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The Formation of a Neptunium(V)–Rhodium(III) Complex. Kinetics and Equilibria in Acidic Solutions[1]

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A Np(V)·Rh(III) complex has been prepared and separated from the reaction mixture, and the absorption spectrum characterized. A value for the equilibrium quotient $Q = [\mathrm{Np(V)\cdot Rh(III)}]/[\mathrm{Np(V)}][\mathrm{Rh(III)}]$ of $3.31 \pm 0.06\ M^{-1}$ at 25° has been determined spectrophotometrically. Values of $\Delta H = -3.6 \pm 0.9$ kcal mole^{-1} and $\Delta S = -10 \pm 3$ eu have been determined. The rate of approach to equilibrium and the rate of dissociation have been measured. The HF-catalyzed rates of dissociation of the Np(V)·Rh(III) and Np(V)·Cr(III) complexes are compared. A kinetic study of the exchange between the aquated ions Cr(III), Rh(III), and Np(V) and O^{18}-labeled solvent water has been carried out with and without added HF. Rates of approach to equilibrium between Np(V) and $[\mathrm{Cr(H_2O)_5Cl}]^+$ and $[\mathrm{Co(en)_2(OH_2)_2}]^{3+}$ are reported.

Introduction

There are a large number of examples of dimeric metal ion species observed during hydrolysis of aquated cations. Such species have been fairly well established for Fe(III) and Cr(III). However, there are a much smaller number of dimeric species known comprised of two different metals. The majority of these have been observed as intermediates in oxidation–reduction processes. Examples of these are the Cr(II), U(VI) reaction to give Cr(III)·U(V)[3] and the Cr(II), Np(VI) reaction to give Cr(III)·Np(V).[4]

In the last example Sullivan showed that Cr(III)·Np(V) was produced by the direct reaction of Cr(III) and $\mathrm{NpO_2^+}$ and the equilibrium quotient as well as the kinetics of formation and dissociation of the dimer was measured. He further showed that many +2 and +3 aquated metal ions associated with $\mathrm{NpO_2^+}$ but that only Cr(III) was kinetically slow. Since of the ions studied, only Cr(III) exchanges its waters slowly, it was of interest to study another nonlabile aquo ion to see if the kinetic lability of the dimer was directly related to the kinetics of water exchange of the aquo ion. With the work of Plumb and Harris[5] showing the slow $\mathrm{H_2O}$ exchange of $\mathrm{Rh(H_2O)_6^{3+}}$ this ion looked especially promising and had the further advantage of being diamagnetic [as opposed to Cr(III)] eliminating possible magnetic interaction with the paramagnetic $\mathrm{NpO_2^+}$.

This paper reports experiments on the thermodynamic and kinetic interaction of $\mathrm{NpO_2^+}$ and $\mathrm{Rh(H_2O)_6^{3+}}$ in acid media and compares the results with those previously obtained with $\mathrm{Cr(H_2O)_6^{3+}}$. Preliminary studies were also made on the association of $\mathrm{NpO_2^+}$ with $[\mathrm{Co(en)_2(OH_2)_2}]^{3+}$ and $[\mathrm{Cr(H_2O)_5Cl}]^{2+}$. For reasons which will be obvious from the text the rate of oxygen exchange between water and $\mathrm{NpO_2^+}$ was studied and the effect of $\mathrm{F^-}$ on the rates of formation and dissociation of Rh(III)·Np(V) and on the water exchange of $\mathrm{Rh(H_2O)_6^{3+}}$, $\mathrm{Cr(H_2O)_6^{3+}}$, and $\mathrm{NpO_2^+}$ were studied.

Experimental Section

Aqueous solutions of $\mathrm{NpO_2^+ClO_4^-}$ were prepared and analyzed as previously described.[6] $\mathrm{Rh(H_2O)_6(ClO_4)_3}$ was prepared as a solid as described by Harris and Plumb.[5] Several samples were made which showed identical spectral properties agreeing with a spectrum kindly supplied by Harris.[5] The salt was not entirely free of $\mathrm{HClO_4}$, and stock solutions were analyzed spectrally and by titration of the excess acid produced when the $\mathrm{Rh^{3+}}$ was absorbed on an ion-exchange resin. Agreement between the two methods was approximately ±1%. Stock solutions 1–3 M $\mathrm{Rh^{3+}}$, 1–2 M $\mathrm{HClO_4}$ did not show any spectral changes over a period of 3 months. Within the experimental error of the kinetic measurements, no kinetic differences were observed which could be attributed to differences in the Rh(III) preparations.

$[\mathrm{Co(en)_2(OH_2)_2}](\mathrm{ClO_4})_3$ was prepared by grinding a mixture of highly purified *trans*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl}$,[7] dilute $\mathrm{HClO_4}$, and $\mathrm{AgClO_4}$ and adding traces of $\mathrm{AgClO_4}$ until the equivalence point was reached. The solution resulting upon filtration gave no test for $\mathrm{Ag^+}$ or $\mathrm{Cl^-}$ and after further acidification was concentrated under vacuum at room temperature. It consisted of primarily the *cis* isomer.[8] The stock solution was analyzed for free $\mathrm{H^+}$ by $\mathrm{OH^-}$ titration and for complex after absorbing it on an ion-exchange resin.

$[\mathrm{Cr(H_2O)_5Cl}]\mathrm{SO_4}$[9] was treated with slightly less than the stoichiometric amount of acidic $\mathrm{Ba(ClO_4)_2}$ until the equivalence point was reached. It was concentrated by vacuum evaporation below room temperature and used immediately. Analysis for acid, total chromium, and hydrolyzed chloro complex is described in the Results section.

All other salts were of reagent grade prepared as standard stock solutions, and these solutions were analyzed for metal ion and free acid by standard procedures.

Solutions for the rate and equilibrium studies were made by injecting small samples of $\mathrm{NpO_2^+}$ or Np(V)·Rh(III) complex solutions into solutions at the proper μ, $[\mathrm{H^+}]$, $[\mathrm{Mg^{2+}}]$, and $[\mathrm{Rh^{3+}}]$. The latter were prepared by weighing the calculated amounts of the appropriate salt stock solutions, diluting to a known volume, and reweighing to obtain the solution density. In the HF catalysis studies the stock HF solution in a polyethylene container was standardized by base titration and small known volumes were injected into the salt solutions just before the

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Resident Research Associate. On leave from the University of Missouri, Columbia, Mo.

(3) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **1**, 368 (1962).

(4) J. C. Sullivan, *ibid.*, **3**, 315 (1964).

(5) W. Plumb and G. M. Harris, *ibid.*, **3**, 542 (1964).

(6) J. C. Sullivan, A. J. Zielen, and J. C. Hindman, *J. Am. Chem. Soc.*, **82**, 5288 (1960).

(7) J. C. Bailar, Jr., *Inorg. Syn.* **2**, 223 (1946).

(8) *cis/trans* = 58: J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

(9) A generous sample was provided by P. Moore and F. Basolo of Northwestern University.

NpO_2^+ or Np(V)·Rh(III) complex was added. In the brief period (1–5 min) between the addition of F^- to the Rh(III) solutions and the start of the reaction, no appreciable F^- is complexed by Rh(III). Further at the concentrations of HF used, little was lost by reaction with the cells during the time of the kinetic measurements even at the elevated temperatures used. However, over longer periods of time (1 day) the [HF] does decrease as evidenced by slower reaction rates.

Concentrated solutions of the complex were made by slowly evaporating (under vacuum) a 1–1 mixture of NpO_2ClO_4 (nearly neutral) with $[Rh(H_2O)_6](ClO_4)_3$ (in dilute acid) to a very small volume. Spectral analysis indicated that approximately 90% of the Np was converted to the complex under these conditions. Further evaporation caused dissociation of the complex and crystallization of $NpO_2ClO_4 \cdot xH_2O$. When a small amount of this concentrated complex solution was added to a cold solution, approximately 1 *M* in HF and NaF, a yellow precipitate was obtained which was the complex fluoride. After careful washing with CH_3OH and acetone and vacuum drying, it gave the following analysis. *Anal.* Calcd for $[NpO_2 \cdot Rh(H_2O)_5]F_4$: Np, 44.1; F, 14.1. Found: Np, 42 ± 2; F, 11 ± 3. This solid complex dissolved in dilute $HClO_4$ and showed the spectrum of the complex with less than 10% free NpO_2^+. However, the complex decomposed very rapidly due to catalysis by F^- as shown more quantitatively later. Although the complex was isolated as a solid fluoride it was never entirely pure. Numerous other attempts to precipitate the complex were made which were uniformly unsuccessful.

Spectrophotometric Measurements.—A Cary Model 14 MR recording spectrophotometer with a thermostated cell compartment was used for all spectral studies. Detailed procedures used in the spectrophotometric studies have been previously described.[4]

Separation Procedures.—The inorganic exchanger, Bio-Rad Zp-1, a zirconium phosphate crystal, was used in a column *ca.* 5–7 cm high, 1 cm in diameter. The exchanger was pretreated with 1 *M* $HClO_4$ and washed with water. An aliquot of the reaction mixture (50–200 λ) was placed at the top of the column. The Rh(III) and Np(V) ions were washed off with 0.5 *M* $HClO_4$ and the Np(V)·Rh(III) complex eluted in 1–2 column volumes with 1.0 *M* $HClO_4$.

After the major portion of this investigation had been completed, it was found possible to separate the complex from a reaction mixture using a low cross-linked Dowex 50W-X2 resin.[10]

The procedure was similar to that described above. The Np(V) and Rh(III) were eluted in 2.0 *M* $HClO_4$. The complex, which was adsorbed as a golden yellow band at the top of the column, was then eluted with 4.0 *M* $HClO_4$.

The ratio of Rh/Np in the complex fraction was 1.05. Successive fractions were analyzed to yield ratios of 1.04 and 1.06, respectively.

Calculations.—The equilibrium under consideration is

$$\text{O–Np–O}^+ + \text{Rh(H}_2\text{O)}_6^{3+} \underset{k_2}{\overset{k_1}{\rightleftarrows}} [\text{O–Np–O–Rh(H}_2\text{O)}_5]^{4+} + \text{H}_2\text{O} \tag{1}$$

where the equilibrium quotient *Q* is defined as[11]

$$Q = [\text{Np(V)}\cdot\text{Rh(III)}]/[\text{Np(V)}][\text{Rh(III)}] \tag{2}$$

Under the experimental conditions, Rh(III) *ca.* 1–0.25 *M* and Np(V) *ca.* 1–4 × 10^{-3} *M*, the initial concentration of the rhodium can be used as the stoichiometric concentration.

At 9912 A, where the complex has a maximum in the absorption spectrum, the equilibrium spectrophotometric data are adequately summarized by the usual expression

$$\epsilon = \epsilon_0 + \epsilon_1 Q[\text{Rh}]/1 + Q[\text{Rh}] \tag{3}$$

where the ϵ are defined in the standard manner[12] and designate, respectively, the test solution, Np(V), and the complex. The least-squares adjustment of the data in terms of (3) was carried out on a CDC 3600 using a nonlinear program developed by the Applied Mathematics Division of this laboratory.

Based upon the assumption that the approach to equilibrium can be described in terms of a first-order process under the experimental conditions employed, the conventional integrated form of the rate equation was used.[13] In terms of the observed absorbance at 9912 A linear plots were obtained for the function

$$\ln (A_e - A) = \alpha + k't \tag{4}$$

where A_e is the absorbance at equilibrium, *A* that at time *t*; the significance of k' will be discussed later; and α is the constant of integration. For the reverse reaction the expression is identical except k' is replaced by k_2.

Use of (4) allows a straightforward graphical estimate of the rate parameter. However, for a least-squares adjustment of the data this expression must be weighted because of the functional form even though the precision in the measured value of the absorbance is the same for all observations. If eq 4 is put into the exponential form

$$A = A_e + (A_0 - A_e)e^{kt} \tag{5}$$

the weighting is not necessary.

Since both forms of the integrated rate expression were used, it is of interest to compare the results of the calculations for a given data set. The experimental observations were on a system where the rate of approach to equilibrium at 35° was under study. There were 65 *A*,*t* observations used in the computation.

In eq 4 $A_e = 0.496$. The calculated values of the rate parameter and constant of integration were $k' = 8.42 \pm 0.04 \times 10^{-4}$ sec^{-1} and $A_e - A_0 = 0.3889 \pm 0.0009$. Values calculated from eq 5 were: $A_e = 0.492 \pm 0.005$, $k' = 8.66 \pm 0.05 \times 10^{-4}$ sec^{-1}, and $A_e - A_0 = 0.3861 \pm 0.0005$.

The differences in the parameters calculated by the two equations (which are not statistically significant at the 3σ level) are due to the fact that the two expressions while mathematically equivalent are not equivalent in the computational procedure. In (4) the value of A_e is fixed while this is a floating parameter in (5).

Use of eq 4 has the advantage that the parameters to be determined enter the expression in a linear manner. Equation 5 utilized a Gaussian iterative procedure which cannot be guaranteed to converge.

Choice of the form of the integrated expression that should be used is not solely dictated by such considerations. If the experiments are carried out at elevated temperatures over a period of several days (as was the case in the present study) there are a number of factors which give rise to concern over the correct value of A_e. For example, possible evaporation of water from the reaction mixture, leaching of material from the cell walls, etc., would suggest eq 5 provides a more significant computational procedure.

O^{18} Exchange Experiments.—The rate of exchange study of H_2O with the Rh(III) and Cr(III) aquo ions was carried out by diluting concentrated, equilibrated rhodium(III) and chromium(III) perchlorate solutions in normal water with enriched water. At time intervals, samples were precipitated with an HF–NaF[14] solution, and after drying a portion of the complexed water was removed under vacuum at 90–120°. The water was collected, weighed, and equilibrated for 3 days with a known weight of CO_2 of known isotopic composition. The CO_2 was then separated from the water and the 46/44 ratio measured on a CEC mass spectrometer, or in the later experiments the 46/(44 + 45) ratio was measured on a Nuclide RMS spectrometer. Both instruments were shown to be linear in the region 0.004 to 0.040 [46/(44 +

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[10] Dr. T. J. Weeks, University of Colorado, suggested the use of this resin.

[11] The water molecules coordinated to the linear O–Np–O$^+$ ion in the equatorial plane and those in the first coordination sphere of the Rh(III) will not be generally represented. Equation 1 is meant to indicate that bonding in the complex is between Rh(III) and one of the neptunyl ion oxygen atoms.

[12] J. A. Christiansen, *J. Am. Chem. Soc.*, **82**, 5520 (1960).

[13] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 186.

[14] L. B. Anderson and R. A. Plane, *Inorg. Chem.*, **3**, 1470 (1964).

45)] using standards. The precision was ±1% and ±0.1% over this range, respectively. The isotope ratios were all normalized to a value of 0.002 for O^{18}/O^{16} in normal water. Conversion of the CO_2 enrichments to those of H_2O were made following the expression given by Dostrovsky.[15]

Simultaneous rate measurements were made in the presence and absence of F^-. The primary function of these experiments was to show the presence or absence of a F^- catalysis of the water exchange.

In order to ascertain the magnitude of the rate of exchange of neptunyl ion oxygens with water, nearly neutral solutions of $NpO_2^+ClO_4^-$ were evaporated to near dryness[16] under vacuum at 30–35°. Water of different O^{18} content was added with cooling and as soon as mixing was complete, a sample of water was evaporated and collected. At time intervals water samples were obtained. The final sample was taken after several days at 25° and 8 hr at 50°. The O^{18}/O^{16} ratio of the water was obtained after equilibration with CO_2 as given above. A definite change in the O^{18} content of the water was found with time in the direction expected for slow exchange of the NpO_2^+ oxygens with water which could not be due to a fractionation factor in the solvent evaporation. This is also verified by the fact that the same conclusion was reached whether enriched H_2O and normal NpO_2^+ or normal H_2O and enriched NpO_2^+ was used. From the t_0 and t_∞ values, making a correction for the amount of water removed between the t_0 and t_∞ samples, the number of neptunyl oxygens could be calculated using atom % O^{18} calculated as $100R/(2 + 2R)$. Since the mass spectrometer used at this time was only good to ±1%, precise rates could not be obtained and the reproducibility in the number of neptunyl oxygens is not as good as expected.

Attempts were made to find a satisfactory precipitating agent of NpO_2^+ for isotopic rate studies. After numerous trials were made, no entirely satisfactory precipitating agent was found. The hydroxide, if of constant composition, might have served. Experiments designed to evaluate $NpO_2(OH)(xH_2O)$ showed that (a) it did not have a constant composition and (b) OH^- precipitation did not cause oxygen exchange between NpO_2^+ and H_2O. The experiments were carried out in two ways.

(1) Neptunyl hydroxide (normal) was precipitated from normal water with dilute $NaOH–H_2O$ and washed and dried under vacuum. It was dissolved in 8× enriched water with a drop or two of $HClO_4$ (11 M) and reprecipitated with 1 or 2 drops of 50% NaOH solution in normal water. The neptunium hydroxide was washed with 8× enriched H_2O and then acetone and dried under vacuum. The solid was treated by the Anbar method[17] to convert it to CO_2 and this analyzed for O^{18} content. The opposite of these experiments was also carried out where the enriched and normal oxygens were reversed

(2) Neptunyl perchlorate was equilibrated for 3–8 days with enriched H_2O and the solvent removed under vacuum. The solid was dissolved in normal water and precipitated with dilute NaOH. The neptunyl hydroxide was washed with normal H_2O and dried under vacuum. It was then converted to CO_2 (by the Anbar method[17]), which was analyzed for O^{18} content. The reverse was also tried where the enrichment was opposite that given. This method was used for the rate studies carried out by the "hydroxide method" with sampling at various times after solution in normal water.

The final $NpO_2^+–H_2O$ exchange experiments were carried out using 71% O^{18} water. A purified acid-free NpO_2ClO_4 (normal) solution was evaporated to dryness under vacuum at 45° and dissolved in 71% O^{18} water. The ~2 M solution was equilibrated for 4 days during which time complete exchange was expected to occur. (It was found later that complete exchange had not occurred.) The solvent water was removed to near dryness and 0.05 M $HClO_4$ (normal H_2O) added. The mixture was divided into two portions, to one of which a very small volume of concentrated NaF in normal H_2O was added. Aliquots of each solution (at 25°) were taken at time intervals and frozen in liquid N_2, and a portion (~50%) of the solvent water was transferred under vacuum. This water was weighed and equilibrated with a known amount of CO_2 (normal) for 3 days at 25°. The CO_2 was separated and its O^{18} content determined on the RMS mass spectrometer. Calculations involved in obtaining the $H_2O–O^{18}$ atom per cent from the CO_2 enrichment followed that given above. The over-all rate of exchange R of NpO_2^+ was calculated using the expression.

$$R = \frac{0.693}{t_{1/2}} \frac{2[NpO_2^+][H_2O]}{2[NpO_2^+] + [H_2O]}$$

and the rate constants were calculated using $R = k[NpO_2^+]$.

Infrared Spectra.—The infrared spectra were obtained on Beckman IR-10 and Perkin-Elmer 421 instruments as Nujol mulls, thin ground solids, or concentrated aqueous solutions. In the brief contact time necessary, no reaction between the AgCl cells and the concentrated neptunium solutions was observed. $K_3[Np(OX)_2O_2]$[18] and $K[NpCO_3O_2]$[19] were prepared by previously described procedures. The iodates were prepared by precipitation of NpO_2^+ or the complex with a concentrated $NaIO_3$ solution, NpO_2F and the $Rh^{3+}–NpO_2^+$ fluoride were prepared analogously using a concentrated NaF–HF solution, and NpO_2Cl and NpO_2ClO_4 were prepared as nearly saturated solutions from the hydroxide by the addition of the appropriate acid in slight excess followed by evaporation under vacuum.

A study was made of the infrared changes in the 1000–500 cm^{-1} region as an equimolar mixture of NpO_2ClO_4 and $Rh(H_2O)_6ClO_4$ converted to the binuclear complex. In this study $Rh(H_2O)_6ClO_4$ and NpO_2ClO_4 were brought together and evaporated to a high concentration, and samples were taken at timed intervals. Each sample was analyzed for free NpO_2^+ and for complex by dissolving in 1 M $HClO_4$ and measuring the spectra (9800 and 9912.5 A). The samples were also used for infrared analysis sandwiched between AgCl disks. It was not possible to get exactly the same thickness of absorbing solution each time but any major changes in the infrared spectra upon complexation of NpO_2^+ with $Rh(H_2O)_6^{3+}$ would have been observed.

Results

Spectrophotometric.—The molar extinction coefficients of the characteristic bands of the Np(V)·Rh(III) complex determined on solutions of the pure complex which had been separated by the exchange procedure are presented in Table I. The values listed are averages of three independent determinations and the average standard deviation is between 3 and 4%.

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF CHARACTERISTIC BANDS OF Np(V)·Rh(III) COMPLEX IN 1.0 M $HClO_4$ AT 25°

λ, A	ε, l. M^{-1} cm^{-1}	λ, A	ε, l. M^{-1} cm^{-1}
11,200	9.1	7850	10.8
11,030	33.0	6870	7.9
10,250	13.4	6650	9.5
9,912.5	244	6125	25.3
9,800	22.3	5770	7.7
9,210	3.3	4790	24.4
8,370	23.4	4130	93.1
		2200	3726

Equilibrium Data.—The summary of the least-squares adjustment of the equilibrium observations is presented in Table II. The uncertainties listed are the com-

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[15] I. Dostrovsky and F. S. Klein, *Anal. Chem.*, **24**, 414 (1952).

[16] The dried NpO_2ClO_4 was shown by infrared to contain water, and by isotopic dilution methods (O^{18}) to contain slightly less than one water per NpO_2ClO_4.

[17] M. Anbar and S. Guttmann, *J. Appl. Radiation Isotopes*, **5**, 233 (1959).

[18] D. M. Gruen and C. A. Hutchison, Jr., *J. Chem. Phys.*, **22**, 386 (1954).

[19] T. K. Keenan and F. H. Kruse, *Inorg. Chem.*, **3**, 1231 (1964).

TABLE II

SUMMARY OF LEAST-SQUARES ADJUSTMENT OF EQUILIBRIUM DATA AT 9912.5 A (μ = 8.00 WITH $Mg(ClO_4)_2$; [Np(V)] = (1.0–4.0) × 10^{-3} M)

T, °C	ϵ_0, M^{-1} cm^{-1}	ϵ_1, M^{-1} cm^{-1}	Q, M^{-1}
25	23 ± 1	185 ± 20	3.31 ± 0.06[a]
35	17 ± 2	190 ± 15	2.37 ± 0.28[b]
35	29 ± 5	220 ± 22	3.53 ± 0.64[c]
50	20 ± 3	181 ± 17	2.16 ± 0.22[d]

[a] [Rh] = 0.25–1.00 M, [H$^+$] = 0.50–2.00 M. [b] [Rh] = 0.25–1.00 M, [H$^+$] = 1.0–2.00 M. [c] [Rh] = 0.20–1.20 M, [H$^+$] = 2.00 M, μ = 10.0. [d] [Rh] = 0.25–1.00 M, [H$^+$] = 0.50–2.00 M.

puted standard deviations for from 10 to 15 independent observations at each temperature. The observations at 35 and 50° include those made on solutions initially 2.1 × 10^{-3} M in HF, as well as those in which the ionic strength was maintained by $Y(ClO_4)_3$. Replicate measurements with two or three different rhodium perchlorate preparations gave consistent results.

From the data presented in Table II the calculated values of the partial molar heat and entropy changes at 25° are $\Delta H = -3.6 \pm 0.9$ kcal mole^{-1} and $\Delta S = -10 \pm 3$ eu.

Kinetic Data.—Table III contains a summary of the first-order rate constants measured for the reaction

$$\text{Np(V)}\cdot\text{Rh(III)} \xrightarrow{k_2} \text{Np(V)} + \text{Rh(III)} \qquad (6)$$

TABLE III

SUMMARY OF RATE CONSTANTS FOR THE REACTION

$$\text{Np(V)}\cdot\text{Rh(III)} \xrightarrow{k_2} \text{Np(V)} + \text{Rh(III)}$$

T, °C	k_2, sec^{-1}	[HClO$_4$], M	Added salt	μ
50	8.39 ± 0.08 × 10^{-4}	0.01	$LiClO_4$	1.00
50	5.46 ± 0.05 × 10^{-4}	0.10	$LiClO_4$	1.00
50	4.38 ± 0.14 × 10^{-4}	1.00		1.00
50	4.50 ± 0.02 × 10^{-4}	2.00	$Mg(ClO_4)_2$, $Y(ClO_4)_3$[a]	8.00
50	4.69 ± 0.08 × 10^{-4}	2.00	$Y(ClO_4)_3$	8.00
35	7.31 ± 0.30 × 10^{-5}	2.00	$Y(ClO_4)_3$	8.00
35	6.03 ± 0.06 × 10^{-5}	2.00	$Mg(ClO_4)_2$, $Y(ClO_4)_3$[a]	8.00
35	5.59 ± 0.05 × 10^{-5}	1.00		1.00
25	1.20 ± 0.01 × 10^{-5}	1.00		1.00
25	1.94 ± 0.08 × 10^{-5}	2.00	$Y(ClO_4)_3$	8.00
50	4.65 ± 0.18 × 10^{-4}	0.991	0.009 M SCN$^-$	1.00
50	3.13 ± 0.03 × 10^{-4}		1 M HCl	1.00

[a] 0.5 M $Y(ClO_4)_3$, 1.0 M $Mg(ClO_4)_2$.

The majority of the measurements were performed by diluting a concentrated equilibrium mixture by a factor of *ca.* 100. Measured rates with solutions of the complex that had been separated from such a mixture were the same (within their respective standard deviations) as those obtained by the dilution procedure.

Most of the values were obtained by measuring the rate of disappearance of the complex at 9912 A. In a number of cases the rate of the reaction was determined by measuring the rate of appearance of Np(V) at 9800 A. The values obtained for k_2 at both wavelengths were the same within the precision indices assigned to either set of observations.

A value for the experimental activation energy, E = 27.3 ± 0.4 kcal, is obtained from a weighted least-squares adjustment of the rate constants determined in 1.00 M perchloric acid. The value calculated for ΔS^* in the usual manner from the equation of absolute reaction rate theory[20] is 8.6 ± 0.9 eu at 25°.

The specific rate for the approach to equilibrium is pseudo-first order, as is to be expected since the concentration of Rh(III) is 10^2–10^3 times greater than that of Np(V). In Table IV is presented a summary of the values obtained for this apparent first-order rate constant. All entries represent the average value of k' determined for duplicate or triplicate measurements including sets with different initial stock solutions. The uncertainties are the standard deviations from these average values presented. It was found that HF at concentrations of the order of 10^{-3} M catalyzed the formation of the complex without altering its spectral characteristics or its equilibrium value. For example, at 50° and [Rh] = 0.50 M, k' = 76.0 ± 0.2 × 10^{-5} sec^{-1}. Under identical conditions with 2.1 × 10^{-3} HF added k' = 236 ± 3 × 10^{-5} sec^{-1}. The catalyzed path was shown to be first order with respect to F$^-$ added.

TABLE IV

SUMMARY OF k' VALUES

(μ = 8.00 with $Mg(ClO_4)_2$, [H$^+$] = 2.00 M, [Np(V)] = (1.8–3.6) × 10^{-3} M)

T, °C	k' × 10^5, sec^{-1}	Rh(III), M	T, °C	Rh(III), M	k' × 10^5, sec^{-1}
25	4.73 ± 0.05	1.74[a]	35	1.200	27.1 ± 0.9[c]
25	3.09 ± 0.24	1 06[b]	35	0.80	22.4 ± 0.4[c]
25	3.09 ± 0.03	1.00	35	0.60	21.6 ± 0.3[c]
25	6.13 ± 0.06	0.80[c]	35	0.40	18.5 ± 0.8[c]
25	3.45 ± 0.14	0.75	35	0.20	12.7 ± 0.7[c]
25	3.60 ± 0.71	0.50	35	1.00	11.77 ± 0.04
25	1.57 ± 0.04	0.50[d]	35	0.75	11.91 ± 0.03
25	2.74 ± 0.04	0.50[e]	35	0.50	11.52 ± 0.03
25	2.37 ± 0.03	0.50[f]	35	0.50	9.52 ± 0.03
25	2.81 ± 0.13	0.25	35	0.25	10.08 ± 0.05
50	89.0 ± 2.4	1.00			
50	84.3 ± 0.5	0.75			
50	76.0 ± 0.2	0.5			
50	65.8 ± 0.3	0.25			
50	56.3 ± 0.5	0.5[g]			

[a] μ = 10.44, [H$^+$] = 0.45 M. [b] μ = 6.36, [H$^+$] = 1.61 M. [c] μ = 10.00. [d] μ = 5.00. [e] [H$^+$] = 1.00 M. [f] [H$^+$] = 0.50 M. [g] μ maintained with $Y(ClO_4)_3$.

The catalysis of the dissociation of the Cr(III) and Rh(III) complexes by HF is demonstrated in Figure 1. From these data the rate expression that describes the catalyzed path is $R = k$[complex][F$^-$] with $k = 6.4 \times 10^{-1}$ and 1.1×10^{-1} M^{-1} sec^{-1} for the Rh and Cr systems, respectively, at 50°, 1 M $HClO_4$, and ~10^{-3} M complex.

Results of some additional spectrophotometric studies using *trans*-diaquobis(ethylenediamine)cobalt(III) perchlorate (1.0 M in 1 M $HClO_4$) show that the rate constant for approach to equilibrium with NpO_2^+ at 9890 A at 50° is $k' = 1.3 \times 10^{-4}$ sec^{-1}. Under comparable concentration conditions for Rh(III), $k' = 8.9 \times 10^{-4}$, and Cr(III), $k' = 2.0 \times 10^{-4}$ sec^{-1}. With 1.41 M $[(H_2O)_5CrCl](ClO_4)_2$ and 1.06 M $HClO_4$, k' =

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[20] S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp 195–199.

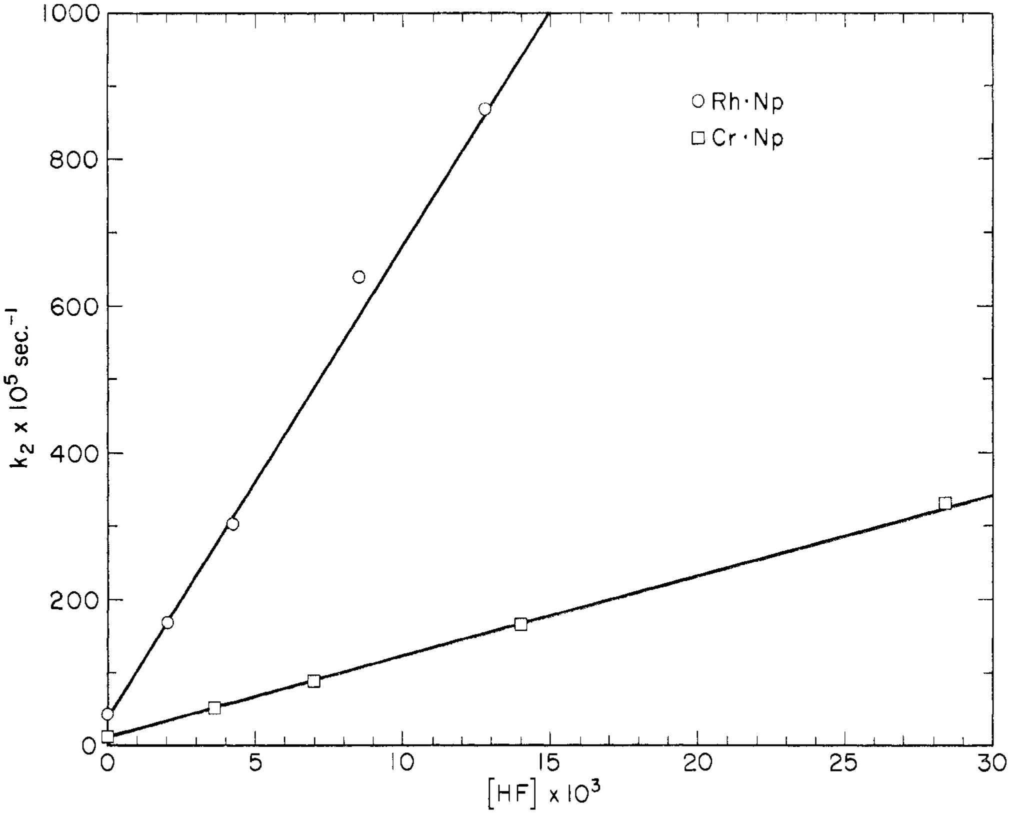

Figure 1.—Effect of HF on the dissociation of the Rh(III)·Np(V) and Cr(III)·Np(V) complexes at 50°, 1.0 *M* $HClO_4$, and complex concentrations *ca.* 10^{-3} *M*.

$1.24 \pm 0.03 \times 10^{-4}$ $\sec^{-1}$ at 9800 A and $1.30 \pm 0.02 \times 10^{-4}$ $\sec^{-1}$ at 9925 A at 25°. After equilibrium had been attained less than 8% of the monochloro species had aquated and at 50% reaction less than 4% as determined by ion-exchange–spectrophotometric analysis.[21] It is interesting to note the *k'* is at least a factor of 10 greater than the previously measured value, $k' = 6.5 \times 10^{-6}$ $\sec^{-1}$ (0.96 *M* $Cr(H_2O)_6^{3+}$, 2.0 *M* $HClO_4$).

$Rh(H_2O)_6^{3+}$, $Cr(H_2O)_6^{3+}$–H_2O Exchange.—The graph of ln $(1 - F)$ *vs.* *t* for the two metal ions in the absence and presence of F^- is shown in Figure 2. It is apparent that at these concentrations no fluoride catalysis can be discerned. There is some curvature to the graphs which does not alter the above conclusion. It results from a small error in N_∞ or in some induced exchange during precipitation. The observed half-time for exchange with Rh(III) was 510 min, Rh = 0.87 *M*, $HClO_4$ = 0.74 *M*, 75° compared to that calculated from the data of Plumb and Harris,[5] 421 min. With Cr(III) $t_{1/2}$ = 3200 min (Cr = 1.09 *M*, $HClO_4$ = 0.82 *M*, 25°), which is apparently somewhat slower than the estimated value of 2400 min calculated from previous measurements.[22]

NpO_2^+–H_2O Exchange.—Table V gives a summary of the over-all rates of NpO_2^+–H_2O exchange under different conditions and by different methods. Table VI shows a summary of experiments leading to the determination of the number of slowly exchanging oxygens attached to Np(V). The average value is 2.1 ± 0.2. Table VIII shows the results of studies on $NpO_2OH \cdot xH_2O$ as a potential precipitating agent for use in NpO_2^+–H_2O exchange studies. Analysis of one sample of the carefully dried hydroxide gave 78.7 ± 1.1% Np. (No Np(IV) or Np(VI) was present.) This is to be compared with $NpO_2(OH) \cdot H_2O$, 77.96% Np.

Table VII shows the measurements of the rate of NpO_2^+–H_2O exchange in the presence and absence of F^-. From this, using a linear least-squares calculation, the following values were obtained (25°, $[H^+] = 5 \times 10^{-2}$ *M*, $[NpO_2^+] = 7.38 \times 10^{-2}$ *M*)

	No F^-	10^{-3} *M* F^-
$t_{1/2}$, min	143.8 ± 8.4	152.4 ± 8.9
$10^5 R$, *M* $\sec^{-1}$	1.182 ± 0.069	1.116 ± 0.068

An empirical form of the rate law is $R = k[Np(V)]^2 \cdot [H^+]^{0.5}$. The third entry in Table V does not conform to this expression, presumably due to the fact that the hydrogen ion concentration changed markedly during the sampling procedure. The most reliable value of the rate constant calculated from the data of Table VII is 9.45 ± 0.28 $M^{-2.5}$ $\sec^{-1}$.

Table IX gives the absorption frequencies for the asymmetrical Np–O_2^+ stretch for a group of related compounds. The band is rather diffuse and is shifted somewhat by the presence of coordination ions. Figure 3 shows the changes in the infrared spectrum of a 1–1 mixture of Rh^{3+} and NpO_2^+ as aquated perchlorates at approximately 2 *M* concentration as a function of

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(21) We are indebted to Dr. R. Thompson for help in analyzing these solutions.

(22) (a) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **18**, 757 (1950); (b) J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954).

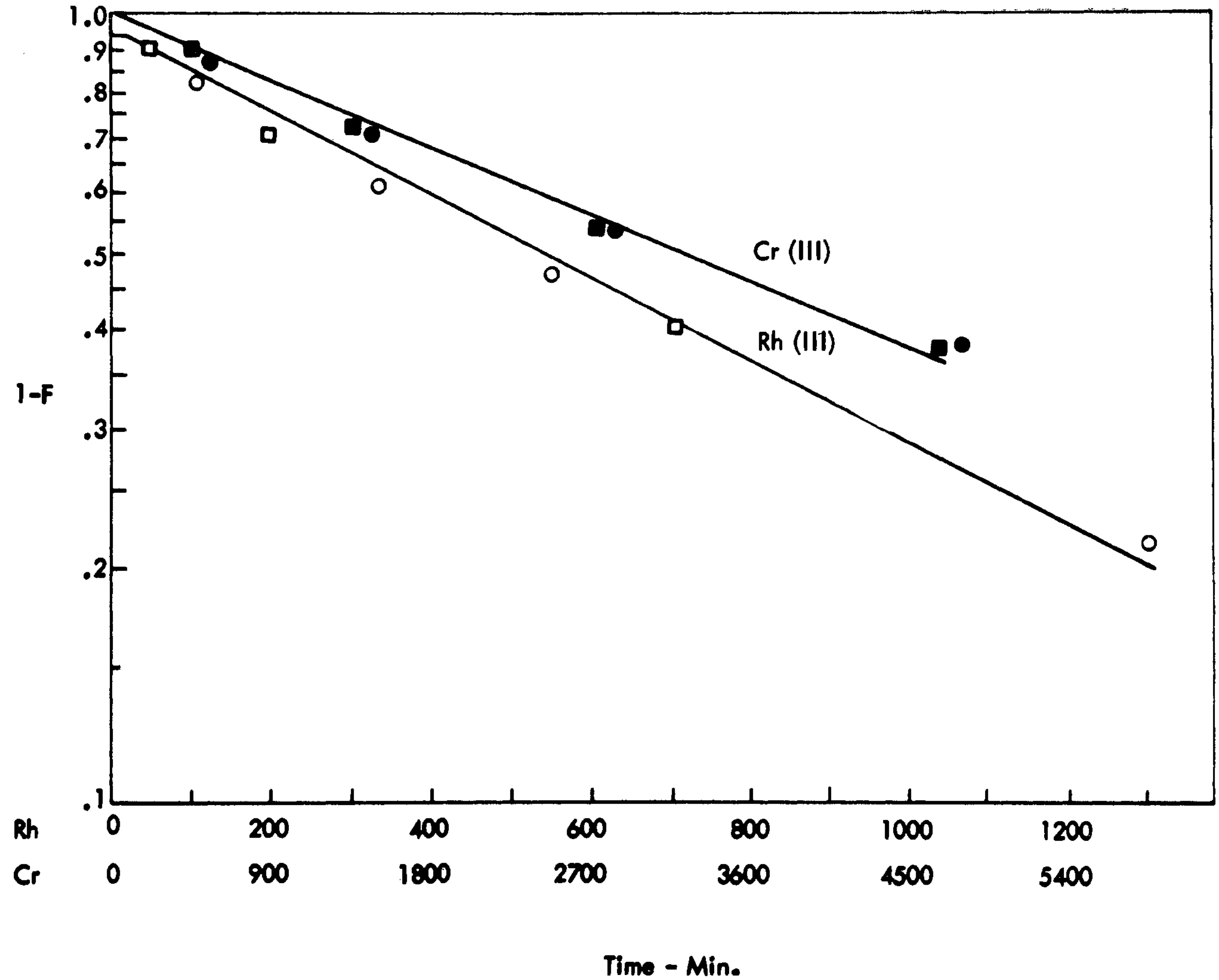

Figure 2.—$M(H_2O)_6{}^{3+}$–H_2O exchange rates. Cr: [Cr(III)] = 1.09 *M*; $[H^+]$ = 0.815 *M*; No F^- (●), F^- (■) = 9.9 × 10^{-3} *M*; 25.0° Rh: [Rh(III)] = 0.871 *M*; $[H^+]$ = 0.741 *M*; No F^- (○), F^- (□) = 9.9 × 10^{-3} *M*; 75°.

TABLE V

RATE OF $NpO_2{}^+$–H_2O EXCHANGE AT 25°

Method	$[NpO_2{}^+]$, *M*	$[H^+]$, *M*	$t_{1/2}$, min	*R*, *M* sec^{-1}
Hydroxide[a]	2.28 × 10^{-3}	3.35 × 10^{-2}	3900 ± 240	1.35 ± 0.08 × 10^{-8}
H_2O[b]	1.72	2.0 × 10^{-5}	230 ± 6	1.63 ± 0.04 × 10^{-4}
H_2O[b]	0.862	0.20	18.3 ± 1.8	1.06 ± 0.09 × 10^{-3}
H_2O[b,c]	0.0738	0.050	148.1 ± 8.7	1.15 ± 0.10 × 10^{-5}

[a] Normal $NpO_2{}^+$, enriched H_2O, $(NpO_2)OH$ sampled. [b] Enriched $NpO_2{}^+$, normal H_2O, water sampled. [c] Average of two runs, A and AF.

TABLE VI

OXYGEN ISOTOPE DILUTION STUDIES

$[NpO_2{}^+]$, *M*	$[H^+]$, *M*	Temp, °C	Neptunyl oxygens/Np
3.44[a]	10^{-4}	0	2.21
0.862[b]	0.20	25	2.29
1.72[b]	2 × 10^{-5}	25	1.89
		Av	2.1 ± 0.2

[a] Normal $NpO_2{}^+$, enriched H_2O. [b] Enriched $NpO_2{}^+$, normal H_2O.

fraction converted to the complex. No significant changes occur, suggesting that bond formation is weak and disrupts the $NpO_2{}^+$ entity only slightly. This is in accordance with the small spectral shifts observed in the visible region.

TABLE VII

$NpO_2{}^+$–H_2O EXCHANGE RATES

($[NpO_2{}^+]$ = 0.0738 *M*, $[H^+]$ = 0.050 *M*, 25.0 ± 0.1°)

Run A		Run AF ($[F^-]$ = 1 × 10^{-3} *M*)	
Time, min	*N* × 10^3	Time, min	*N* × 10^3
3.4	7.205	3.8	7.202
29.6	7.226	30.1	7.220
70.1	7.254	70.8	7.261
135.0	7.281	134.3	7.287
249.8	7.345	250.3	7.338
326.5	7.378	327.4	7.384
390.7	7.397	390.0	7.388
458.5	7.413	459.2	7.410
1346	7.438	1346	7.439
1832	7.436	1832	7.436
∞	7.437	2781	7.438
		∞	7.437
Slope = 8.03 ± 0.47 × 10^{-5}		Slope = 7.58 ± 0.46 × 10^{-5}	

TABLE VIII

APPARENT O^{18} CONTENT OF $NpO_2(OH)\cdot xH_2O$

(25°, $[NpO_2^+] = 1.03 \times 10^{-2}$ *M*, $[H^+] = 3.5 \times 10^{-3}$ *M*)

Time, min	$N \times 10^3$		$N \times 10^3$
2.6	4.063	Final H_2O	2.036
41.4	4.115[a]	Final Washes	2.000
62.4	3.897[a]	NpO_2^+ oxygens (from equilibrated H_2O)	6.095
96.5	4.134		
122	3.998		
188	3.957[a]		
300	4.098		

Type	*T*, °C	$[NpO_2^+]$, *M*	$[H^+]$, *M*	Labile O/NpO_2^+ [d,e]
b	25	0.00228	0.0335	0.75
c	25	0.010	8×10^{-4}	2.97
c	25	0.0035	0.0035[f]	2.04
c	0	0.0172	0.004	4.47
b	0	0.086	1×10^{-4}	1.02

[a] $Hg(CN)_2\cdot HgCl_2–NpO_2OH\cdot H_2O$ heated for an additional 9 hr at 400–420°. [b] Normal NpO_2^+, enriched H_2O. [c] Enriched NpO_2^+, normal H_2O. [d] Assuming two nonexchanging oxygens per NpO_2^+. [e] For pure $[NpO_2]OH$, assuming Anbar method converts both types of oxygen equivalently to CO_2, this ratio would be 1.0. [f] F^- present 0.0027 *M*.

TABLE IX

Compound	State	NpO_2^+ asym str, cm^{-1}
$[NpO_2–Rh]^{4+}(ClO_4^-)$	Concd aq soln	830
$NpO_2ClO_4(aq)$	Concd aq soln	819
$KNpO_2CO_3$	Nujol mull	848, 828
$NpO_2ClO_4\cdot H_2O$	Solid	800, 760
$K_3Np(OX)_2O_2$	Nujol mull	790
$NpO_2(OH)\cdot xH_2O$	Nujol mull	800, 760
NpO_2Cl	Concd aq soln	750 br
$[NpO_2–Rh]^{4+}(F^-)$	Solid	775

Discussion

Spectra.—The spectrum of the Np(V)·Rh(III) complex is characterized by an intense band at 2200 A, a broad band with a maximum at 4130 A, and sharp bands with maxima at 6125 and 9912 A.

The absorption band at 2200 A was not observed for the Np(V)·Cr(III) complex which, as is the case for the hydrated Np(V) ion, exhibits what is presumably the shoulder of an intense allowed transition in this region. The band at 4130 A may be tentatively identified as a modification of the original Rh(III) band at 3960 A.

The hydrated Np(V) ion has a sharp absorption band at 6160 A. Upon complex formation with both Cr(III) and Rh(III) the maximum of this transition is shifted very slightly toward the ultraviolet. It should be noted that Rh(III) is transparent at this wavelength.

At 9912 A the new absorption band probably arises from the original transition that is observed at 9800 A.

The same types of changes between complex and constituent absorption spectra were observed for the Np(V)·Cr(III) complex and are again not amenable to a simple ligand field interpretation.

Equilibrium.—The value obtained for the association quotient of the Np(V)·Cr(III) complex at 25° was 2.62 ± 0.48. The fact that this is essentially the same value[23] as obtained in this investigation for the Np(V)·Rh(III) complex suggests that there is no strong dependence on the electronic structure of the trivalent cations in this association reaction. This is a bit surprising when one remembers that the ground state of the Cr(III) ion is $3d^3$ (paramagnetic) while Rh(III) has a $4d^6$ spin-paired ground state. This implies that electrostatic interactions may be of primary importance in the association reactions under consideration. The fact that the enthalpies of formation for the rhodium (−3.6 ± 0.9 kcal $mole^{-1}$) and chromium (−3.3 ± 0.6 kcal $mole^{-1}$) complexes are the same within the experimental uncertainties is consistent with such an interpretation.

Kinetic Behavior.—The set of data in Table IV provides the basis for the following: (a) the rate of approach to equilibrium is dependent upon the initial Rh(III) concentration; (b) any hydrogen ion dependent path is not of primary importance if indeed the observed variation of k' with hydrogen ion indicates the existence of such a path and is not the operation of a medium effect, and (c) there are significant changes in k' caused by variation of solution composition and ionic strength.

If k' is evaluated as

$$k' = k_1^0[\mathrm{Rh(III)}]e^{\alpha[\mathrm{Rh(III)}]} + k_2^0e^{\alpha[\mathrm{Rh(III)}]}$$

the parameters k_1^0 and k_2^0 are approximately corrected for medium effects. Operationally, k_2 is determined at essentially zero Rh(III) concentration. As has been noted[24] the above treatment corrects the observed k' values to the same solution composition conditions under which k_2 was measured.

The numerical evaluation of k_1 was carried out by a least-squares adjustment of the data in the form

$$k' - k_2/[\mathrm{Rh(III)}] = k_1 + \alpha[\mathrm{Rh(III)}]$$

Values calculated for k_1 are $8.89 \pm 0.63 \times 10^{-4}$, $1.60 \pm 0.05 \times 10^{-4}$, and $7.23 \pm 0.41 \times 10^{-5}$ sec^{-1} $mole^{-1}$ at 50, 35, and 25°, respectively. The associated values calculated for α are $(-4.6 \pm 0.8) \times 10^4$, $(-1.0 \pm 0.1) \times 10^{-4}$, and $(-5.4 \pm 0.4) \times 10^{-5}$, respectively.

From these values of k_1 and the measured values of k_2 (in 2.0 *M* perchloric acid and an ionic strength of 8.0) calculated values of $Q = k_1/k_2$ are 1.93 ± 0.14, 2.40 ± 0.25, and 3.73 ± 0.26 at 50, 35, and 25°, respectively.

It is evident that the kinetic and equilibrium data are consistent within the stated limits.

A comparison of the values obtained for the rates of dissociation of the Rh and Cr complexes ($1.20 \pm 0.01 \times 10^{-5}$ and 2.28 and 0.03×10^{-6} sec^{-1}, respectively at 25° and 1.00 *M* $HClO_4$) with the rates of water exchange at 25° (3.0×10^{-8} and 3.5×10^{-5} sec^{-1} for Rh(III) and Cr(III), respectively) provides the basis for the following mechanistic interpretation.

It is highly unlikely that the water exchange process is rate determining in the dissociation of the Np·Rh complex. This coupled with the fact that the experi-

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(23) The difference between the two numbers probably represents the difference in activity coefficients of 1 *M* chromium perchlorate as compared to 1 *M* rhodium perchlorate.

(24) This interpretation of the treatment was suggested by Professor E. L. King during the course of conversations.

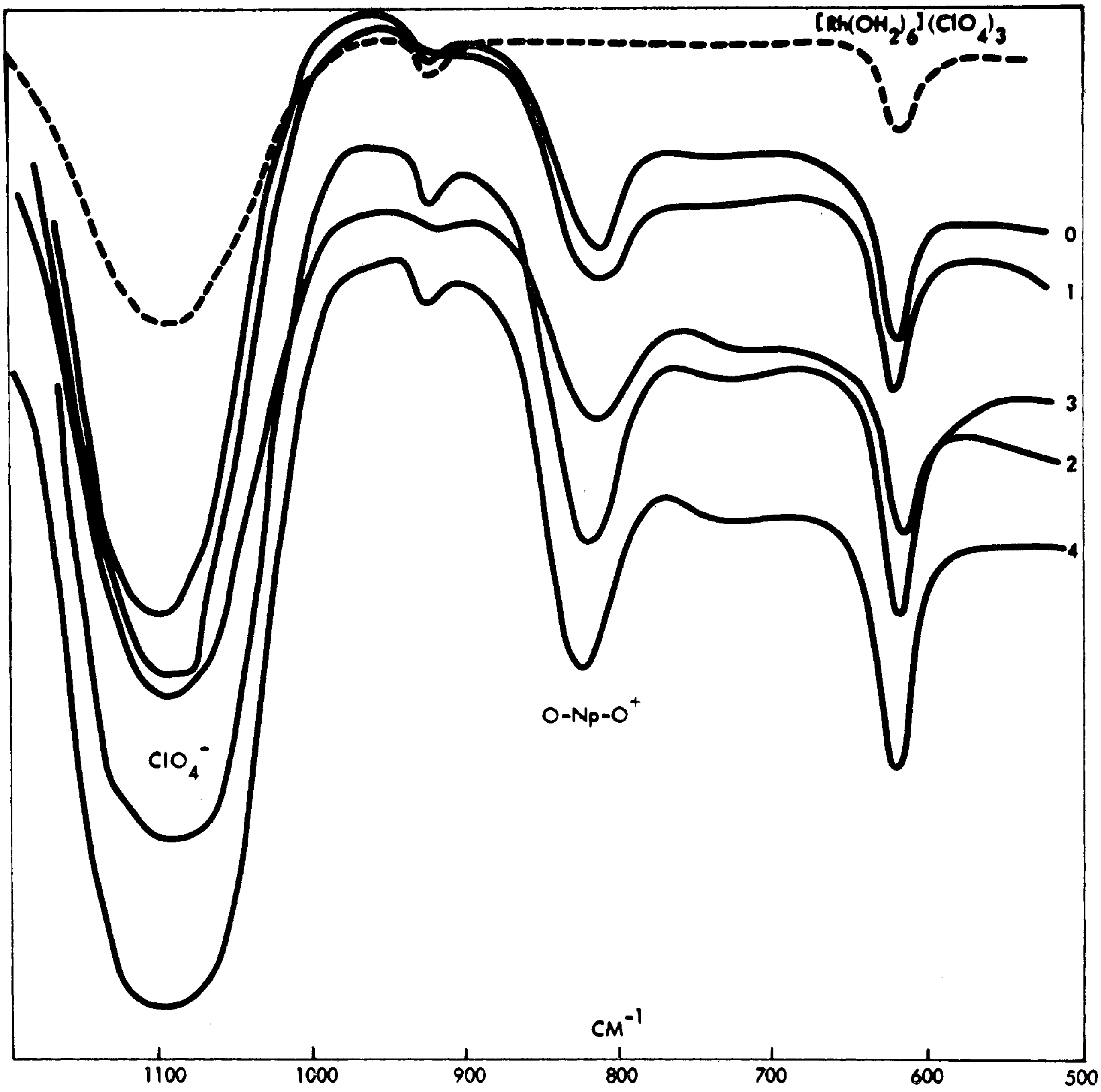

Figure 3.—Infrared spectra of a 1–1 Rh(III)–NpO_2^+ mixture as a function of fraction of complex formed. NpO_2^+ free/NpO_2^+ complexed: 0, 4.83; 1, 2.73; 2, 0.88; 3, 0.73; 4, 0.67.

mental activation energies for the dissociation of the Np·Rh and Np·Cr complexes are the same within the experimental uncertainties, 27.3 ± 0.4 and 28.3 ± 0.8 kcal, respectively, provides the basis for the hypothesis that the complexes are formed by substitution on the $O–Np–O^+$ ion.

Rabideau[25] has reported oxygen-exchange studies on NpO_2^{2+} and explained his data in terms of a path involving fast oxygen exchange with trace amounts of NpO_2^+ followed by fast electron exchange with NpO_2^{2+}. Thompson and Sullivan have shown[26] that in 1 *M* perchloric acid the Np(V)–oxygen exchange is not instantaneous. In order to compare the kinetics of Rh(III)–Np(V) formation with the $NpO_2^+–H_2O$ exchange, it was necessary to measure the exchange rate in a direct fashion. At low acid concentrations the rate of $H_2O–NpO_2^+$ exchange was directly measurable. Although we were not able to measure the rate constant for oxygen exchange with NpO_2^+ under the conditions of Rh(III)–Np(V) complex formation because of the extremely low $[NpO_2^+]$ and the presence of foreign ions (Rh^{3+}, Mg^{2+}) it was possible to demonstrate that the rate increased with acid concentration and with either $[NpO_2^+]$ or with increasing ionic strength.

A possible means of demonstrating that $NpO_2^+–H_2O$ exchange is intimately connected with the formation and dissociation of the Rh(III)–Np(V) complex was suggested by the fact that F^- (or HF) catalyzed the latter reactions. If the $NpO_2^+–H_2O$ exchange was catalyzed by HF then it would be highly likely that the

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[25] S. W. Rabideau, *J. Phys. Chem.*, **67**, 2655 (1963).

[26] R. C. Thompson and J. C. Sullivan, *J. Am. Chem. Soc.*, **89**, 1098 1967).

rate-determining step in the formation and dissociation of the complex involved Np–O fission. However, the presence of HF at concentrations comparable to those in the formation–dissociation studies did not alter the NpO_2^+–H_2O exchange rate. Further HF did not modify the rates of H_2O exchange with either Rh(III) or Cr(III). Unfortunately, it was not possible to study fluoride catalysis of the NpO_2^+–H_2O exchange at $\mu = 8$ to 10 and 1 *M* $HClO_4$ where the complex formation was studied. On the basis of this work 10^{-3} *M* F^- or HF catalyzes the formation and dissociation of the complex but does not affect the rate of H_2O exchange of NpO_2^+, Cr(III), or Rh(III).

These observations are even more perplexing in view of the result that 1 *M* HCl has little or no effect on the rate of dissociation.

The only metal ions which form binuclear complexes with NpO_2^+ at a slow rate are those whose water exchange rates are slow. If the rapidly exchanging equatorial waters of $NpO_2^+ \cdot H_2O$ were being substituted by $M(H_2O)_6^{3+}$, one would expect fast reactions in all cases. Thus it is doubtful that equatorial waters play the dominant role in complex formation or dissociation. Rather it appears that a neptunyl oxygen is replaced in the kinetically important step.

At $\mu = 8$–10 and 1–2 *M* $HClO_4$ the NpO_2^+–H_2O exchange can be estimated from this work to be very rapid compared to the formation and dissociation of the complex. In view of the fact that Rh(III) and Cr(III) are nearly identical in their behavior it is reasonable to suggest that $M(H_2O)_6^{3+}$ competes with solvent H_2O for the active intermediate formed in the oxygen exchange of NpO_2^+. Because of its high (3+) charge, the metal ion is relatively unsuccessful compared to water, and the rate of water exchange is much greater than that for complexation. Since it was not possible to demonstrate fluoride catalysis of the rate of oxygen exchange of the metal ions in question the catalytic effect is not useful in attempting to more fully understand the mechanism of complex formation. We are unable to present a plausible and meaningful explanation for this marked fluoride catalysis.

The infrared spectra on neptunium complexes establish a small change in the asymmetrical stretching frequency, ν_3, as a function of equatorial environment. In the solid state several frequencies are sometimes observed, suggesting that all lattice positions are not equivalent. In aqueous media at low acid concentrations there is only a small observable change in the stretching frequency as association with Rh^{3+} takes place. The infrared spectra of the solid complex fluoride also showed no significant change. These observations suggest either that bonding is so weak that the O–Np–O bonds are hardly altered or that bonding is not through the axial oxygens. For reasons cited above, the former explanation appears more reasonable.

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Magnetic Properties of Potassium Tribromocuprate(II) and Cesium Tribromocuprate(II)

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The magnetic susceptibilities of potassium tribromocuprate(II) and cesium tribromocuprate(II) have been determined over a temperature range of 80–300°K. The magnetic behavior of potassium tribromocuprate(II) conforms to a modified Bleaney–Bowers equation, indicating the existence of a weak antiferromagnetic spin interaction between $[Cu_2Br_6]^{2-}$ dimer ions as well as of a strong spin coupling within the dimers. On the other hand, the slight paramagnetism of cesium tribromocuprate(II) obtained after corrections for diamagnetic contributions shows no variation with temperature, indicating that the unpaired electrons are completely coupled.

Introduction

The binuclear structure of copper(II) acetate monohydrate has been established by X-ray crystal analysis.[1] The compound is a typical example of isolated binuclear clusters, the temperature dependence of its magnetic susceptibility being clearly interpreted by a simple singlet–triplet formula proposed by Bleaney and Bowers.[2]

A recent X-ray crystal analysis carried out by Willett, *et al.*,[3] has shown that potassium trichlorocuprate(II) contains $[Cu_2Cl_6]^{2-}$ dimer ions piled on top of one another to form one-dimensional infinite arrays. They have also reported that potassium tribromocuprate(II) is isomorphous with potassium trichlorocuprate(II). In view of the crystal data, one would suspect a possible spin interaction between copper atoms belonging to different dimer ions as well as between copper atoms within the dimers. However, the magnetic moment of

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(1) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

(2) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* (London), **A214**, 451 (1952).

(3) R. D. Willett, C. Dwiggins, Jr., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, **38**, 2429 (1963).