electrostatic repulsion and electron conductivity should be quite similar.

From the available potentials,[15] $\Delta F° = -5.6$ kcal for (6) and $\Delta F° = -13.0$ kcal for (7). This contribu-

tion to the free energy of activation would make the rate of (7) greater than that of (6).

The fact that the specific rate constants under consideration are of the opposite order may very well reflect the importance of the reorganization free energy of activation in the two examples. A considerable portion of this difference would arise from the fact that the d electron being transferred to a 5f orbital is e_g in the case of Cr^{2+} and t_{2g} in the case of Fe^{2+}.

(15) Fe(II)–Fe(III) and Cr(II)–Cr(III) couples are from W. H. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," Prentice-Hall, Inc., New York, N. Y., 1938. The neptunium and plutonium couples are from J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley and Sons, Inc., New York, N. Y., 1957.

The Reaction between Excess Neptunium(V) and Chromium(II) in Perchlorate Solution[1]

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Abstract: The kinetics of the reaction Np(V) + Cr(II) = Np(IV) + Cr(III) have been studied in acid perchlorate solutions from 0.02 to 0.20 M HClO$_4$. The reaction is complicated by a competitive consecutive reaction between the Cr(II) reactant and the Np(IV) product. The rate law for the 1-equiv reduction of Np(V) by Cr(II) is $-d[\text{Np-}(V)]/dt = k_1[\text{Np(V)}][\text{Cr(II)}][\text{H}^+]^{0.78}$, where $k_1[\text{H}^+]^{0.78}$ is interpreted to equal $k_0[\text{H}^+]e^{\beta[\text{H}^+]}$. Values of ΔH^* and ΔS^* appropriate to the k_0 term were found to be 1.85 kcal/mole and -38.4 eu. Oxygen-18 tracer results indicate the formation of an inner-sphere activated complex.

The reduction of the oxycations NpO_2^{2+} and NpO_2^+ by chromium(II) is complicated by the existence of competitive and perhaps parallel paths. The reduction of excess neptunium(VI) by chromium(II) in 1 M perchloric acid is reported to yield predominantly neptunium(IV) along with smaller amounts of neptunium(V) and neptunium(V)–chromium(III) complex.[3] Preliminary experiments revealed the presence of a neptunium(III) intermediate in the reduction of excess Np(V) by Cr(II) at hydrogen ion concentrations $\leqq 0.2$ M. Appelman and Sullivan[4] also report a Np(III) intermediate in the V(III)–Np(V) reaction at low acidities. Kinetic, stoichiometric, and oxygen-18 tracer results for the Np(V)–Cr(II) reaction are reported in this communication.

Experimental Section

Reagents. The neptunium(V), chromium(II), and lithium perchlorate and perchloric acid solutions were prepared and standardized as described previously.[5,6] Neptunium(III) perchlorate solutions were prepared by reduction of a Np(V) solution over amalga-

mated zinc in the absence of oxygen. The extinction coefficients for Np(V) at 9800 A were determined at each solution composition and temperature, but the variations from the reported value[7] of $A = 403$ M^{-1} cm^{-1} were small.

Kinetic Experiments. The procedures used were essentially the same as previously reported.[5] Since up to 10 hr was required for completion of the Np(V)–Np(III) reaction in some experiments, the serum caps were covered with Apiezon T grease approximately 5 min after initiation of the reaction to prevent entry of oxygen gas. The Np(III) intermediate was monitored at 2670 A and the formation of Np(IV) at 7230 A; the absorbance by the other reactants or products is small at these wavelengths. The hydrogen ion concentration of the reaction mixture was determined by titration with standard base after completion of the reaction.

Stoichiometry and Tracer Experiments. In the stoichiometry experiments, the hexaaquochromium(III) product was separated from the other species in a spent reaction mixture by ion-exchange techniques employing Bio-Rad AG 50W-X8 resin in the hydrogen ion form. The excess Np(V) was eluted with 1 M perchloric acid, and the $Cr(OH_2)_6^{3+}$ was eluted from the Np(IV) and any possible dimeric chromium(III) with 3 M perchloric acid. The hexaaquochromium(III) eluent was analyzed spectrophotometrically at 4075 and 5750 A, where values of $A = 15.9$ and 13.6 M^{-1} cm^{-1}, respectively, were used.

For the tracer experiments, oxygen-18 enriched Np(V) was prepared by removing the solvent water from a neptunium(V) perchlorate solution under reduced pressure until the green solid began crystallizing and then equilibrating with a large excess of 1.5% H$_2$O^{18} (YEDA). The enriched water was then distilled from the enriched Np(V) solution and collected for analysis. The dry, enriched neptunium(V) perchlorate (~0.4 mmole) was dissolved in ca. 1 ml of unenriched triply distilled water and quickly injected with vigorous stirring into less than the stoichiometric amount of Cr(II) in unenriched, oxygen-free perchloric acid solution adjusted to the desired hydrogen ion concentration. The O^{18} enrichment of the Np(V) used in these experiments was taken to be that of the removed, equilibrated water. This assumption will only be correct

(1) (a) Research performed under the auspices of the U. S. Atomic Energy Commission. (b) A preliminary account of this investigation was presented before the Inorganic Chemistry Division, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(2) Resident Research Associate.

(3) J. C. Sullivan, *Inorg. Chem.*, 3, 315 (1964).

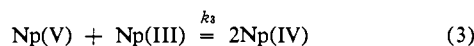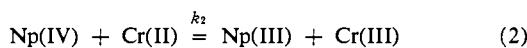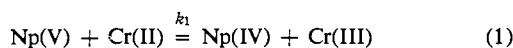(4) E. H. Appelman and J. C. Sullivan, *J. Phys. Chem.*, 66, 442 (1962).

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

(6) J. C. Sullivan, A. J. Zielen, and J. C. Hindman, *ibid.*, 82, 5488 (1960).

(7) R. Sjoblom and J. C. Hindman, *ibid.*, 73, 1744 (1951).

provided that oxygen exchange between the Np(V) and solvent in nearly neutral solution is negligible for the minute or so between dissolution and injection, and also negligible during the time necessary for reaction with Cr(II) in the acidic reaction solution (*ca.* 5-10 sec). This assumption is supported *a priori* by recent exchange experiments[8] and by the nearly maximum theoretical transfer of Np(V) oxygen to the hexaaquochromium(III) in 1 *M* perchloric acid (*vide infra*). The $Cr(OH_2)_6{}^{3+}$ was separated as described above with the exception that 3 *M* HCl was used as eluent. Hexaaquochromium(III) fluoride was precipitated and dried over $CaSO_4$, and the coordinated water was separated from the solid *in vacuo* as described previously.[9,10] The water was then transferred to a weighed sample tube and reweighed, and a known amount of CO_2 of normal isotopic abundance was added. After isotopic equilibration, the CO_2 was distilled and analyzed in an isotopic ratio mass spectrometer.[11]

Data Treatment. In preliminary experiments at 25° and [$HClO_4$] = 0.2 *M*, both the disappearance of Np(V) at 9800 A and the appearance of Np(IV) at 7230 A were characterized by an initial rapid reaction followed by a slower one. The rapid portion did not obey either a first- or second-order rate law. The formation and consumption of Np(III) intermediate was verified by monitoring the Np(III) peak at 2670 A. Again, the formation of Np(III) did not follow first- or second-order kinetics. Three competitive, consecutive second-order reactions (eq 1-3) were postulated

$$Np(V) + Cr(II) \overset{k_1}{=} Np(IV) + Cr(III) \qquad (1)$$

$$Np(IV) + Cr(II) \overset{k_2}{=} Np(III) + Cr(III) \qquad (2)$$

$$Np(V) + Np(III) \overset{k_3}{=} 2Np(IV) \qquad (3)$$

to account for both the Np(III) intermediate and the over-all stoichiometry. However, the differential equations associated with this set of chemical reactions cannot be integrated in closed form. Consequently, the kinetic data were analyzed by means of a computer program in which the integration was done numerically using the Runge-Kutta method,[12] and the best value for the rate constant k_1 in the individual runs was determined by a nonlinear least-squares technique.[13] Computational uncertainties in k_1 were minimized by independently determining the values of the rate constants k_2 and k_3 for the conditions of each experiment. Thus, k_1 was the only determined parameter in the computer treatment. Initial estimates of k_1 were obtained by an analog computer technique and by interpolation after sufficient data had been collected and analyzed.
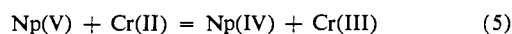
The Np(V)-Np(III) rate data were analyzed by means of the computer program used for the Np(IV)-Cr(II) reaction.[5] The rate expression used was

$$-d[Np(V)]/dt = k_3[Np(V)][Np(III)] \qquad (4)$$

at constant hydrogen ion concentration.

Results

Stoichiometry. The formal potential for the reaction

$$Np(V) + Cr(II) = Np(IV) + Cr(III) \qquad (5)$$

(8) R. K. Murmann and J. C. Sullivan, to be published.
(9) L. B. Anderson and R. A. Plane, *Inorg. Chem.*, 3, 1470 (1964).
(10) R. C. Thompson and G. Gordon, *ibid.*, 5, 562 (1966).
(11) The equilibration and mass spectrometric analysis of the CO_2 were generously performed by Professor R. K. Murmann at the University of Missouri.
(12) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p 469.
(13) The general program is based on R. H. Moore and R. K. Ziegler, Los Alamos Scientific Laboratory Report LA-2367, Office of Technical Services, U. S. Department of Commerce, Washington, D. C., 1959. We wish to acknowledge the assistance of Dr. T. W. Newton for adapting the necessary subroutines to suit our particular application. The further adaptation of the program for use on the CDC3600 (program C-169) was performed by M. Matthies, Applied Mathematics Division of the Argonne National Laboratory.

is 1.16 v,[14] and thus it was assumed that the reaction goes essentially to completion.

The yields of hexaaquochromium(III) ion at 25° were determined in both 1.0 and 0.10 *M* perchloric acid. In the high acid experiment the initial concentrations of Np(V) and Cr(II) were 1.14×10^{-2} and 9.05×10^{-3} *M;* and 9.43×10^{-3} and 6.99×10^{-3} *M* in the lower acid. The ratio (millimoles of $Cr(OH_2)_6{}^{3+}$ found)/ (millimoles of Np(V) consumed) was 1.0_5 at 1.0 *M* $HClO_4$ and 1.0_9 at 0.10 *M* $HClO_4$.[15]

Np(IV)-Cr(II) and Np(V)-Np(III) Reactions. As mentioned earlier, the kinetics of the Np(IV)-Cr(II) and Np(V)-Np(III) reactions at low acidities and ionic strength were essential in order to analyze the Np(V)-Cr(II) kinetic data. The Np(IV)-Cr(II) reaction had been studied in detail at $I = 1.00$ *M* (maintained with $LiClO_4$) and [$HClO_4$] = 0.11-1.00 *M*. The reported rate law[5] is

$$-d[Np(IV)]/dt = k_2[Np(IV)][Cr(II)][H^+]^{-1.27} \qquad (6)$$

with $k_2 = 4.29$ sec^{-1} at 25°. Correction of the data to $I = 0.20$ resulted in only a 10% decrease in k_2. It was necessary to extrapolate the hydrogen ion dependence from 0.11 to 0.025 *M;* however, the reported data at the lowest hydrogen ion concentration appears to be as reliable as that at higher acidities. The temperature dependence of k_2 was calculated using the reported activation parameters.

The reported rate law[16] for the Np(V)-Np(III) reaction is

$$-d[Np(V)]/dt = k_3[Np(V)][Np(III)][H^+] \qquad (7)$$

with $k_3 = 43.2$ M^{-2} sec^{-1} at 25°, $I = 2.0$ *M* ($NaClO_4$), and [$HClO_4$] = 0.11-1.91 *M*. However, Appelman and Sullivan[4] briefly reinvestigated this system and found a hydrogen ion dependence of 0.35-0.65 at [$HClO_4$] = 0.13-0.37 *M* and $I = 3.0$ *M*. Therefore, this reaction was investigated at $I = 0.25$ *M* ($LiClO_4$) and [$HClO_4$] = 0.06-0.22 *M*. The results of these experiments are summarized in Table I. Extensive scatter and rather large standard deviations in the individual experiments (*ca.* 6%) occurred. However, the data do indicate that the rate is markedly dependent on the ionic strength, and that the hydrogen ion dependence under these conditions is definitely less than unity. A least-squares treatment of the first seven entries in Table I yields a hydrogen ion dependence of 0.56 ± 0.16 at $I = 0.25$ *M;* 10^{-3} *M* HCl had little detectable effect on the value of k_3, but 10^{-3} *M* $HSO_4{}^-$ markedly catalyzed the rate. As will be seen, the value of k_1 appropriate to reaction 1 is generally rather insensitive to the value of k_3. Input values of k_3 were calculated from the rate expression

$$-d[Np(V)]/dt = k_3[Np(V)][Np(III)][H^+]^{0.56} \qquad (8)$$

with $k_3 = 5.40$ at 25° and $I = 0.2$ *M*. Temperature corrections for k_3 were calculated assuming an activa-

(14) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952.
(15) No dimeric chromium(III) was observed in the ion-exchange separation of the products; however, trace amounts could have been obscured by the Np(IV) band.
(16) J. C. Hindman, J. C. Sullivan, and D. Cohen, *J. Am. Chem. Soc.*, 80, 1812 (1958).

Table I. Apparent Second-Order Rate Constants for the Np(V)–Np(III) Reaction at 25° ([Np(V)] = 1.20 × 10⁻³–2.58 × 10⁻³ M, [Np(III)] = 6.99 × 10⁻⁴–2.46 × 10⁻³ M)

HClO₄, M	I(LiClO₄), M	k_3, M^{-1} sec^{-1} [a]
0.0599	0.240	1.84 ± 0.06
0.0848	0.245	2.68 ± 0.03
0.104	0.244	2.48[b]
0.127	0.247	2.35[b]
0.135	0.255	5.39[b]
0.150	0.250	3.36 ± 0.37
0.199	0.249	3.67 ± 0.35
0.227	0.227	2.32 ± 0.16
0.225	0.225	2.37 ± 0.05[c]
0.230	1.03	7.22 ± 0.02
0.130	3.03	78.7 ± 3.2
0.150	0.250	17.9 ± 0.3[d]

[a] Unless otherwise noted, entries represent the average of duplicate runs. Uncertainties are the average deviations. [b] One run only. [c] 10⁻³ M HCl. [d] 10⁻³ M HSO₄⁻.

only negligible portions of the reaction at low hydrogen ion concentrations and higher temperatures (*vide infra*).

Values of k_1 = 124 ± 2 and 122 ± 3 M^{-1} sec^{-1} were obtained at 5° in 0.20 M HClO₄ with 10⁻³ M added HCl and no added HCl, respectively. However, small amounts of HSO₄⁻ markedly increase the reaction rate. At 17° and 0.107 M HClO₄, values for k_1 = 305 ± 15 and 65 ± 0.2 M^{-1} sec^{-1} were obtained with 10⁻³ M HSO₄⁻ and no added HSO₄⁻, respectively. The effect of Cl⁻ and HSO₄⁻ in this system thus resembles that noted in the Np(V)–Np(III) reaction.

The variation of k_1 as a function of hydrogen ion concentration and temperature is summarized in Table II. The rate was found to be markedly dependent on the ionic strength at constant hydrogen ion concentration. At 25° and [HClO₄] = 0.106 M, k_1 = 302 ± 14, 119 ± 4, and 73 ± 0.1 M^{-1} sec^{-1} at I = 1.01,

Table II. [H⁺] and Temperature Dependencies of k_1[a]

	5°		10°		17°		25°[b]
[H⁺], M	k_1, M^{-1} sec^{-1}	[H⁺], M	k_1, M^{-1} sec^{-1}	[H⁺], M	k_1, M^{-1} sec^{-1}	[H⁺], M	k_1, M^{-1} sec^{-1}
0.202	116 ± 5.5	0.207	157 ± 1.4	0.209	174 ± 4.4	0.207	188 ± 0.3
0.154	92.5 ± 0.9	0.156	121 ± 1.7	0.156	135 ± 1.6	0.156	141 ± 8.2
0.104	79.2 ± 0.2	0.104	82.1[c]	0.104	89.4 ± 3.5	0.106	110 ± 9.1
0.0851	62.6 ± 0.5	0.0845	72.6 ± 0.2	0.0861	78.0 ± 4.1	0.0863	85.2 ± 9.3
0.0675	49.7 ± 0.1	0.0678	58.7[c]	0.0646	65.5 ± 4.1	0.0656	69.3 ± 1.3
0.0476	33.9 ± 0.1	0.0473	38.4 ± 1.2	0.0477	36.1 ± 0.5	0.0465	55.9 ± 2.9
0.0263	22.6 ± 0.2	0.0267	24.6 ± 0.1	0.0271	31.9 ± 1.0	0.0262	38.6 ± 0.2

[a] I = 0.207 M maintained with LiClO₄. Uncertainties are the average deviations. [Np(V)]₀ = 4.28–11.2 × 10⁻⁴ M, [Cr(II)]₀ = 1.87–9.34 × 10⁻⁴ M. [b] The 25° entries were also calculated by altering the input values for k_3 by 100% and again by changing k_2 by 10%. In both computations the resulting values for k_1 deviated a maximum of 4% from those listed here. [c] One experiment only.

tion energy of 6.52 kcal/mole, as reported by Hindman, *et al.*[16]

Rate Law for the Np(V)–Cr(II) Reaction. Values of k_1 associated with reaction 1 were computed over a wide range of experimental conditions. The rate data for over 3 half-lives were adequately correlated by the computer treatment, with standard deviations in k_1 of 1–3%. This result supports the assumption that reaction 1 is second order, first order each with respect to Np(V) and Cr(II).

Two checks on the computational method for obtaining values of k_1 were made. Most of the 25° data were analyzed by an analog computer technique in which the best value of k_1 was obtained by a curve-fitting procedure after numerical integration of the rate equations for various trial values of k_1. The maximum deviation in k_1 as calculated by this method and the previously described one was 5%. Also, when the ratio k_1/k_2 for a given experiment is large, the over-all reaction rate is second order over a certain fraction of the reaction. In general, the rate constants determined over the portion of the reaction that obeyed second-order kinetics agreed closely with those obtained over 3 half-lives by the numerical integration procedure. For example, at 5° and 0.20 M HClO₄ (where k_1/k_2 = 35), second-order kinetics are followed for 3 half-lives with k_1 = 117 ± 0.8 M^{-1} sec^{-1}; the computed value of k_1 was 119 ± 1.3 M^{-1} sec^{-1} for the same data. In most of the experiments, however, over-all second-order kinetics were observed for less than 1 half-life and for

0.206, and 0.106 M (LiClO₄), respectively. The variation in k_1 with change in the hydrogen ion concentration can be correlated by the expression

$$k_1 = k'[H^+]^N \tag{9}$$

Values determined for N from a least-squares adjustment of all the individual experiments were 0.787 ± 0.029, 0.856 ± 0.044, 0.761 ± 0.072, and 0.760 ± 0.027 at 25, 17, 10, and 5°, respectively. These values suggest that the rate is predominantly proportional to [H⁺]; the deviations from first-order dependence can most simply be ascribed either to medium effects as the hydrogen ion concentration is varied at constant ionic strength or to a contribution from a hydrogen ion independent path. The striking dependence of k_1 on [LiClO₄] suggests that even at constant ionic strength, the activity coefficients associated with the activated complex may well be quite sensitive to the substitution of H⁺ by Li⁺. For this reason, it is concluded that the inclusion of more than one parameter to correlate the deviations from first-order hydrogen ion dependence is not justified. The data in Table II were analyzed by means of eq 10. The $e^{\beta[H^+]}$ term is of the form of a

$$k_1 = k_0[H^+]e^{\beta[H^+]} \tag{10}$$

Harned term, where β is an adjustable parameter. Values of k_0 and β at the four working temperatures are

Table III. Values of k_0 and β as a Function of Temperature

Temp, °C	k_0, M^{-2} sec^{-1}	β, M^{-1}
5	865 ± 49	−2.234
10	905 ± 21	−0.9396
17	1002 ± 38	−0.9401
25	1146 ± 61	−1.142

summarized in Table III. The values of β are much larger than are usually encountered. One explanation for this result is that the activity coefficients of the activated complex are unusually sensitive to the composition of the medium. Also, there may be a contribution from a hydrogen ion independent term to the value of β; however, to compute such a contribution necessitates the unwarranted use of two additional parameters.[17] The activation energy for the net activation process

$$NpO_2^+ + Cr^{2+} + H^+ = (NpO_2 \cdot Cr \cdot H^{4+}) \qquad (11)$$
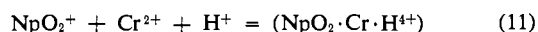
as calculated from the data in Table III was 2.44 ± 0.23 kcal/mole. Values of $\Delta H^* = 1.85 \pm 0.23$ kcal/mole and $\Delta S^* = -38.4 \pm 0.8$ eu at 25° were calculated by use of the expression from the absolute reaction rate theory[18]

$$k = \frac{ekT}{h} \exp(-\Delta E/RT) \exp(\Delta S^*/R) \qquad (12)$$

where $\Delta H^* = \Delta E - RT$. If the data in Table III are analyzed by the expression

$$k_1 = k'' + k'''[H^+] \qquad (13)$$

the determined values for k'' as a function of temperature yield a nonlinear Arrhenius plot.

Tracer Results A limited set of experiments designed to test possible oxygen transfer from O-Np-O$^+$ to the nonlabile hexaaquochromium(III) product were made: $[Np(V)]_0 = 1.28-1.59 \times 10^{-2}$ M and $[Cr(II)]_0 = 1.13-1.18 \times 10^{-2}$ M at 25°. In two independent experiments at 1.0 M HClO$_4$, 0.90 ± 0.08 water on the Cr(III) product was found to have the same enrichment as the NpO$_2^+$ reactant. In a single experiment at 0.169 M HClO$_4$, 0.68 Np(V) oxygen was transferred. The ratio of the relevant rate constants, k_1/k_2, was estimated to be ca. 530 and 6.4 for the high and low acid experiments, respectively.

Discussion

A number of reactions involving the reduction of MO$_2^+$ ions have been studied.[4,19,20] A term in the rate

law proportional to [H$^+$] has been found in nearly all these systems and again appears as the dominant term in the present study. The most notable exception to this generalization is the V(III)–Np(V) system, but this is a special case since addition of a proton to the activated complex would presumably lead to the formation of an unstable intermediate, VOH^{3+}.[4] The possible existence of a minor path independent of [H$^+$] cannot be ruled out in the Np(V)–Cr(II) reaction, since the marked medium effect prohibits characterization of such a path over the acid range studied. Large ionic strength effects have also been observed in the reduction of Np(V) by Np(III) and probably Fe^{+2},[20] and in the reduction of VO$_2^+$ by Fe^{2+}.[19] These medium effects may well be involved in an unclear manner in the structural change necessary in the conversion of the MO$_2^+$ entity to the M(IV) species.

The present study is particularly enlightening in that the tracer results strongly suggest a predominantly, if not exclusively, inner-sphere activated complex. The result that the oxygen transfer from the Np(V) to Cr(III) decreases with decreasing [H$^+$] is consistent with the increasing importance of the competition for the Cr(II) by the Np(IV) product. The latter path would not be expected to allow transfer. The exclusive formation of hexaaquochromium(III) as the Cr(III) product is consistent with evidence that one-electron oxidations of Cr(II) produce only this species.[21]

The possibility that the Np(III) intermediate is generated through a two-electron reduction of Np(V) by Cr(II)

$$Np(V) + Cr(II) \overset{k_a}{=} Np(III) + Cr(IV) \qquad (14)$$

$$Cr(II) + Cr(IV) \overset{\text{very fast}}{=} 2Cr(III) \qquad (15)$$

$$Np(III) + Np(V) \overset{k_b}{=} 2Np(IV) \qquad (16)$$

can be discarded on the basis of the data presented. First, dimeric chromium(III) would be the expected Cr(III) product;[21] none was detected. Secondly, a maximum[22] of 0.50 Np(V) oxygen could be transferred to the Cr(III); considerably greater transfer was observed even in low acid. Finally, the kinetic data could be correlated by this reaction scheme only by allowing k_b to be ca. 40 times the observed value.[23]

The thermodynamic activation parameters of related, formally similar activation processes are listed in Table IV. Although all the activated complexes are shown as if a single atom lies between the metal ions, this

(17) It is tempting to analyze the data by the equation $k_1 = (k_a + k_b \cdot [H^+])e^{\beta[H^+]}$, which contains only three parameters. However, in view of the large medium effects there is no reason to assume that the $e^{\beta[H^+]}$ term should be the same for two activated complexes differing in composition by a proton; but to include such a term for each of the rate constants k_a and k_b results in a four-parameter equation.
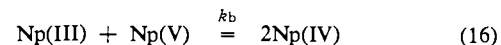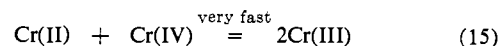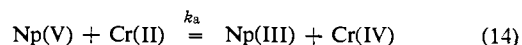
(18) S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp 197-199.

(19) N. A. Daugherty and T. W. Newton, J. Phys. Chem., 67, 1090 (1963).

(20) J. R. Huizenga and L. B. Magnusson, J. Am. Chem. Soc., 73, 3202 (1951).

(21) M Ardon and R. A. Plane, ibid., 81, 3197 (1959).

(22) This optimistic maximum possible transfer is surely too high, since Cr(IV) is thought to be labile.

(23) A computer program, C148, was written by M. Howe of the Applied Mathematics Division of this laboratory. The computational procedure was based on the method of D. French, J. Am. Chem. Soc., 72, 4806 (1950). Np(V) concentrations were calculated from the rate data from the expression

$$[Np(V)] = [Np(V)]_0 - [Cr(II)]_0 \times$$

$$\left[1 + \frac{k_a e^{-k_b \theta} - k_b e^{-2k_a \theta} + k_a e^{-2k_a \theta}}{k_b - 2k_a} \right]$$

where $\theta = \int_0^t [Np(V)]dt$. Values of θ were obtained by numerical integration by means of Simpson's rule, and best values of k_a and k_b were determined by a nonlinear least-square adjustment of the data.

Table IV. Activation Parameters at 25°

	ΔH^*, kcal/mole	ΔS^*, eu	S^* (complex),[19] eu	Ref
$NpO_2^+ + Cr^{2+} + H^+ = (H \cdot NpO_2 \cdot Cr^{4+})^*$	1.85	−38	−66	This work
$NpO_2^+ + Fe^{2+} + H^+ = (H \cdot NpO_2 \cdot Fe^{4+})^*$	8.6	−38	−69	20
$VO_2^+ + Fe^{2+} + H^+ = (H \cdot VO_2 \cdot Fe^{4+})^*$	1.52	−37	−70	19
$NpO_2^+ + Np^{3+} + H^+ = (H \cdot NpO_2 \cdot Np^{5+})^*$	5.9	−31	−72	16

inner-sphere structure has direct experimental evidence only in the case of the first entry. All of these reactions listed are characterized by low heats of activation, but this is especially true in the V(V)–Fe(II) and Np(V)–Cr(II) reactions. The ΔS^* values for the first three reactions are in remarkable agreement, and the surprising correlation between the charge of the activated complex and the associated S^* value as noted by Newton and Rabideau[24] for actinide elements is fol-

lowed by the Np(V)–Cr(II) reaction. The Np(V)–Np(III) system has a S^* value expected for +4 charged activated complexes rather than those with +5 charge. The results presented in this paper suggest that some of this discrepancy may be due to the contribution by a path independent of (H⁺), at least at (HClO₄) ≤0.2 M.

(24) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

Phosphiran[1a]

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Abstract: The novel heterocycle phosphiran (phosphacyclopropane) has been prepared by two routes. It has been characterized by mass, infrared, and nuclear magnetic resonance spectra. Phosphiran is thermally unstable and decomposes to a viscous, involatile liquid.
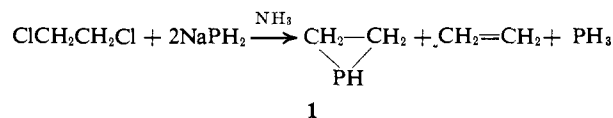
The preparation of phosphiran (phosphacyclopropane, 1) has been briefly described,[2] but no details of its characterization or of its spectral properties have yet appeared. The present paper describes in detail both the original preparation of the heterocycle[2] and a novel preparative method and describes its characterization and some of its properties.

During the course of some further work on phosphorus–boron polymer chemistry,[3] an attempt was made to prepare 1,2-diphosphinoethane by reaction between 1,2-dichloroethane and phosphinide ion in anhydrous ammonia. The reaction did not follow the nucleophilic substitution pathway usually observed with simple alkyl halides, but yielded phosphiran, phosphine, and ethylene.
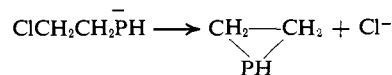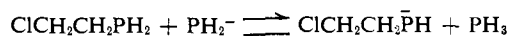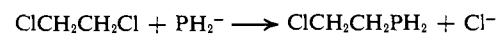
(2) R. I. Wagner, U. S. Patent 3,086,056 (1963).
(3) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

$$ClCH_2CH_2Cl + 2NaPH_2 \xrightarrow{NH_3} \underset{\underset{PH}{\diagdown \diagup}}{CH_2 - CH_2} + .CH_2{=}CH_2 + PH_3$$

1

A tentative mechanism for this ring-closure reaction is

$$ClCH_2CH_2Cl + PH_2^- \longrightarrow ClCH_2CH_2PH_2 + Cl^-$$

$$ClCH_2CH_2PH_2 + PH_2^- \rightleftharpoons ClCH_2CH_2\bar{P}H + PH_3$$

$$ClCH_2CH_2\bar{P}H \longrightarrow \underset{\underset{PH}{\diagdown \diagup}}{CH_2 - CH_2} + Cl^-$$

The reaction is efficient and has yielded up to 74% of phosphiran based on starting 1,2-dichloroethane. Unusual reactions between phosphinide ions and vicinal dihaloalkanes have been reported by other workers[4] although the phosphorus-containing products which were obtained were quite different from those reported here

(4) K. Issleib and K. Stanktke, *Ber.*, **96**, 279 (1963).