text{ sec}^{-1}$. Experimentally determined equilibrium parameters are used to calculate values of the formal oxidation potential and $S^\circ_{(2+)} - S^\circ_{(3+)}$, for the $(\text{NH}_3)_5\text{RuOH}_2^{2+,3+}$ and $(\text{NH}_3)_6\text{Ru}^{2+,3+}$ couples of -0.084 ± 0.004 V, $+17.5 \pm 1.1$ eu and -0.066 ± 0.003 V, $+4.1 \pm 1.9$ eu, respectively. Kinetic parameters are discussed in terms of both the orthodox outer-sphere transition state and an unorthodox transition state in which ruthenium attains coordination number 7. The importance of ΔS° in determining the rate of reaction between highly charged ions is pointed out.

Introduction

Initial experiments showed that *both* Np(IV) and Np(III) result from the reduction of Np(V) by ruthenium(II)-ammine complexes. Therefore, in order to be able to characterize the Np(V)-Ru(II) system, it became necessary to conduct a detailed equilibrium and dynamic investigation of the reaction



(where Ru(III) is either $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+}$ or $\text{Ru}(\text{NH}_3)_6^{3+}$, and Ru(II) the corresponding reduced species), the results of which are reported in this paper. This reaction is also of interest in light of recent studies by Taube and coworkers⁴ on the electron-transfer reactions of ruthenium-ammine complexes with d transition metal ions, the present work providing an opportunity to obtain comparable kinetic parameters for reactions which involve 5f electrons. In addition, the equilibrium data presented in this report bear upon the discrepancy in the reported values of the formal potentials for the $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+,3+}$ and $\text{Ru}(\text{NH}_3)_6^{2+,3+}$ couples.^{4a,4c,5} It should be noted that the use of trifluoromethanesulfonate as the common anion allowed these studies to be conducted in an acidic medium where complex ion formation is minimal⁶ and the extraneous oxidation of Ru(II) by perchlorate^{4c} is avoided.

Experimental Section

Reagents. Trifluoromethanesulfonic Acid. The starting material was obtained from the 3M Co., purportedly as the anhydrous acid. It was purified *via* distillation of the monohydrate (bp 96° (1 mm), mp 34°) in an all-Pyrex, preconditioned system with no greased or Teflon joints.⁷ Solutions were standardized by conventional titrimetric procedures.

(1) A portion of this investigation was conducted under the auspices of the United States Atomic Energy Commission.

(2) University of Chicago.

(3) Argonne National Laboratory.

(4) (a) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968);

(b) H. J. Price and H. Taube, *ibid.*, **7**, 1 (1968); (c) J. E. Endicott and H. Taube, *ibid.*, **4**, 437 (1965); (d) J. A. Stritar and H. Taube, *ibid.*, **8**, 2281 (1969).

(5) H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11**, 1460 (1972). We are grateful to the authors for making the manuscript for this reference available before publication.

(6) A. Scott and H. Taube, *Inorg. Chem.*, **10**, 62 (1971).

(7) *Warning!* This is a very corrosive acid. Solutions as dilute as 1 *F* will cause painful irritation upon contact with skin.

Lithium Trifluoromethanesulfonate. Reagent grade lithium carbonate was recrystallized according to a published procedure⁸ and then neutralized with a standardized solution of trifluoromethanesulfonic acid.

Silver Trifluoromethanesulfonate. Equimolar quantities of reagent grade silver oxide and 2 *F* HO_3SCF_3 were combined and heated to boiling for *ca.* 5 hr. The resulting solution was filtered and used in subsequent preparations.

Aquopentaammineruthenium(III) Trifluoromethanesulfonate. Chloropentaammineruthenium(III) chloride was prepared from $\text{Ru}(\text{NH}_3)_5\text{Cl}_2$ as previously described.⁹ This was treated with excess AgO_3SCF_3 solution in dilute HO_3SCF_3 and the mixture stirred at 35° until the formation of AgCl ceased (about 5–7 days). The solution was filtered and reduced in volume and the product was precipitated by addition of 4 *F* HO_3SCF_3 . This salt was recrystallized three times from 1 *F* HO_3SCF_3 aqueous solutions and dried at 60° (over P_2O_5 , under vacuum) for 48 hr. *Anal.* Calcd for $(\text{NH}_3)_5\text{RuOH}_2[\text{O}_3\text{SCF}_3]_3$: C, 5.53; H, 2.63; N, 10.75; S, 14.77. Found: C, 5.62; H, 2.60; N, 10.73; S, 14.92. The apparent molar absorptivity at 268 nm was determined to be $719 \pm 9 F^{-1} \text{ cm}^{-1}$ (average of six determinations) in reasonable agreement with previously reported values (770,^{10a} 757^{10b}).

Hexaammineruthenium(III) Trifluoromethanesulfonate. $\text{Ru}(\text{NH}_3)_6\text{Cl}_2$ was treated with 3 equiv of AgO_3SCF_3 solution (*ca.* 0.1 *F* in HO_3SCF_3), the AgCl was filtered off, and the product was precipitated by the addition of 4 *F* HO_3SCF_3 . This salt was recrystallized three times from warm aqueous solution (*ca.* 10^{-3} *F* in HO_3SCF_3) and dried at 35° (over P_2O_5 , under vacuum) for 24 hr. *Anal.* Calcd for $(\text{NH}_3)_6\text{Ru}[\text{O}_3\text{SCF}_3]_3$: C, 5.54; H, 2.79; N, 12.92. Found: C, 5.42; H, 2.87; N, 13.03. The apparent molar absorptivity at 275 nm was determined to be $472 \pm 8 F^{-1} \text{ cm}^{-1}$ (average of three determinations) in good agreement with the reported value (475^{4a}).

Solutions of aquopentaammineruthenium(II) (usually *ca.* 0.01 *F* in Ru(II), 0.05–0.10 *F* in HO_3SCF_3) were prepared by reduction of the trivalent salt with amalgamated zinc under an argon atmosphere. Solutions of Np(V) in perchloric acid were prepared as previously described.¹¹ These were converted to solutions of Np(V) in trifluoromethanesulfonic acid by the following procedure. Neptunium(V) hydroxide was precipitated with NaOH, washed three times with water, dissolved in 1 *F* HO_3SCF_3 , reprecipitated with base, washed three times with water, and finally redissolved in 1 *F* HO_3SCF_3 . Fresh solutions of Np(V) were prepared at the beginning of every series of experiments. Np(III) solutions were prepared by reduction of Np(V) stock solutions with amalgamated zinc under an argon atmosphere.

(8) E. R. Caley and P. J. Elving, *Inorg. Syn.*, **1**, 1 (1939).

(9) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).

(10) (a) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964); (b) J. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **84**, 4985 (1962).

(11) R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, **89**, 1096 (1967).

Np(IV) solutions were prepared *via* the reaction of equivalent amounts of Np(III) and Np(V) under an atmosphere of argon. The apparent molar absorptivities of Np(IV) and Np(III) (in 1 *F* HO₃SCF₃) determined in this work at 9605, 7235, and 7150 Å, respectively, were 230 and 7.8, 158 and 1.7, and 75 and 1.2 *F*⁻¹ cm⁻¹ with standard deviations of 3%. None of the ruthenium species studied herein have any significant absorbance at these wavelengths.

Procedures. Solutions of all reagents, except either the Np(III) or Ru(II), were pipetted into 2- or 5-cm absorption cells, ionic strength being maintained usually with HO₃SCF₃, but sometimes with LiO₃SCF₃. [Ionic strength was 1.00 *F* for all aquopentaammineruthenium experiments, but the low solubility of hexaammineruthenium(III) trifluoromethanesulfonate limited the ionic strength that could be used for the majority of experiments to 0.500 *F*. A few experiments performed with the hexaammine salt at *I* = 1.00 *F* showed that doubling the ionic strength produced no detectable change in the equilibrium parameter, but caused a 50% increase in the rate parameter.] The cells were then stoppered with a rubber serum cap, placed in a constant-temperature bath, and deoxygenated for at least 40 min with an argon stream which had been passed through a bubbling tower. The cell was then placed in the compartment of a Cary Model 14 MR spectrophotometer, which was thermostated at the working temperature, and an aliquot of the Np(III) or Ru(II) solution was introduced through the serum cap using a glass syringe fitted with a Pt needle. The optical density at either 9605, 7235, or 7150 Å was recorded as a function of time. Calculated rate parameters were shown not to be dependent on the wavelength used. Twenty to thirty absorptivity-time data points were taken in each kinetic experiment, the first significant observation usually corresponding to 10 sec after mixing of reactant solutions. The optical density at time zero (OD₀) was obtained by extrapolation of log (OD_t - OD_∞) plots. When Np(III) was the injected reagent, there was usually a small amount of Np(IV) present in the reaction mixture at time zero. This initial concentration of Np(IV) can be determined from OD₀ (see next section for appropriate equations).

Results and Calculations

Determination of Rate Law. Published values of the relevant oxidation potentials^{5,12} may be used to estimate an equilibrium quotient of ca. 0.1 for reaction 1. This result, plus the general shape of the absorbance-time recordings, provides the basis for postulating that reaction 1 proceeds according to the rate law

$$d[\text{Np(IV)}]/dt = k_f[\text{Np(III)}][\text{Ru(III)}] - k_r[\text{Np(IV)}][\text{Ru(II)}] \quad (2)$$

The integrated form of the rate law governing a second-order approach to equilibrium has been presented,¹³ and it adequately describes this system (Figure 1). However, it was observed that the data obtained from the reaction of the trivalent cations could apparently be described equally well by the integrated expression for a first-order approach to equilibrium (see Figure 1). It was therefore deemed prudent to test the proposed rate law in the differential form, and individual sets of OD-time data were treated by the method of fourth differences¹⁴ in order to obtain values of d(OD_t)/dt at every point. In terms of optical densities, eq 2 can be expressed as

$$d(\text{OD}_t)/dt = a + b(\text{OD}_t - \text{OD}_0) + c(\text{OD}_t - \text{OD}_0)^2 \quad (3)$$

where

$$a = Fk_f[\text{Ru}^{\text{tot}}][\text{Np}^{\text{tot}}]$$

$$b = -k_f([\text{Ru}^{\text{tot}}] + [\text{Np}^{\text{tot}}])$$

$$c = (k_f - k_r)/F$$

$$F = i(\epsilon_{\text{Np(IV)}} - \epsilon_{\text{Np(III)}})$$

and the terms [Ru^{tot}] and [Np^{tot}] refer to the total concen-

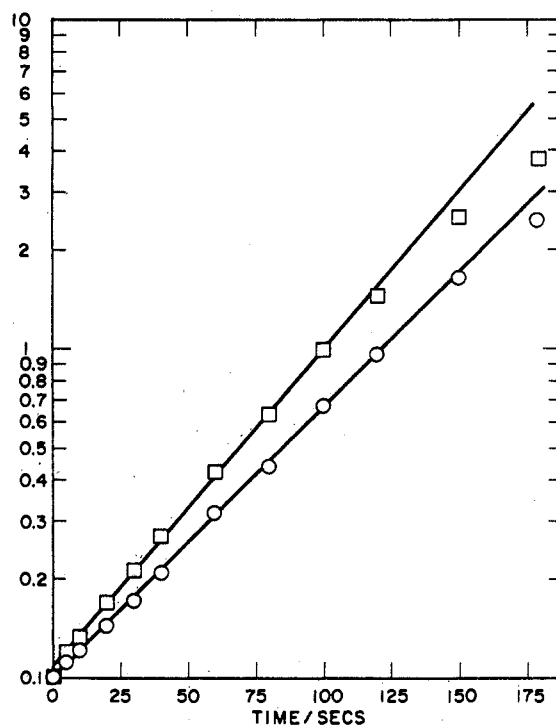


Figure 1. Reaction between aquopentaammineruthenium(III) and neptunium(III). Conditions: $T = 25^\circ$, $I = 1.00 F$, $[\text{Np(III)}]_0 = 1.120 \times 10^{-2} F$, $[\text{Ru(III)}]_0 = 1.208 \times 10^{-2} F$, $[\text{Np(IV)}]_0 = 4.7 \times 10^{-3} F$, $[\text{H}^+] = 0.827 F$. Circles represent the function governing first-order approach to equilibrium, while squares represent the function governing second-order approach (both functions taken from ref 13). When the data from this particular experiment are adjusted to fit the expression $d(\text{OD}_t)/dt = a + b(\text{OD}_t) + c(\text{OD}_t)^2$, the resulting values of a , b , and c , with their standard deviations, are 0.012 ± 0.004 , -0.008 ± 0.002 , and $-0.010 \pm 0.003 \text{ sec}^{-1}$, respectively.

tration of these elements in both oxidation states, [Np(IV)]₀ being assumed to be zero. Nonlinear least-squares¹⁵ analysis of 19 independent experiments on the reaction of aquopentaammineruthenium(III) with neptunium(III) (conditions: $[\text{Np(III)}]_0 = (1.37-27.0) \times 10^{-3} F$, $[\text{Ru(III)}]_0 = (4.50-49.1) \times 10^{-3} F$, $[\text{Ru(III)}]_0/[\text{Np(III)}]_0 = 0.17-16.5$) showed that while the c parameter was not always statistically defined, the a and b parameters depended upon [Ru^{tot}] and [Np^{tot}] in the fashion predicted by eq 3. This analysis yielded a value of $k_f(\text{Np}^{3+} + (\text{NH}_3)_5\text{RuOH}_2^{3+}, 25^\circ, I = 1.00 F)$ of $0.29 \pm 0.03 F^{-1} \text{ sec}^{-1}$. An equivalent differential analysis of six independent reactions of hexaammineruthenium(III) with neptunium(III) (conditions: $[\text{Np(III)}]_0 = 1.37 \times 10^{-3} F$, $[\text{Ru(III)}]_0 = (1.48-2.95) \times 10^{-3} F$) yielded a value of $k_f(25^\circ, I = 0.50 F)$ of $0.38 \pm 0.02 F^{-1} \text{ sec}^{-1}$. Eight independent experiments on the reaction of aquopentaammineruthenium(II) and neptunium(IV) were also analyzed by the differential technique (conditions: $[\text{Np(IV)}]_0 = 3.0 \times 10^{-3} F$, $[\text{Ru(II)}]_0 = (1.59-6.37) \times 10^{-3} F$). In these cases the c term was always a well-defined quantity and a value of $k_r(25^\circ, I = 1.00 F)$ was calculated to be $4.4 \pm 0.8 F^{-1} \text{ sec}^{-1}$.

These results are inconsistent with a first-order approach to equilibrium and in addition provide strong evidence for the validity of the postulated rate law (eq 2). Therefore, all further calculations are based on the assumption that the reac-

(12) D. Cohen and J. C. Hindman, *J. Amer. Chem. Soc.*, **74**, 4679 (1952).

(13) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 186.

(14) C. Lanczos, "Applied Analysis," Prentice-Hall, Englewood Cliffs, N. J., 1956, pp 315-324.

(15) R. H. Moore and R. K. Zeigler, Report No. LA-2367 plus addenda, Los Alamos Scientific Laboratory, 1959. We are very grateful to Dr. T. W. Newton (Los Alamos Scientific Laboratory, CMF-2) for providing us with a copy of this program and for assisting us with its adaptation to the University of Chicago Computation Center IBM/360 system.

tions under discussion follow a second-order approach to equilibrium.

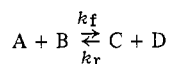
Treatment of Data. In the reactions of Np(III) with Ru(III) species, the concentration of Np(IV) present at time zero may be calculated from OD_0 and $[Np^{tot}]$ by the expression

$$[Np(IV)]_0 = Z = (OD_0 - l\epsilon_{Np(III)}[Np^{tot}])/F \quad (4)$$

where F is defined as in eq 3. The total absorbance change of each individual kinetic run ($T = OD_\infty - OD_0$) provides an independent determination of the equilibrium quotient

$$Q = \frac{[Np(IV)][Ru(II)]}{[Np(III)][Ru(III)]} = \frac{(T/F + Z)(T/F)}{([Ru^{tot}] - T/F)([Np^{tot}] - Z - T/F)} \quad (5)$$

It is seen that Q is a very sensitive function of T and that small errors in T will produce large uncertainties in Q . The integrated form of the rate law governing second-order approach to the equilibrium



was expressed^{15,16} as

$$OD_t = OD_0 + \left[\frac{T}{A_0 - A_\infty} \right] \left[\frac{\sqrt{q}(\theta + 1)}{(1 - \theta)} - \beta \right] \left[\frac{1}{k_f - k_f/Q} \right] \quad (6)$$

where

$$\theta = \left[\frac{\beta - \sqrt{q}}{\beta + \sqrt{q}} \right] e^{t\sqrt{q}}$$

$$\beta = -k_f(A_0 + B_0) - (k_f/Q)(C_0 + D_0)$$

$$q = k_f^2(A_0 - B_0)^2 + (k_f/Q)^2(C_0 - D_0)^2 + 2(k_f^2/Q)[(A_0 + B_0)(C_0 + D_0) + 2(A_0B_0 + C_0D_0)]$$

$$A_\infty = [-b + (b^2 + 4ac)^{1/2}]/2a$$

$$a = Q - 1$$

$$b = Q(B_0 - A_0) + 2A_0 + C_0 + D_0$$

$$c = A_0(A_0 + C_0 + D_0) + C_0D_0$$

and a nonlinear least-squares program¹⁵ was used to adjust the absorptivity-time data with respect to the parameters OD_0 , OD_∞ , and k_f . This adjustment was shown to be very insensitive to the value of Q used in the calculation. For example, data from an experiment with $[Np(III)]_0 = 3.04 \times 10^{-3} F$, $[Np(IV)]_0 = 1.06 \times 10^{-4} F$, and $[Ru(NH_3)_5OH_2^{3+}]_0 = 4.36 \times 10^{-2} F$ were treated using three different values of Q . The resulting values of the adjusted parameters OD_0 , OD_∞ , and k_f ($F^{-1} \text{ sec}^{-1}$), and their standard deviations, were respectively 0.044 ± 0.002 , 0.624 ± 0.001 , and 0.265 ± 0.002 for $Q = 0.06$, 0.044 ± 0.002 , 0.628 ± 0.001 , and 0.277 ± 0.002 for $Q = 0.07$, and 0.041 ± 0.002 , 0.627 ± 0.001 , and 0.292 ± 0.002 for $Q = 0.08$. Thus a large uncertainty in Q does not strongly affect the final fit or the values of the adjusted parameters (of course the error in $k_r = k_f/Q$ is directly determined by the uncertainty in Q). This allows the following iterative procedure to be used effectively.

For the reaction between aquopentaammineruthenium(III) and neptunium(III), initial values of the equilibrium quotient were calculated for 47 independent experiments. The average calculated value, $Q = 0.07 \pm 0.01$, was fixed and initial es-

timates of OD_0 , OD_∞ , and k_f were obtained graphically for use in eq 6. Adjusted values thus obtained for OD_0 and OD_∞ were then used for a second calculation of individual Q values. The resulting average Q was again fixed and the values of OD_0 , OD_∞ , and k_f obtained in the first adjustment were used as starting estimates for a second iteration. The entire procedure was repeated twice again, with no change in the values obtained for Q and the adjustable parameters occurring between the third and fourth iterations. In this example the final value of Q was 0.062 ± 0.007 . This same procedure, with obvious appropriate modifications, was used to calculate the values of the rate parameter and equilibrium quotient for the other reactions (at each temperature) considered in this work. This iterative calculation reproduced the observed absorptivities with an average standard deviation of ± 0.002 optical density unit for the 94 independent experiments summarized in this communication (total absorbance change usually 0.6–0.9 unit). Precision indices estimated for the rate parameters (based on external consistency) ranged from 0.3 to 1.0%. The spread in the reproducibility of the rate parameter is illustrated by the following results for the reaction between aquopentaammineruthenium(III) and neptunium(III). At 25° , $I = 1.00 F$, $[Np(III)]_0 = 3.0 \times 10^{-3} F$, $[Ru(III)]_0 = 43.5 \times 10^{-3} F$, and $[H^+] = 0.71 F$, duplicate determinations of k_f ($F^{-1} \text{ sec}^{-1}$) gave values of 0.283 ± 0.003 and 0.266 ± 0.002 . For a second set of determinations, under the same conditions except with a different preparation of reagents, the values calculated for k_f were 0.251 ± 0.002 , 0.255 ± 0.001 , 0.252 ± 0.002 , and 0.252 ± 0.001 .

Representative data for the reaction between aquopentaammineruthenium(III) and neptunium(III) are presented in Table I. These data were selected from 47 independent experiments in order to show the wide range of initial concentrations of metal ions used in this work. They demonstrate that the second-order approach to equilibrium is an adequate description of the system over this entire range. In addition, there is no compelling evidence for a significant contribution of a hydrogen ion dependent kinetic path over the limited range of hydrogen ion concentration data presented. A substantial effort was expended to extend significantly the range of initial hydrogen ion concentration. The kinetic parameters at the lower acid concentrations (0.052–0.10 F) were irreproducible (although the values fell within the range reported in Table I) but values of Q were invariant within the assigned error limit already noted.

The values of Q and k_f determined for the reactions of Np(III) with ruthenium(III)-ammine complexes are summarized in Table II. It should be noted that these values of k_f are in substantial agreement with those values calculated from the differential treatment of the data. In addition to these results, a value for k_r for the aquopentaammineruthenium(III) reaction was directly determined by monitoring the reaction of Np(IV) with aquopentaammineruthenium(II). It was not feasible to carry out this same type of experiment with hexammineruthenium(II) because of the relative lability of this species.¹⁷ At 25° , $I = 1.00 F$, $[H^+] = 0.95 F$, $[Np(IV)]_0 = 3.0 \times 10^{-3} F$, and $[Ru(II)]_0 = (1.7\text{--}6.8) \times 10^{-3} F$, the value calculated for k_r from eight independent determinations is $4.37 \pm 0.21 F^{-1} \text{ sec}^{-1}$. This is in good agreement with the value $k_r = 0.270/0.062 = 4.35 F^{-1} \text{ sec}^{-1}$ calculated from the data in Table II and with the value obtained from the differential treatment of the data.

A nonlinear least-squares procedure¹⁵ was used to calculate

(16) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 29.

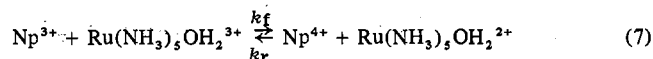
(17) P. Ford and H. Taube, *Inorg. Chem.*, 7, 1976 (1968).

Table I. Representative Data^a from 47 Independent Experiments on Reaction 7

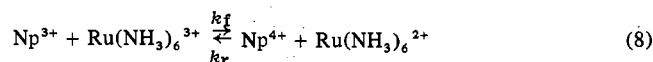
$10^3 \times$ [Np(III)] ₀ <i>F</i>	$10^3 \times$ [Ru(III)] ₀ <i>F</i>	$10^3 \times$ [Np(IV)] ₀ <i>F</i>	[Ru]/[Np]	[H ⁺], <i>F</i>	k_f , ^b <i>F</i> ⁻¹ sec ⁻¹
1.172	3.86	0.046	3.17	0.968	0.273
2.837	49.12	0.14	16.5	0.679	0.277
6.68	56.94	0.15	8.33	0.594	0.261
26.42	4.54	0.58	0.17	0.731	0.269
28.74	6.28	0.00	0.22	0.699	0.243

^a *T* = 25°, *I* = 1.00 *F*. ^b Range of calculated values of k_f = 0.243–0.327 *F*⁻¹ sec⁻¹ for the total set of 47 determinations.

values of ΔH° and ΔS° from the variation of *Q* with temperature. For the reaction



$\Delta H^\circ = -8.7 \pm 0.2$ kcal/mol and $\Delta S^\circ = -34.8 \pm 0.8$ eu, where the uncertainties are computed standard deviations. For the reaction

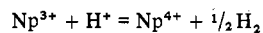


$\Delta H^\circ = -11.5 \pm 0.7$ kcal/mol and $\Delta S^\circ = -45.4 \pm 1.7$ eu. The variation of rate parameters, k_f , with temperature were adjusted in terms of the Eyring formalism by the nonlinear least-squares procedure.¹⁵ For k_f (eq 7), $\Delta H_f^\ddagger = 4.24 \pm 0.25$ kcal/mol and $\Delta S_f^\ddagger = -46.9 \pm 0.9$ eu. For k_f (eq 8), $\Delta H_f^\ddagger = 3.9 \pm 1.0$ kcal/mol and $\Delta S_f^\ddagger = -48.1 \pm 3.5$ eu.

Discussion

Equilibrium Data. From the values obtained for *Q* at 25° and the formal potential of the Np(III)–Np(IV) couple,¹² calculated values of the formal oxidation potential of the (NH₃)₅RuOH₂^{2+,3+} and (NH₃)₆Ru^{2+,3+} couples are -0.084 ± 0.004 and -0.066 ± 0.003 V, respectively. Comparable values determined by cyclic voltammetry⁵ are -0.066 and -0.051 V, respectively, in good agreement with our evaluation of hexaammineruthenium(II) being the better reductant by 18 ± 5 mV. The systematically more positive cyclic voltammetry values can reasonably be accounted for by differences in ionic strength, supporting electrolyte, and junction potential corrections. The difference between the *E*^o reported in ref 4a and the *E*^f calculated herein for the (NH₃)₆Ru^{2+,3+} couple could arise from the appropriate activity coefficient term (a factor of 10 in this term would correspond to 50 mV). However, the *E*^o value reported in ref 4a for the (NH₃)₅RuOH₂^{2+,3+} couple appears to be somewhat too negative.

Using the value of $\Delta S^\circ = -31.2 \pm 0.8$ eu determined by Cohen and Hindman¹² for the reaction



taking $\frac{1}{2}S^\circ_{\text{H}_2}$ as 15.6 eu¹⁸ and assuming $S^\circ_{\text{H}^+} = -5.5$ eu,^{19,20} values of $S^\circ_{(2+)} - S^\circ_{(3+)}$ may be calculated from the ΔS° values determined for reactions 7 and 8. These entropy differences, along with similarly calculated values for related ion pairs, are listed in Table III. The first two entries in this table provide a reference point for the relative ordering of these entropy differences since the large bipyridyl ligands effectively shield the surrounding water structure from the effect of

Table II. Rate Parameters and Equilibrium Quotients for the Reactions of Np(III) and Ru(III)^a

Ru(III) species	k_f , <i>F</i> ⁻¹ sec ⁻¹	<i>Q</i>	<i>T</i> , °C	Determinations ^b
(NH ₃) ₅ RuOH ₂ ³⁺ ^c	0.270 ± 0.019	0.062 ± 0.008	25.0	47
	0.197 ± 0.009	0.110 ± 0.008	15.0	15
	0.150 ± 0.014	0.204 ± 0.017	3.0	10
(NH ₃) ₆ Ru ³⁺ ^d	0.305 ± 0.036	0.031 ± 0.003	25.0	7
	0.226 ± 0.005	0.061 ± 0.002	15.0	7

^a Uncertainties are standard deviations of the sets of measurements. ^b Number of independent determinations. ^c *I* = 1.00 *F*. Range of concentrations of reactants delineated in Table I. ^d *I* = 0.500 *F* (solubility of hexaammineruthenium(III) trifluoromethanesulfonate limits the ionic strength and temperatures that can be studied). [Np(III)]₀ = (1.29–22.6) × 10⁻³ *F*, [Ru(III)]₀ = (9.25–29.5) × 10⁻³ *F*, [Ru(III)]₀/[Np(III)]₀ = 0.37–21.5, [H⁺] = 0.24–0.40 *F*.

Table III. Standard Entropy Differences, in eu^a

Ion pair	$S^\circ_{(2+)} - S^\circ_{(3+)}$	Ref
Fe(bipy) ₃ ^{2+,3+}	-1.4 ± 2.0	20, 21
Ru(bipy) ₃ ^{2+,3+}	+0.4 ± 2.0	21
Ru(NH ₃) ₆ ^{2+,3+}	+4.1 ± 1.9	This work
Ru(NH ₃) ₅ OH ₂ ^{2+,3+}	+17.5 ± 1.1	This work
Fe(OH ₂) ₆ ^{2+,3+}	+48.5	18

^a Calculated by taking $\frac{1}{2}S^\circ_{\text{H}_2} = 15.6$ eu and $S^\circ_{\text{H}^+} = -5.5$ eu.

the charge on the central metal ion, causing $S^\circ_{(2+)} - S^\circ_{(3+)}$ to be essentially zero.^{20,21} The smaller ammonia ligand is not as effective an insulator as bipyridyl and a small positive entropy difference is observed between the hexaammineruthenium 2+ and 3+ ions. This is consistent with the fact that the Ru–N bond distances of these two complexes differ by only 0.04 Å in the solid state.²² The larger entropy difference between the 2+ and 3+ aquopentaammineruthenium ions is consistent with previously correlated data²³ which show that the entropies of complex ions with aquo ligands are more sensitive to variation in charge than those with ammonia ligands. Presumably this effect arises from preferential hydrogen bonding between the structurally similar ligand and solvent,²³ culminating in the large positive $S^\circ_{(2+)} - S^\circ_{(3+)}$ value observed for the hexaquoiron ions.

Kinetic Data. The saturated ligands and substitution-inert character of the (NH₃)₆Ru³⁺ ion preclude its reduction by Np³⁺ through a classical inner-sphere transition state.²⁴ A comparison of the very similar activation parameters for this reaction and the corresponding reduction of the (NH₃)₅RuOH₂³⁺ ion could be used to argue that the same mechanism is involved in both cases. However, this comparison cannot be considered diagnostic for classical outer-sphere reactions since the activation parameters of the reverse reactions do not have similar values. It is possible that these reactions involve a transition state in which one of the oxygens bound to neptunium attacks an octahedral face of the ruthenium complex, thus expanding the ruthenium coordination number to 7.^{24,25} The seven-coordinate transition state for the microscopic reverse reaction, Np⁴⁺ + (NH₃)₆Ru²⁺, is analogous to the previously postulated¹⁷ electrophilic attack by H⁺ on the t_{2g} orbitals of (NH₃)₆Ru²⁺.

The number of systems to which the present study may be compared is limited by the fact that the majority of electron-transfer reactions between highly charged aquo cations pro-

(21) P. George, G. I. H. Hanania, and D. H. Irvine, *J. Chem. Soc.*, 2548 (1959).

(22) H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, 10, 2304 (1971).

(23) P. George, G. I. H. Hanania, and D. H. Irvine, *J. Chem. Phys.*, 22, 1616 (1954).

(24) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1972, Chapter II.

(25) E. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968).

(18) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952.

(19) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill, New York, N. Y., 1953.

(20) J. Lin and W. G. Breck, *Can. J. Chem.*, 43, 766 (1965).

ceed through kinetic paths with inverse hydrogen ion dependencies. White and Newton²⁶ have tabulated the available information on hydrogen ion independent oxidations of f-electron reductants. They note that the activation entropies of these reactions are surprisingly similar (ca. -30 to -35 eu) despite differences in charge type and in the nature of the oxidant. The much more negative activation entropy (ca. -47 eu) observed herein for the oxidation of Np(III) by $(\text{NH}_3)_6\text{Ru}^{3+}$ and $(\text{NH}_3)_5\text{RuOH}_2^{3+}$ is consistent with an unorthodox transition state²⁴ being involved in these reactions. It is interesting to note that it is the more favorable entropy term which provides almost the entire difference in rate between the U(III)- $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ reaction ($k = 1.64 \times 10^3 \text{ F}^{-1} \text{ sec}^{-1}$ at 25°, $\Delta H^* = 3.67 \pm 0.04 \text{ kcal/mol}$, $\Delta S^* = -31.5 \pm 0.3 \text{ eu}$)²⁶ and the Np(III)-Ru(III) reactions. While the greater rate of the U(III)-Co(III) reaction is not unexpected in light of the fact that U(III) is a better reductant than Np(III) by 0.79 V and Co(III) is a better oxidant than Ru(III),^{4b} it is not clear from *a priori* considerations that the predominant factor should be the difference in entropies of activation.

It has been observed that rate ratios of closely related reactions can often be correlated using the Marcus cross relation,²⁷ even though the mechanisms involved may not be outer sphere.^{26, 28} Thus, assuming that the Marcus relation holds in the Np(III)-Ru(III) reactions, the data in Table II may be used to calculate that the $(\text{NH}_3)_6\text{Ru}^{2+,3+}$ exchange rate is 2.5 times as fast as the $(\text{NH}_3)_5\text{RuOH}_2^{2+,3+}$ exchange rate at both 25 and 15°. From Meyer and Taube's^{4a} hexaammine exchange rate of $8.2 \times 10^2 \text{ F}^{-1} \text{ sec}^{-1}$ (25°, $I = 0.013$), the aquopentaammine exchange rate can be estimated as $3.3 \times 10^2 \text{ F}^{-1} \text{ sec}^{-1}$.

For the reverse reactions of eq 7 and 8, values calculated

(26) J. D. White and T. W. Newton, *J. Phys. Chem.*, **75**, 2117 (1971).

(27) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

(28) (a) R. C. Patel and J. F. Endicott, *J. Amer. Chem. Soc.*, **90**, 6364 (1968); (b) T. W. Newton and N. A. Daugherty, *J. Phys. Chem.*, **71**, 3768 (1967).

for k_r ($\text{F}^{-1} \text{ sec}^{-1}$) at 25°, ΔH^* (kcal/mol), and ΔS^* (eu) are 4.37 ± 0.21 , 12.9 ± 0.4 , -12.1 ± 1.2 and 9.8 ± 0.5 , 15.4 ± 1.2 , 3 ± 4 , respectively. The very small activation entropy associated with the $\text{Np}^{4+} + (\text{NH}_3)_6\text{Ru}^{2+}$ reaction is noteworthy. These results may be compared with the kinetic parameters obtained for the hydrogen ion independent path in the reaction between V(II) and Np(IV):²⁹ $k = 2.53 \text{ F}^{-1} \text{ sec}^{-1}$, $\Delta H^* = 9.72 \pm 0.05 \text{ kcal/mol}$, $\Delta S^* = -24.0 \pm 0.2 \text{ eu}$. The authors noted that for this reaction the hydrogen ion, chloride ion, and temperature-dependence data are inconsistent with an inner-sphere mechanism. Thus, the specific rate constants for the reductions of Np(IV) by the t_{2g} -electron donors V(II), $(\text{NH}_3)_6\text{Ru}^{2+}$ and $(\text{NH}_3)_5\text{RuOH}_2^{2+}$ are remarkably similar despite the fact that ΔS^* and ΔH^* vary markedly from system to system. A similar phenomenon has been reported by Price and Taube^{4b} for the reduction of a series of carboxylatopentaamminecobalt(III) complexes by hexaammineruthenium(II) in perchlorate media. This lack of any readily discernible correlation precludes further discussion of the results.

The salient point to be emphasized, however, is the importance of the ΔS^* term in determining the rate of reactions between highly charged ionic species of the type considered in this work. Further developments necessary to aid in the understanding of such observations have been pointed out by Linck.³⁰

Registry No. $\text{Ru}(\text{NH}_3)_6^{2+}$, 19052-44-9; $\text{Ru}(\text{NH}_3)_6^{3+}$, 18943-33-4; $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$, 21393-88-4; $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, 25590-52-7; Np, 7439-99-8.

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(29) M. J. Burkhart and T. W. Newton, *J. Phys. Chem.*, **73**, 1741 (1969).

(30) R. G. Linck in "Transition Metals in Homogenous Catalysis," G. N. Scauzer, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 7.

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Kinetics of the Dissociation of Decavanadate Ion in Basic Solutions

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The kinetics of dissociation of decavanadate ion, $\text{V}_{10}\text{O}_{28}^{6-}$, in basic solution was studied spectrophotometrically from 15 to 50°. At pH 8-10, the rate is independent of pH. In hydroxide ion solution of constant $[\text{M}^+]$ ($\text{M} = \text{Li}, \text{Na}, \text{or K}$), a $[\text{OH}^-]$ -dependent dissociation path exists as well. The rate of dissociation equals $\{k_1 + k_2[\text{OH}^-]\}[\text{V}_{10}\text{O}_{28}^{6-}]_{\text{tot}}$, where $[\text{V}_{10}\text{O}_{28}^{6-}]_{\text{tot}}$ is the total (free and ion-paired) decavanadate ion concentration. k_2 depends on the alkali metal, increasing in the order $\text{Li} < \text{Na} < \text{K}$; $k_2 = 0$ for $(\text{CH}_3)_4\text{N}^+$. The linear dependence of k_2 on $[\text{Na}^+]$ at $\mu = 2.5$ is explained by the presence of a reactive ion pair.

Introduction

Although serious studies on the aqueous solution chemistry of alkali metal vanadates(V) commenced with Dullberg¹ in 1903, it has only been within the last 10 or 15 years that the degree of aggregation of the aqueous vanadates has been reasonably well understood and agreed upon. In particular,

the degree of condensation of the decavanadate ion, $\text{V}_{10}\text{O}_{28}^{6-}$, was difficult to ascertain, partly because of the presence of the weak acids $\text{HV}_{10}\text{O}_{28}^{5-}$ and $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ and because of the slow attainment of equilibrium of the decavanadate ion with the more basic vanadates. Very carefully performed potentiometric studies² and X-ray diffraction analyses of

(1) P. Dullberg, *Z. Phys. Chem.*, **45**, 129 (1903).

(2) F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, **10**, 957 (1956).