

between five and six  $F^-$ ) is similar to spectra obtained at the lowest  $NH_4F$  concentrations (2  $M$ ) which could be studied. These observations are consistent with the hypothesis that the average ligand number is about six in 2  $M$   $NH_4F$  and approaches eight in saturated  $NH_4F$ .

As noted in the Experimental section, the molar extinction coefficient of U(IV) at 662  $m\mu$ ,  $E_{662}$ , shows a fairly small but clearly established decrease with increasing U(IV) concentration in 7  $M$   $NH_4F$  (see Fig. 4). In contrast,  $E_{662}$  is independent of U(IV) concentration in 12  $M$   $NH_4F$ . These observations can be explained assuming that U(IV) forms dimers (or other polymers) with a low  $E_{662}$  in 7  $M$   $NH_4F$  and that these are depolymerized in the presence of very high  $F^-$  concentrations. Such dimers might well involve hydroxide or oxide bridging, particularly since the  $NH_4F$  solutions are slightly basic. However, at least one case of fluoride bridging is well established,<sup>23</sup> and this may constitute another example. The observed decrease ( $E_{662} = 29.4 - 200M$ ) is consistent with the formation of dimers with a constant  $K_d = [U(IV)_2]/[U(IV)]^2$  greater than 3.4 l./mole. This minimum value is obtained if  $E_{662}$  for the dimer is assumed equal to 0.

**Anion-Exchange Absorption of  $UF_4$ .**—Dissolution of insoluble salts by cation exchangers is well known (e.g.,  $BaCO_3$  by  $H^+$ -form resin).<sup>24</sup> The absorption of  $UF_4$  by fluoride-form anion exchanger differs in that no reaction product is given off, but instead the  $UF_4$  enters the resin and adds to the exchangeable  $F^-$  originally present. The anion-exchange absorption of  $UF_4$  from

(23) R. L. Rau and J. C. Bailar, Jr., *J. Electrochem. Soc.*, **107**, 745 (1960).

(24) F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 226.

a water slurry provides a striking demonstration of the tendency of U(IV) to form anionic complexes with  $F^-$ . Examination of the U(IV) spectrum also is made possible in a system similar in many respects to aqueous solutions but with the additional advantage that an indication of the ligand number may be obtained from the stoichiometry. This type of ion-exchange absorption has apparently not been reported previously. It should be useful with a wide variety of systems in which complex anionic species are formed readily.

In the Experimental section it was noted that saturation was reached when 0.60 mole of  $UF_4$  were absorbed for each mole of  $F^-$  originally present in the resin. Thus, for each 0.6 mole of U(IV) there are 3.4 moles of  $F^-$ . This composition is consistent with the presence of 0.4 mole of  $UF_6^{-2}$  and 0.2 mole of  $UF_5^-$  per equivalent of exchange capacity. This high degree of absorption of  $UF_4 \cdot 2.5H_2O$  (which is very sparingly soluble in water) indicates correspondingly large formation constants for  $UF_5^-$  and  $UF_6^{-2}$  in the resin phase. In fact, the absorption can be most readily explained by assuming a formation constant  $k = (UF_5^-)/(UF_4)(F^-)$  several orders of magnitude larger than that found in dilute HF solutions.<sup>11</sup> On the other hand, the visible spectra of resin samples containing only small amounts of  $UF_4$  were indistinguishable in form from those of resin saturated with  $UF_4$ . This suggests that higher complexes such as  $UF_7^{-3}$  and  $UF_8^{-4}$  have far less tendency to form within the resin than in concentrated  $NH_4F$  solutions.

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CONTRIBUTION FROM THE CHEMISTRY DIVISION  
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## The Formation of a Neptunium(V)-Chromium(III) Complex. Kinetics and Equilibria in Perchlorate Solutions<sup>1</sup>

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A value for the equilibrium quotient  $Q = [Np(V) \cdot Cr(III)]/[Np(V)][Cr(III)]$  of  $2.62 \pm 0.48$  at 25° has been determined spectrophotometrically. Values of  $\Delta H = -3.3 \pm 0.6$  kcal. and  $\Delta S = -9.0 \pm 1.9$  e.u. have been determined. The rates of formation and aquation of the complex  $Np(V) \cdot Cr(III)$  have been measured. The complex is also formed by the reduction of Np(VI) with Cr(II).

### Introduction

It has been demonstrated previously that Np(V) and Cr(III) ions, in aqueous perchloric acid-perchlorate media, react to produce a substituted chromic complex ion.<sup>2</sup> A detailed study of the thermodynamic and kinetic variables of this reaction is of interest since (a) complex ion formation between cations, in a non-complexing medium, extends our knowledge of ionic

interactions in solution; (b) this represents a convenient system to study the properties of a species analogous to the intermediates U(V)-Cr(III)<sup>3</sup> and Pu(V)-Fe(III)<sup>4</sup> which have been investigated by Newton in the course of kinetic studies.

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

(2) J. C. Sullivan, *J. Am. Chem. Soc.*, **84**, 4256 (1962).

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

(4) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

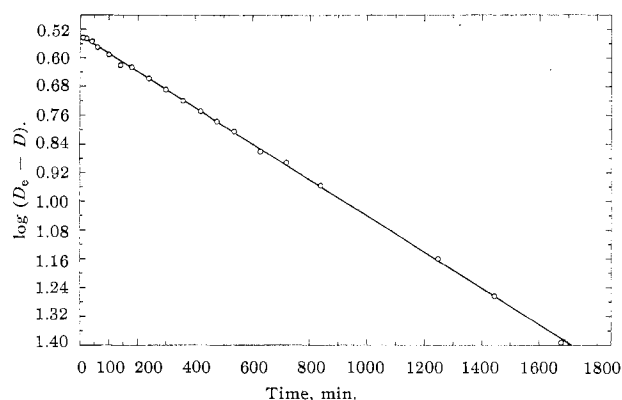


Fig. 1.—A typical plot of the variation of  $\log(D_e - D)$  as a function of time: 0.500 *M* chromic perchlorate, 0.500 *M* yttrium perchlorate, 2.00 *M* perchloric acid,  $2.42 \times 10^{-3}$  *M* Np(V) at 35°. The line is drawn for the calculated slope of  $(5.01 \pm 0.04) \times 10^{-4}$ .

Anticipating results to be presented, the fact that the Np(V)–Cr(III) complex is formed upon reduction of Np(VI) with Cr(II) is direct evidence that this species can be produced by an oxidation–reduction reaction.

### Experimental

**Reagents.**—The preparation and standardization of stock solutions of perchloric acid, sodium, magnesium, Np(V), Np(VI), and yttrium perchlorates have been described in a previous publication.<sup>5</sup> Chromic perchlorate solutions prepared by twice recrystallizing G. F. Smith material and by the method of Postmus and King<sup>6</sup> gave completely equivalent results in kinetic and equilibrium studies. Both preparations were relatively free of polymeric Cr(III) species, based on the criteria suggested by Altman and King,<sup>7</sup> with values for  $\epsilon_{230}/\epsilon_{260}$  of 0.55 and 0.20, respectively, for the two preparations. The Cr(II) perchlorate was prepared, stored, and dispensed essentially in the manner described by Lingane<sup>8</sup> with the apparatus scaled down by a factor of *ca.* 50. Conventional radiometric and analytical techniques were used to standardize the solutions.

**Procedures.**—In studying the approach to equilibrium 2 or 5 cm. silica absorption cells were filled with a measured volume of the Cr(III) perchlorate solution containing the appropriate amount of inert perchlorate salt and perchloric acid. Absorption measurements were made from 10,000 to 9500 Å. with a Cary Model 14 spectrophotometer. An aliquot of Np(V) solution was then introduced into the cell, and the measurements were repeated as a function of time.

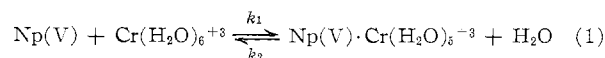
In studies of the aquation reaction, samples of the separated complex were introduced into the absorption cells, and the optical density (from 10,000 to 9500 Å.) was measured as a function of time. Additional experiments used a dilution technique. A solution originally 1.3 *M* in Cr(III), 1.0 *M* in HClO<sub>4</sub>, and 0.14 *M* in Np(V) (all as perchlorates) was equilibrated for several weeks. An aliquot of this solution was then introduced into the absorption cell containing the indicated salt solutions. The dilution factor was *ca.* 60.

The sample compartment of the spectrophotometer was thermostated to within  $\pm 0.05^\circ$ . A thermostated water bath was used to store the absorption cells between readings and until equilibrium was attained.

The average precision of the optical density measurements of the equilibrium solutions was  $\pm 0.003$ .

The reduction experiments were performed using either a 2-cm. absorption cell or a three-necked pear-shaped flask. The Np(VI) was placed in the reaction vessel and flushed with CO<sub>2</sub>.<sup>8</sup> The Cr(II) solution was then introduced while the solution was stirred by gas bubbling. The absorption cell, or an aliquot measured into an absorption cell in the latter case, was then placed in the spectrophotometer for measurement. These experiments were performed at  $25 \pm 1^\circ$ .

**Calculations.**—For the reaction



an equilibrium quotient,  $Q$ , is defined as

$$Q = [\text{Np(V)·Cr(III)}]/[\text{Np(V)}][\text{Cr(III)}]^3 \quad (2)$$

At 9925 Å. the equilibrium spectrophotometric data are adequately represented by the familiar expression

$$\epsilon = \epsilon_0 + \epsilon_1 Q[\text{Cr(III)}]/1 + Q[\text{Cr(III)}] \quad (3)$$

where the  $\epsilon$ 's are defined in the standard manner<sup>10</sup> and designate, respectively, the test solution, Np(V), and the complex. It should be noted that under the conditions of the experiments, [Cr(III)] *ca.* 1–0.3 *M* and [Np(V)] *ca.*  $2\text{--}4 \times 10^{-3}$  *M*, the initial concentration of Cr(III) can be used as the stoichiometric concentration.

The weighted least-squares adjustment of the data in terms of (3) was carried out on an IBM 704 using a generalized least-squares program developed by the Applied Mathematics Division of this laboratory. The weighting factor arises from the functional relationship since the precision in the measured optical densities was the same for all observations.

Based upon the assumption that the approach to equilibrium in eq. 1 is a first-order process under the experimental conditions employed, the conventional integrated form of the rate equation was used.<sup>11</sup> In terms of the observed optical density at 9925 Å. linear plots (see Fig. 1) were obtained with the function

$$\ln(D_e - D) - \alpha + k't \quad (4)$$

where  $D_e$  is the optical density at equilibrium and  $D$  that at any time  $t$ ; the significance of  $k'$  will be discussed later, and the parameter  $\alpha$  allows the best fit to the data without the restriction that the extrapolated value of  $D_0$  is used. Such a treatment is desirable to minimize the effect of errors in the true zero time and/or accelerated reaction speed due to high local concentrations before complete mixing of the reactants. The values calculated for  $\alpha$ , which were in all cases in satisfactory agreement with those obtained by graphical methods, were then used as starting estimates for  $\epsilon_0$  in eq. 3.

For the reverse reaction the appropriate expression is identical.

After the preliminary graphical analysis actual treatment of the data was accomplished by weighted least squares calculations using an IBM 704 computer. Again weighting was introduced because of the functional form employed since the precision of the observed optical density values was the same at all points.

### Results and Discussion

**Equilibria.**—The nature of this system coupled with experimental expediency necessitated that the association reaction be studied in solutions *ca.* 1 *M* in chromic perchlorate. It is with trepidation that one uses the concept of “constant ionic strength” in such a medium. However, to investigate the system in any detail it is necessary to vary the Cr(III) concentration.

(9) The water molecules coordinated to the linear O–Np–O<sup>+</sup> ion in the equatorial plane and those in the first coordination sphere of the Cr(III) will not be generally represented. Equation 1 is meant to imply bonding between Cr(III) and one of the linear oxygen atoms of the Np(V).

(10) J. A. Christiansen, *J. Am. Chem. Soc.*, **82**, 5520 (1960).

(11) A. A. Frost and R. G. Pearson, “Kinetics and Mechanism,” 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 186.

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

(6) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1209 (1955).

(7) C. Altman and E. L. King, *J. Am. Chem. Soc.*, **83**, 2826 (1961).

(8) J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **20**, 425 (1948).

TABLE I  
SUMMARY OF LEAST-SQUARES ADJUSTMENT OF EQUILIBRIUM DATA AT 9925 Å.  
 $\mu = 8.0$ ,  $[\text{HClO}_4] = 2.0 \text{ M}$ ,  $[\text{Np(V)}] = 2-4 \times 10^{-3} \text{ M}$ ,  $[\text{Cr(III)}] = 0.25-0.95 \text{ M}$

Series	Temp., °C.	Added salt	$\epsilon_0$	$\epsilon_1 Q$	$Q$
A	50.0	$\text{Mg}(\text{ClO}_4)_2$	$19.58 \pm 0.08$	$340 \pm 13$	$1.99 \pm 0.12$
B	50.0	$\text{Y}(\text{ClO}_4)_3$	$19.6 \pm 0.5$	$339 \pm 18$	$2.12 \pm 0.19$
C	35.0	$\text{Mg}(\text{ClO}_4)_2$	$16.2 \pm 0.1$	$432 \pm 17$	$2.71 \pm 0.16$
D	25.0	$\text{Mg}(\text{ClO}_4)_2$	$15.70 \pm 0.08$	$439 \pm 52$	$2.62 \pm 0.48$

The results of one such a series of experiments are presented graphically in Fig. 2. Table I contains a summary of the values calculated for the parameters in eq. 3, along with their standard deviations, for the equilibrium data.

The choice of trivalent cations that are suitable as substitutes for the chromic ion is limited since interaction between Np(V) and a number of such cations is known to occur.<sup>2</sup> Of the salts that do not exhibit such interaction, yttrium perchlorate was chosen on the basis of qualitative similarity between the variation of the activity coefficient (with concentration) of  $\text{YCl}_3$  and  $\text{CrCl}_3$  or  $\text{Cr}(\text{NO}_3)_3$ .<sup>12</sup>

As long as one is plagued with the impracticality of evaluating activity coefficients in solutions of mixed electrolytes (especially in a concentration range such as is under consideration here) it is not possible to assert that a physical interpretation of an equilibrium quotient, as defined by eq. 2, is unique. A comparison of the results presented in series A and B does, however, increase the probability that the given interpretation is valid.<sup>13</sup>

At 9925 Å, a value may be calculated for  $\epsilon_1 = 168 \pm 37$  from the results of series D. The value previously determined for the complex at that wave length is  $223 \pm 4$  in a medium of 1 M perchloric acid. This implies that the physical significance attached to  $\epsilon_1 Q$  in eq. 3 is valid and at the same time indicates the magnitude of the uncertainties to be expected in the spectrum of a weak complex when derived in this manner.

From the data presented in Table I, the partial molar heat and entropy changes have been calculated<sup>14</sup> for reaction 1. At 25°  $\Delta H = -3.3 \pm 0.6$  kcal. and  $\Delta S = -9.0 \pm 1.9$  e.u.

The salient feature of the model for the  $[\text{O-Np-O-Cr}(\text{OH}_2)_5]^{+4}$  complex previously presented,<sup>2</sup> *i.e.*, that the Cr(III) ion is not in a strong repulsive electrostatic field, is consistent with the small negative value obtained for  $\Delta H$ . Because of the original drastic assumptions in the calculations based upon this model, any

attempts at refinements utilizing the experimental data are not warranted.

The negative value of the entropy change provides additional evidence confirming this point as is evident from the following considerations.

King<sup>15</sup> has pointed out the importance of correcting  $\Delta S$  values for the symmetry numbers of reactant and product species in complex ion reactions. In applying this procedure to reaction 1, it is assumed that: (a) the molecules of water in the equatorial plane of the Np(V) ion are left unchanged upon complex formation and (b) the spatial arrangement of the five molecules of water left in the coordination sphere of the Cr(III) ion is the same before and after complex ion formation. The correction factor calculated on this basis is +3.9 e.u.<sup>16</sup>

If the number of water molecules in the equatorial plane of Np(V) decreases upon complex formation, there would be an increase in this calculated value. In addition, there would be a significant increase in  $\Delta S$  for the reaction due to the liberation of the water molecule or molecules.

The spectrophotometric changes used for the evaluation of  $Q$  are due only to the formation of an inner-sphere complex between Np(V) and Cr(III). No evidence was found for the existence of an outer-sphere complex. This is not surprising in view of the observations discussed by King<sup>17</sup> concerning the stability of the outer-sphere complexes of hexaquo-chromium(III) ion.

**Kinetic Studies of the Dissociation and Formation of the Np(V)·Cr(III) Complex.**—Table II contains a summary of the first-order rate constants measured for the reaction  $\text{Np(V)} \cdot \text{Cr(III)} \xrightarrow{k_2} \text{Np(V)} + \text{Cr(III)}$ . Most of these values were obtained by following the disappearance of the complex as measured at 9925 Å. In a number of experiments the course of the reaction was followed by measuring the appearance of Np(V) as measured at 9800 Å. The values obtained for  $k_2$  at both wave lengths were the same within the standard deviation computed for either set of observations.

The data presented in Table II form a set that is sufficient to support the following conclusions: (a) The reaction is first order in the complex over a concentration range of a factor of 3. (b) The presence of the products, in concentrations *ca.* 20 times greater for Cr(III) and equal to  $[\text{Np(V)}]$ , the initial concentra-

(12) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1959, p. 502.

(13) As has been pointed out by Professor T. F. Young, this does not imply that we can expect  $Q$  to be invariant when salts other than Mg and Y perchlorates are used to maintain the ionic strength.

(14) Standard least-squares techniques were used for the calculation of  $\Delta H$  and the error is the standard deviation based upon external consistency. The error in  $\Delta H$  is based upon the computations previously described and that in  $\Delta S$  upon the familiar "Propagation of Errors." These computational techniques were used only to present an objective assessment of the results for  $\Delta H$  and  $\Delta S$  and do not imply that the conditions necessary for an unambiguous application of these calculational procedures were rigorously fulfilled.

(15) E. L. King and P. K. Gallagher, *J. Phys. Chem.*, **63**, 1073 (1959).

(16) This computation only provides for changes in the rotational partition functions. It is not feasible to estimate changes in the vibrational partition functions based upon the same models.

(17) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).

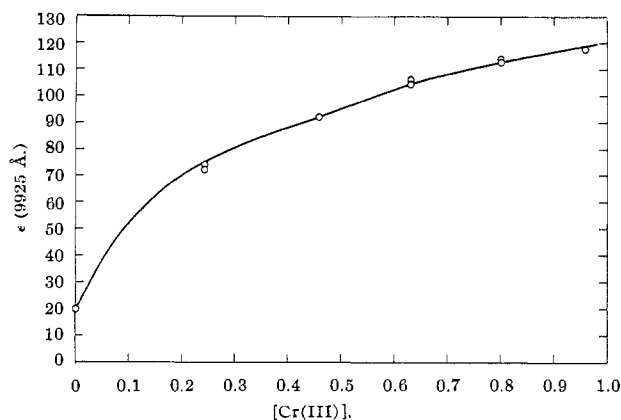


Fig. 2.—The variation of  $\epsilon$  at 9925 Å. with Cr(III) concentration. The smooth curve was calculated from the parameters of series A in Table I.

TABLE II  
SUMMARY OF RATE CONSTANTS FOR THE REACTION

T, °C.	$\text{Np(V)} \cdot \text{Cr(III)} \xrightarrow{k_2} \text{Np(V)} + \text{Cr(III)}^a$			
	$k_2$ , sec. <sup>-1</sup>	[HClO <sub>4</sub> ], M	Added salt	$\mu$
25.0	$(2.34 \pm 0.08) \times 10^{-6}$	1.00	<i>b</i>	1.02
25.0	$(2.28 \pm 0.03) \times 10^{-6}$	1.00		1.16
25.0	$(4.97 \pm 0.05) \times 10^{-6}$	0.023		0.15
25.0	$(1.91 \pm 0.03) \times 10^{-6}$	0.023	NaClO <sub>4</sub>	8.12
25.0	$(4.14 \pm 0.03) \times 10^{-6}$	0.023	LiClO <sub>4</sub>	0.35
25.0	$(2.51 \pm 0.02) \times 10^{-6}$	0.23		0.35
35.0	$(1.11 \pm 0.01) \times 10^{-5}$	1.00		1.16
35.0	$(1.24 \pm 0.01) \times 10^{-5}$	2.00	Y(ClO <sub>4</sub> ) <sub>3</sub>	8.00
35.0	$(1.14 \pm 0.01) \times 10^{-5}$	2.00	NaClO <sub>4</sub>	8.00
35.0	$(1.00 \pm 0.01) \times 10^{-5}$	0.38	Y(ClO <sub>4</sub> ) <sub>3</sub>	8.00
50.0	$(9.43 \pm 0.04) \times 10^{-5}$	1.00		1.16
50.0	$(10.17 \pm 0.10) \times 10^{-5}$	2.00	Y(ClO <sub>4</sub> ) <sub>3</sub>	8.00
50.0	$(9.71 \pm 0.07) \times 10^{-5}$	2.00	Y(ClO <sub>4</sub> ) <sub>3</sub>	8.00
50.0	$(9.08 \pm 0.17) \times 10^{-5}$	0.38	NaClO <sub>4</sub>	8.00
50.0			Y(ClO <sub>4</sub> ) <sub>3</sub>	
50.0			NaClO <sub>4</sub>	

<sup>a</sup> All errors are twice the standard deviation. In all experiments the concentration of the complex is  $1-3 \times 10^{-3} M$ , [Cr(III)] = 0.02 M, and [Np(V)] =  $8 \times 10^{-4} M$  except *b*. <sup>b</sup> Average value obtained from five independent column separations of the complex from two stock solutions. No Cr(III) or Np(V) initially present.

tion of the complex, has no observable effect on the rate of the reaction. (c) There are no paths that make a significant contribution to the observed rate which involve hydrogen or perchlorate ions.

A value for the experimental activation energy,  $E = 28.3 \pm 0.8$  kcal., is obtained from a weighted least-squares adjustment of the appropriate data.<sup>18</sup>

The value calculated for  $\Delta S^*$ , in the customary manner from the equation of absolute reaction rate theory,<sup>19</sup> is  $8.8 \pm 2.8$  e.u. at 25°. This positive value of  $\Delta S^*$  is consistent with the concept that there is a decrease in the strength of the bond between the Np(V) and Cr(III) molecules in the activated complex.

(18) The calculations were made using the ten independent values of  $k_2$  obtained in molar perchloric acid at the three temperatures. Weights were based on the standard deviations previously computed.

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

TABLE III  
SUMMARY OF  $k'$  VALUES

$\mu = 8.0, 2.0 M \text{ HClO}_4$ ,  $[\text{Np(V)}]_0 = 1-3 \times 10^{-3} M$

T, °C.	$k'$ , sec. <sup>-1</sup>	[Cr], M	Added salt
25.0	$(6.49 \pm 0.02) \times 10^{-6}$	0.9619	
25.0	$(6.04 \pm 0.02) \times 10^{-6}$	0.7986	Mg(ClO <sub>4</sub> ) <sub>2</sub>
25.0	$(5.61 \pm 0.02) \times 10^{-6}$	0.6308	Mg(ClO <sub>4</sub> ) <sub>2</sub>
25.0	$(5.33 \pm 0.02) \times 10^{-6}$	0.4604	Mg(ClO <sub>4</sub> ) <sub>2</sub>
25.0	$(4.61 \pm 0.02) \times 10^{-6}$	0.2936	Mg(ClO <sub>4</sub> ) <sub>2</sub>
35.0	$(2.71 \pm 0.02) \times 10^{-5}$	0.9619	
35.0	$(2.66 \pm 0.02) \times 10^{-5}$	0.7986	Mg(ClO <sub>4</sub> ) <sub>2</sub>
35.0	$(2.42 \pm 0.01) \times 10^{-5}$	0.6308	Mg(ClO <sub>4</sub> ) <sub>2</sub>
35.0	$(2.14 \pm 0.01) \times 10^{-5}$	0.4820	NaClO <sub>4</sub>
35.0	$(1.92 \pm 0.02) \times 10^{-5}$	0.4815	Y(ClO <sub>4</sub> ) <sub>3</sub>
35.0	$(2.20 \pm 0.02) \times 10^{-5}$	0.4606	Mg(ClO <sub>4</sub> ) <sub>2</sub>
35.0	$(2.01 \pm 0.01) \times 10^{-5}$	0.2936	Mg(ClO <sub>4</sub> ) <sub>2</sub>
50.0	$(2.03 \pm 0.01) \times 10^{-4}$	0.9619	
50.0	$(1.94 \pm 0.02) \times 10^{-4}$	0.7986	Mg(ClO <sub>4</sub> ) <sub>2</sub>
50.0	$(1.88 \pm 0.04) \times 10^{-4}$	0.7555	Y(ClO <sub>4</sub> ) <sub>3</sub>
50.0	$(1.75 \pm 0.02) \times 10^{-4}$	0.6672	Y(ClO <sub>4</sub> ) <sub>3</sub>
50.0	$(1.75 \pm 0.01) \times 10^{-4}$	0.6322	Mg(ClO <sub>4</sub> ) <sub>2</sub> , LiClO <sub>4</sub> <sup>a</sup>
50.0	$(1.88 \pm 0.07) \times 10^{-4}$	0.6308	Mg(ClO <sub>4</sub> ) <sub>2</sub>
50.0	$(1.57 \pm 0.01) \times 10^{-4}$	0.4820	NaClO <sub>4</sub>
50.0	$(1.35 \pm 0.02) \times 10^{-4}$	0.4815	Y(ClO <sub>4</sub> ) <sub>3</sub>
50.0	$(1.07 \pm 0.04) \times 10^{-4}$	0.4813	<i>b</i>
50.0	$(1.74 \pm 0.07) \times 10^{-4}$	0.4606	Mg(ClO <sub>4</sub> ) <sub>2</sub>
50.0	$(1.47 \pm 0.02) \times 10^{-4}$	0.2936	Mg(ClO <sub>4</sub> ) <sub>2</sub>
50.0	$(1.20 \pm 0.02) \times 10^{-4}$	0.2095	Y(ClO <sub>4</sub> ) <sub>3</sub>

<sup>a</sup> [H<sup>+</sup>] = 1.00. <sup>b</sup>  $\mu = 5.0$ , [H<sup>+</sup>] = 2.00.

The data presented do not provide any evidence that would be of assistance in distinguishing between a rate-determining step in which the Np(V)·Cr(III) dissociates or one in which a molecule of water adds to Np(V)·Cr(III) to form a seven-coordinated intermediate.

A comparison of the experimental activation energies for the aquation of  $[\text{Cr}(\text{H}_2\text{O})_5\text{O-Np-O}]^{+4}$  ( $28.3 \pm 0.8$  kcal.) and  $\text{Cr}(\text{H}_2\text{O})_5\text{NCS}^{+2}$  ( $28.1$  kcal.) provides the basis for the following speculation concerning details of the mechanisms.

In a unimolecular reaction there is generally an extension of the bond to be broken by about 10%<sup>19</sup> over the equilibrium interatomic distances. It does not seem plausible that the energy necessary to cause such an effect in the bonds  $\alpha$ ,  $[(\text{H}_2\text{O})_5\text{Cr}^\alpha\text{O-Np-O}]^{+4}$ , and  $\beta$ ,  $[(\text{H}_2\text{O})_5\text{Cr}^\beta\text{SCN}]^{+2}$ , be identical. Hence it would appear improbable that both reactions proceed by an SN1 mechanism. There is no basis for either affirming or rejecting the alternate SN2 mechanism for both reactions.

The specific rate for the approach to equilibrium is pseudo-first order as is to be expected since the chromic ion concentration is in such large excess. In Table III are presented a summary of the values obtained for this apparent first-order rate constant.

The following observations are consistent with these data: (a) there is a small but significant variation of  $k'$  with changing initial Cr(III) concentration, (b) there is no clear evidence that  $k'$  is significantly altered by marked changes in solution composition or perchlorate ion concentration, (c) between 1 and 2 M hydrogen

ion concentration  $k'$  is invariant, and (d) there is only a small decrease in  $k'$  when the total ionic strength is varied from 8.0 to 5.0.

For a mechanism indicated by eq. 1 we may write

$$dx/dt = k_1(A - x)B - k_2x \quad (5)$$

where  $x$  is the concentration of the complex formed at any time and  $A$  and  $B$  are the respective initial concentrations of Np(V) and Cr(III). Integration of (5) by standard procedures<sup>11</sup> results in

$$\ln(x_0 - x) = k_1AB/x_0t + C \quad (6)$$

where  $x_0$  is the equilibrium concentration of the complex. Therefore

$$k_1 = k'x_0/AB \quad (7)$$

The average values calculated for  $k_1$  are  $5.80 \pm 0.73 \times 10^{-6}$ ,  $2.42 \pm 0.33 \times 10^{-5}$ , and  $1.63 \pm 0.26 \times 10^{-4}$  sec.<sup>-1</sup> mole<sup>-1</sup> for 25, 35, and 50°, respectively.

The activation energy calculated from these values is  $25.6 \pm 3.1$  kcal. and the entropy of activation  $\Delta S^* = +1.4$  e.u.

From these values of  $k_1$  and the measured values of  $k_2$  (in 2.0 *M* perchloric acid at an ionic strength of 8.0)<sup>20</sup> calculated values of  $Q = k_1/k_2$  are  $2.31 \pm 0.29$ ,  $1.95 \pm 0.33$ , and  $1.60 \pm 0.24$  at 25, 35, and 50°, respectively.

These results are consistent with the assumed mechanism within the stated limits.

**Reduction of Np(VI) with Cr(II).**—At 25°, in 1 *M* perchloric acid, Cr(II) reduces Np(VI) rapidly. The reaction is complete by the time the first spectrophotometric observation was made *ca.* 30 sec. after mixing the reactants.

Over the initial concentration ranges of  $0.14\text{--}2.4 \times 10^{-3}$  *M* Np(VI) and  $0.04\text{--}1.5 \times 10^{-3}$  *M* Cr(II) the reduced products were Np(IV), Np(V), and Np(V)·Cr(III). With excess Np(VI) always present there

was a further slow reaction with Np(IV) to produce additional Np(V).<sup>21</sup>

In the dilute solutions, where extrapolation to the time of mixing was unnecessary, 76% of the reduced Np was present as Np(IV), 15% as the Np(V)·Cr(III) complex, and 9% as Np(V).

The result of primary interest in conjunction with the present work, since these experiments were not designed to obtain kinetic information, is the fact that initial products in the reduction are both Np(V) and the Np(V)·Cr(III) complex. An explanation of these results postulates two types of activated complexes for this stage of the oxidation–reduction reaction.

In one there is penetration of the inner coordination sphere of the chromous ion (presumably a chromous ion with its coordination sphere partially rearranged to resemble that of a chromic ion) immediately prior to or in coincidence with the electron transfer. In a second type there would be no such penetration coincident with the electron transfer.

There are two points germane to these comments.

(a) In a kinetic study of the analogous reduction of U(VI) by Cr(II) Newton and Baker<sup>3</sup> obtained evidence for the existence of two binuclear intermediates. The observations presented here correspond to their interpretation that one of these intermediates may well be  $[(\text{H}_2\text{O})_5\text{CrOUO}]^{+4}$ . (b) Taube<sup>22</sup> has pointed out that for the class of oxidation–reduction processes under consideration both “outer sphere” and “bridged” activated complexes may provide a reaction path. The one-electron reduction of Np(VI) by Cr(II) can be interpreted as an example of this concept.

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(20) The appropriate value to use for  $k_2$  was considered to be the one determined in a medium of *ca.* 1 *M* Y(ClO<sub>4</sub>)<sub>3</sub>. An extrapolated value was used for 25°.