$$L\{f(t)\} = \int_0^\infty e^{-pt} f(t)\,\mathrm{d}t = \bar{f}(p) \qquad (28)$$

From (28) one obtains[12] the relation

$$L\Big\{\underbrace{\int_0^t \cdots \int_0^t}_{n\ \text{times}} f(t)\mathrm{d}t \ldots \mathrm{d}t\Big\} = \frac{1}{p^n}\bar{f}(p) \qquad (29)$$

Thus

$$L\Big\{\underbrace{\int_0^\nu \cdots \int_0^\nu}_{\substack{j-s+1\\ \text{times}}} e^{\delta\nu}\nu^{s-2}\,\mathrm{d}\nu \ldots \mathrm{d}\nu\Big\} = \frac{1}{p^{j-s+1}} L\{e^{\delta\nu}\nu^{s-2}\} \qquad (30)$$

However, since

$$L\{t^n\} = \frac{n!}{p^{n+1}} \qquad (31)$$

(see ref. 12), $1/p^{j-s+1}$ may be represented by

$$\frac{1}{p^{j-s+1}} = L\left\{\frac{\nu^{j-s}}{(j-s)!}\right\} \qquad (32)$$

and eq. 30 may be rewritten in the form

$$L\Big\{\underbrace{\int_0^\nu \cdots \int_0^\nu}_{\substack{j-s+1\\ \text{times}}} e^{\delta\nu}\nu^{s-2}\,\mathrm{d}\nu \ldots \mathrm{d}\nu\Big\} = L\left\{\frac{\nu^{j-s}}{(j-s)!}\right\} L\{e^{\delta\nu}\nu^{s-2}\} \qquad (33)$$

Equation 33 may now be transformed into eq. 35 by making use of the convolution lemma (34).[12]

$$\bar{f}(p)\bar{g}(p) = L\left\{\int_0^\nu f(\nu - y)g(y)\mathrm{d}y\right\} \qquad (34)$$

$$L\Big\{\underbrace{\int_0^\nu \cdots \int_0^\nu}_{\substack{j-s+1\\ \text{times}}} e^{\delta\nu}\nu^{s-2}\,\mathrm{d}\nu \ldots \mathrm{d}\nu\Big\} = L\left\{\int_0^\nu \frac{y^{j-s}}{(j-s)!} e^{\delta(\nu-y)}(\nu - y)^{s-2}\mathrm{d}y\right\} \qquad (35)$$

By Lerch's theorem[12] we finally obtain

$$\underbrace{\int_0^\nu \cdots \int_0^\nu}_{\substack{j-s+1\\ \text{times}}} e^{\delta\nu}\nu^{s-2}\,\mathrm{d}\nu \ldots \mathrm{d}\nu = \int_0^\nu \frac{y^{j-s}}{(j-s)!} e^{\delta(\nu-y)}(\nu - y)^{s-2}\mathrm{d}y \qquad (36)$$

Acknowledgments.—The authors thank Prof. Paul Doty for his help and encouragement in this work. J. D. C. is grateful for the support of the Office of Naval Research (N5 Ori-07654).

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(12) See, for example, F. B. Hildebrand, "Advanced Calculus for Engineers," Prentice–Hall, Inc., New York, N. Y., 1957, p. 52.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY, PITTSBURGH, PENNA.]

Complex Formation in the Phosphorus Tribromide–Trimethylamine System and the Phosphorus Trichloride–Trimethylarsine System Phosphorus Nitrogen Chemistry II.[1,2]

BY ROBERT R. HOLMES

RECEIVED APRIL 9, 1960

The complexes, $Br_3P \cdot N(CH_3)_3$ and $Cl_3P \cdot As(CH_3)_3$ were prepared and characterized. Dissociation pressures were determined for both solids. The heat of reaction of phosphorus tribromide with trimethylamine was determined from Henry's law constants. The solubility relationship of the solid, $Br_3P \cdot N(CH_3)_3$, as a function of temperature was also established. A value of the heat of solution of the latter in phosphorus tribromide resulted. Nearly ideal liquid behavior was established in the phosphorus trichloride–trimethylarsine system above the "melting" range of $Cl_3P \cdot As(CH_3)_3$. Also the trimethylphosphine–trimethylamine system showed ideal behavior. The data provided an estimation of the bond energy in $Br_3P \cdot N(CH_3)_3$ and allowed a discussion of electronic factors in comparing its stability with the corresponding $Cl_3P \cdot N(CH_3)_3$ complex.

Introduction

The phosphorus–nitrogen linkage postulated to account for the existence of $Cl_3P \cdot N(CH_3)_3$ established previously[1] led to further investigation to ascertain more clearly the nature of the interaction. If the interaction involves the establishment of a phosphorus–nitrogen linkage, variation in the groups attached to either the phosphorus or nitrogen atom should show up in measurements of the relative interaction energies of the resultant molecules. Thus phosphorus tribromide–trimethylamine phase equilibria were studied to estimate the relative importance of decreasing electronegativity on the interaction energy. Going to the opposite situation, trimethylphosphine was considered to ascertain the effect of increasing the electron field around phosphorus. Finally, the effect of using an atom of lesser electron field than nitrogen was examined by studying the trimethylphosphine–trimethylarsine system.

Results

The PBr_3–$(CH_3)_3N$ System.—Additions of $(CH_3)_3N$ to 4.36 mmoles of liquid PBr_3 at 0° resulted in the three phase equilibrium ($C = L + V$) having a constant pressure of 1.6 mm., until a mole ratio of $(CH_3)_3N$ to PBr_3 of 1.00:1.03 was reached; after this the pressure rose sharply. It was noted that nice crystals, several mm. in length could easily be obtained from excess PBr_3.

Vapor pressures of the 1:1 complex were determined from 0 to 28° and are listed in the second row of Table I.

TABLE I

DISSOCIATION PRESSURES OF PHOSPHORUS TRIBROMIDE-TRIMETHYLAMINE

t, °C.	0.0	4.30	8.25	11.90	16.00
p, mm.	1.6	3.2	5.2	7.6	12.2
$p(CH_3)_3N$	1.5	3.0	4.8	7.0	11.3
t, °C.	19.90	25.1	25.2	28.0	
p, mm.	19.2	35.1	35.8	48.9	
$p(CH_3)_3N$	17.7	32.8	33.5	46.0	

The procedure followed to obtain the vapor pressures and prove their independence of the relative amount of vapor was similar to that described for the sublimation of $Cl_3P \cdot N(CH_3)_3$.[1]

The third row of Table I lists pressures obtained by subtracting out the contribution due to PBr_3. The latter calculation will be discussed later. However, in this case the correction does not influence

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[1] Presented before the Inorganic Division at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960. Previous paper in this series: R. R. Holmes, *J. Phys. Chem.*, **64**, 1295 (1960).

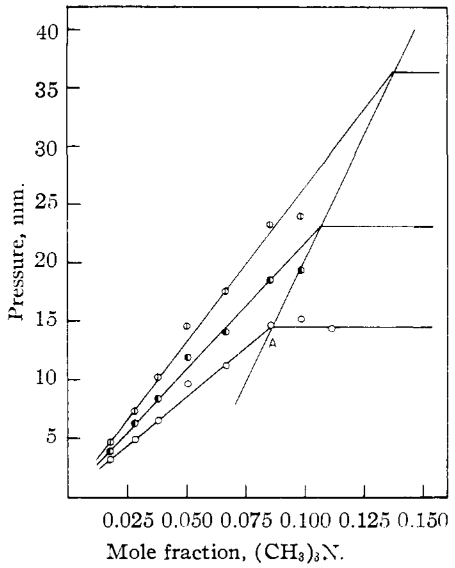

Fig. 1.—Trimethylamine pressures above phosphorus tribromide solutions: O, 18.00°; ◐, 22.0°; ◔, 26.0°.

the resultant heat of dissociation (obtained from the log p *vs.* $1/T$ plot) appreciably, differing by only 0.1 kcal. The heat of dissociation is 19.9 kcal./mole corresponding to the reaction[2]

$$Br_3P\cdot N(CH_3)_3(s) = PBr_3(l) + (CH_3)_3N(g)$$

In order to obtain an estimate for the interaction energy an experiment was designed employing a large mole ratio of PBr_3 to $(CH_3)_3N$. Here it was anticipated that the complex would be sufficiently soluble in excess PBr_3 to allow values of the Henry's law constant to be obtained as a function of temperature.[3] Measurements were made at 18.00, 22.0 and 26.0°. The measured pressures were corrected for the presence of PBr_3. The resulting $(CH_3)_3N$ pressures are listed in Table II and shown graphically in Fig. 1.

TABLE II

VAPOR PRESSURES OF PHOSPHORUS TRIBROMIDE–TRIMETHYLAMINE SOLUTIONS AS A FUNCTION OF TEMPERATURE[a]

18.00°		22.0°		26.0°	
Mole fraction $(CH_3)_3N$	p, $(CH_3)_3N$, mm.	Mole fraction $(CH_3)_3N$	p, $(CH_3)_3N$, mm.	Mole fraction $(CH_3)_3N$	p, $(CH_3)_3N$, mm.
0.0177	3.1	0.0177	3.9	0.0177	4.7
.0279	4.9	.0279	6.3	.0279	7.3
.0379	6.5	.0379	8.4	.0377	10.2
.0503	9.7	.0503	11.9	.0501	14.6
.0666	11.2	.0664	14.1	.0662	17.6
.0855	14.7	.0853	18.6	.0851	23.3
.0986	15.2	.0985	19.4	.0981	24.0
.1113	14.4				

[a] In this experiment 45.684 mmoles of PBr_3 was used.

The Henry's law constants are listed in Table III (included also are the vapor pressures of pure $(CH_3)_3N(p^0)$ for comparison) from which the heat of solution of $(CH_3)_3N(g)$ in $PBr_3(l)$ is calculated to be − 9.5 kcal./mole.

TABLE III

HENRY'S LAW CONSTANTS FOR TRIMETHYLAMINE IN PHOSPHORUS TRIBROMIDE

Temp., °C.	Henry's law constant k, mm.	p^0, $(CH_3)_3N$, mm.
18.00	168	1360
22.0	216	1560
26.0	265	1800

In Fig. 1 the plateaus correspond to the dissociation pressures of the solid complex (14.5 mm. at 18.00°, 23.1 mm. at 22.0° and 36.3 mm. at 26.0°) and were obtained from the log p *vs.* $1/T$ plot of the data of Table I. Their intersections with the $(CH_3)_3N$ pressure curve determine the solubility relationship with temperature of the solid complex in liquid PBr_3 as shown by the straight line connecting these intersections. The resultant solubilities in terms of amine mole fractions were 0.0858 at 18.00°, 0.1068 at 22.0° and 0.1374 at 26.0°. The log (mole fraction)$^{-1}$ *vs.* $1/T$ plot yielded a value of −10.4 kcal./mole for the heat of solution of the complex. The calculation indicated that the complex should "melt" at 64° at a $(CH_3)_3N$ dissociation pressure of 1.6×10^3 mm.

The above variation of solubility with temperature provided a means of estimating the partial pressures of PBr_3 that were used in establishing $(CH_3)_3N$ pressures as discussed in Tables I and II. Extrapolating the solution solubility lines in Fig. 1 to zero amine mole fraction provides values for the vapor pressures of pure PBr_3 as a function of temperature. These values were estimated to be 1.3 mm. at 18.00°, 1.8 mm. at 22.0° and 2.5 mm. at 26.0°. Considering that the measurements involved a maximum amine mole fraction of about 0.1, the magnitude of the vapor pressure lowering even considering complex formation is rather small; for example, at an amine mole fraction of 0.0981 at 26.0°, the highest temperature and concentration in Table II, the lowering amounted to 0.2 mm. Hence, the above pressures of pure PBr_3 were subtracted from the observed values to obtain the values listed in Table II for the vapor pressures of $(CH_3)_3N$. The PBr_3 contributions to be observed pressures from 0.0 to 28.0° in Table I were obtained graphically from the PBr_3 pressures at 18.00, 22.0 and 26.0° reported above. Considering that over the temperature range under study, 0 to 28.0°, the vapor pressure of pure PBr_3 varies between only 1 and 4 mm., it is felt that this procedure provides sufficiently reliable corrections.

The PCl_3–$(CH_3)_3As$ System.—The $Cl_3P\cdot As(CH_3)_3$ complex was previously characterized.[4] Vapor pressure measurements were made on the 1:1 solid and are reported in Table IV. The procedure followed to obtain the vapor pressures was similar to that described for the sublimation of $Cl_3P\cdot N(CH_3)_3$.[1]

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(2) The reaction corresponds to the presence of a three phase equilibrium ($C = L + V$) and not congruent sublimation (a two phase equilibrium, $C + V$) as indicated from the fact that the pressure of 1.6 mm. at 0° (Table I) is the same as the pressure obtained for the three phase equilibrium plateau. Also the pressure variation of the latter plateau with temperature should correspond to the vapor pressure data on the 1:1 complex (at 26.0°, for example, the plateau pressure is 38.3 mm. and the corresponding value in Table I is 38.6 mm.).

(3) The latter type of experiment could not be performed in the PCl_3–$(CH_3)_3N$ system[1] because of the closer volatility relationship of the components and the lower available sublimation pressures of the solid complex.

(4) R. R. Holmes and E. F. Bertaut, THIS JOURNAL, **80**, 2983 (1958).

TABLE IV

SUBLIMATION PRESSURES OF PHOSPHORUS TRICHLORIDE–TRIMETHYLARSINE

t, °C.	−40.8	−34.0	−29.5	−24.3	−20.0
p, mm.	2.8	4.2	6.3	9.1	12.0
t, °C.	−19.8	−15.9	−11.7		
p, mm.	12.8	16.7	22.7		

Measurements of the pressures of the system, gaseous $(CH_3)_3As$ dissolving in liquid PCl_3 at 0°, showed only slight negative deviations from ideal behavior in the $(CH_3)_3As$ mole fraction region of 0.0 to 0.5. Pressure measurements on mixtures of the components in the vapor show no tendency for association. From these two sets of measurements it is implied that little tendency for association of the components exists in either the liquid or gas phase.

Measurements of the vapor pressures of the 1:1 solid were continued up to 25°. The log p vs. $1/T$ plot (Fig. 2) is included to illustrate typical behavior of complexes of this type, the solid, first subliming ($C = V$ line), then the appearance of a liquid phase at point A ($= -10°$, corresponding to the dissociation, $C = L + V$) and finally solution of the complex at point B($= 4°$, $L + V$ equilibrium). The diagram is entirely analogous to that described for the $Cl_3P.N(CH_3)_3$ system[1] where a more elaborate discussion is included.

From the data of Table IV and the ideal behavior of the system the heat of dissociation of the solid complex to the free gaseous components may be evaluated. Equating the equilibrium constant for this process to $(0.5p)^2$ allows a value of the heat of dissociation to be calculated. The value is 18.2 kcal./mole.

The $(CH_3)_3P$–$(CH_3)_3N$ System.—No complex was formed in this system even at −78.5°. Measurements of the pressure composition diagrams in the region of 0.0 to 0.5 amine mole fractions showed ideal behavior at 0 and at −37.5°.

Discussion

The high solubility of $(CH_3)_3N$ in PBr_3 must mean that $(CH_3)_3N$ is predominantly in the form of a complex with PBr_3. The fact that the pressure varied linearly with amine mole fraction in the solution region (Fig. 1) implies that a series of successive equilibria does not exist. By analogy with the closely related system PCl_3–$(CH_3)_3N$, where a 1:1 complex was established in solution,[1] it seems reasonable to assume that such is the case here also.

In view of the above, the data are presented as heats of reaction and summarized in Table V. The last two reactions represent data determined in the preceding paper[1] and are included here for comparison.

Adding the heat of vaporization of $(CH_3)_3N$ of 6.40 kcal.[1] to reaction 1 gives a value of 3.1 kcal. for the estimated P–N bond energy in $Br_3P\cdot N(CH_3)_3$(assuming the heat of mixing of the liquids to be zero in the absence of complexing). The value is appreciably less than the estimated P–N bond energy of 6.4 kcal. in $Cl_3P\cdot N(CH_3)_3$, last reaction of Table V. These results would either imply that the greater electronegativity effect of chlorine increases the bonding in $Cl_3P\cdot N(CH_3)_3$ or the greater steric effect of bromine reduces it in $Br_3P\cdot N(CH_3)_3$. However, no evidence is presented here to decide the issue.

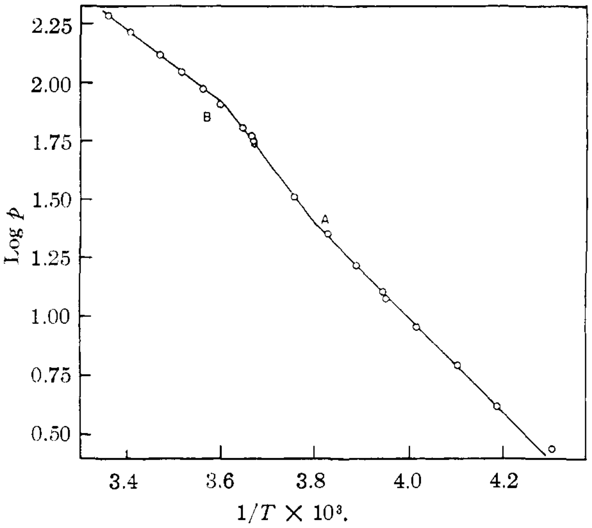

Fig. 2.—Variation with temperature of the dissociation pressure of phosphorus trichloride-trimethylarsine.

The observance of the completely ideal system in $(CH_3)_3P$–$(CH_3)_3N$ and only slight negative deviations in the PCl_3–$(CH_3)_3As$ system shows that either increasing the electron field around phosphorus or decreasing the field around the donor atom precludes "bonding."

TABLE V

HEATS OF REACTION IN THE PHOSPHORUS TRIHALIDE SYSTEMS

	ΔH, kcal./mole
$PBr_3(l) + (CH_3)_3N(g) = Br_3P\cdot N(CH_3)_3$ (soln.)	−9.5
$Br_3P\cdot N(CH_3)_3(s) = Br_3P\cdot N(CH_3)_3$ (soln.)	10.4
$Br_3P\cdot N(CH_3)_3(s) = PBr_3(l) + (CH_3)_3N(g)$	19.9
$Cl_3P\cdot As(CH_3)_3(s) = PCl_3(g) + (CH_3)_3As(g)$	18.2
$Cl_3P\cdot N(CH_3)_3(s) = PCl_3(g) + (CH_3)_3N(g)$	22.4
PCl_3(soln.) + $(CH_3)_3N$(soln.) = $Cl_3P\cdot N(CH_3)_3$(soln.)	−6.4

The absence of complexing in the PCl_3–$(C_2H_5)_3N$ system previously studied[5] indicates the operation of a steric effect since the ethyl groups would tend to increase the electron density around nitrogen and hence one would expect stronger interaction with PCl_3. Brown[6] and Sujishi[7] have postulated that $(C_2H_5)_3N$ does exert a steric effect in addition compound formation with $B(CH_3)_3$ from observations of the order of base strength: Quinuclidine > $(CH_3)_3N$ > $(C_2H_5)_3N$. Assuming the PCl_3 molecule to be about the size of $B(CH_3)_3$, such an effect could explain the lack of complexing with $(C_2H_5)_3N$.

The order of stability indicated by the data in terms of interaction energy in solution, $Cl_3P\cdot N(CH_3)_3 > Br_3P\cdot N(CH_3)_3$, and the non-existence of $Cl_3P\cdot As(CH_3)_3$ and $(CH_3)_3P\cdot N(CH_3)_3$ in solution follows what would be expected if the interaction

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[5] R. R. Holmes and E. F. Bertaut, THIS JOURNAL, **80**, 2980 (1958).

[6] H. C. Brown, *ibid.*, **67**, 1452 (1945).

[7] H. C. Brown and S. Sujishi, *ibid.*, **70**, 2878 (1948).

consisted of the formation of a P–N sigma bond in which an electron pair from nitrogen would be donated to phosphorus. If such is the case, the above complexes would be the first examples in which tricoördinated phosphorus is acting directly as an acceptor in sigma bond formation.

Experimental

Materials.—The purification of trimethylamine and phosphorus trichloride was described in a previous paper.[1]

Both trimethylphosphine[5] and trimethylarsine[4] are from samples used in previous work and whose purification is therein described. The samples were refractionated in the vacuum line and vapor pressures determined. Trimethylphosphine had a vapor pressure of 159.1 mm. at 0°; trimethylarsine 99.6 mm. at 0°.

Phosphorus tribromide (Eastman Kodak) supplied in a sealed glass ampoule exhibited a vapor pressure of 1.0 mm. at 0°.

Procedures.—The vacuum techniques and reaction section used are the same as those reported previously.[1]

All of the components could be measured out in the line except phosphorus tribromide. Sample sizes of the latter were obtained by direct weighing in the reaction ampoule flushed with nitrogen. Dry box techniques were employed for all transfer operations in which it was involved.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF ARGONNE NATIONAL LABORATORY, LEMONT, ILLINOIS]

Kinetics of the Reduction of Neptunium(VI) by Uranium(IV)[1]

BY J. C. SULLIVAN, A. J. ZIELEN AND J. C. HINDMAN

RECEIVED FEBRUARY 4, 1960

The kinetics of the reaction 2 Np(VI) + U(IV) = 2 Np(V) + U(VI) were studied in aqueous perchloric acid solutions and found to follow the rate law: $d[NpO_2^+]/dt = 2k[U^{+4}][NpO_2^{+2}]/[H^+]$. At an ionic strength of 2.00 and 25° the thermodynamic quantities of activation for the complex $(UOH \cdot NpO_2)^{+5}$ were found to be: $\Delta F^* = 16.05 \pm 0.01$ kcal./mole, $\Delta H^* = 18.2 \pm 0.2$ kcal./mole and $\Delta S^* = 7.4 \pm 0.8$ e.u. The effect of deuterium, ionic strength and the charge of the cations used to maintain the ionic strength were determined. The kinetics of analogous reactions of the (IV) and (VI) states of uranium, neptunium and plutonium are discussed.

Introduction

The various possible combinations in the reaction of the (IV) and (VI) states of uranium, neptunium and plutonium are all formally similar in that a quadrivalent ion is oxidized by a MO_2^{+2} ion, and it would therefore appear reasonable to predict a corresponding similarity in the kinetics of the reactions. However, this has not been found to be the case. Quantitative kinetic studies of the Np(IV)–Np(VI)[2] and U(IV)–Pu(VI)[3] reactions have yielded rate laws and postulated mechanisms of different forms, and a third type of rate law for the Pu(IV)–Pu(VI) and U(IV)–U(VI) reactions can be deduced from the disproportionation kinetics of the respective (V) states.[3–5] Thus a kinetic study of the U(IV)–Np(VI) reaction should extend our understanding of this system of reactions.

Experimental

The preparation and standardization of the following stock solutions have been previously described: neptunium (V) and (VI)[6]; perchloric acid, sodium perchlorate and thorium perchlorate[7]; deuterioperchloric acid[8]; and lithium perchlorate.[9] Reagent grade magnesium carbonate, lanthanum oxide and yttrium oxide were treated with perchloric acid followed by recrystallization to obtain the respective perchlorate solutions. Conventional procedures were employed by the analytical division of this Laboratory to standardize these solutions.

For the early experiments pure stock solutions of uranium (IV) perchlorate were prepared by dissolution of uranium trioxide in excess perchloric acid followed by electrolytic reduction with a continuous control potentiostat. However, it was later found more convenient to prepare the solutions by addition of excess granular lead to uranyl perchlorate in 2 molar perchloric acid. The reduction to uranium (IV) is quantitative and rapid, and solutions so prepared remained stable in U(IV) content for many weeks. The small amount of Pb^{+2} introduced in the stock solutions was found to have no detectable effect on the kinetics of the U(IV)–Np(VI) reaction. The uranium(IV) content was determined by addition of excess standard ceric perchlorate and titration with standard ferrous perchlorate to the ferroin end-point. Periodic checks of the stock solutions were also made spectrophotometrically at the 6480 Å. uranium(IV) absorption peak.

The reaction vessels were 5 cm. silica absorption cells, jacketed to allow continuous flow of water thermostated at the desired temperature. Stock solution aliquots of neptunium(VI), perchloric acid and sodium perchlorate (or other added salts) were added at room temperature. The cells were then placed in a Cary Model 14 MR Recording Spectrophotometer, the compartment of which was also independently thermostated at the working temperature. After attainment of temperature equilibrium an aliquot of uranium (IV) stock solution—maintained in a water-bath at the reaction temperature—was quickly squirted into the absorption cell by means of a micro pipet. The course of the reaction was followed by monitoring the growth of the 9800 Å. neptunium (V) absorption peak.

In the absence of added salts intitial concentrations of neptunium(VI) were obtained by radiometric assay of the reaction cell solutions; in all other cases initial concentrations were calculated from the stock solution concentration. Similarly hydrogen ion concentrations were determined by direct micro titration of the cell solutions whenever possible. In nearly all of the experiments neptunium(VI) was present in excess, and this, combined with the excellent stoichiometry observed in the reaction, allowed determination of the initial uranium(IV) concentration from the limiting optical density of each kinetic run. This procedure eliminated any errors due to air oxidation loss of uranium(IV) in transfer.

All concentrations were corrected for changes in solution volume with temperature and are reported in terms of moles/l. representated by the symbol M or by brackets.

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

(2) J. C. Hindman, J. C. Sullivan and D. Cohen, THIS JOURNAL, **81**, 2316 (1959); **79**, 4029 (1957); **76**, 3278 (1954).

(3) T. W. Newton, *J. Phys. Chem.*, **62**, 943 (1958).

(4) S. W. Rabideau, THIS JOURNAL, **79**, 6350 (1957).

(5) D. M. H. Kern and E. F. Orlemann, *ibid.*, **71**, 2102 (1949); H. G. Heal and J. G. N. Thomas, *Trans. Faraday Soc.*, **45**, 11 (1949).

(6) D. Cohen and J. C. Hindman, THIS JOURNAL, **74**, 4679 (1952).

(7) A. J. Zielen, *ibid.*, **81**, 5022 (1959).

(8) J. C. Sullivan, D. Cohen and J. C. Hindman, *ibid.*, **79**, 3672 (1957).

(9) A. J. Zielen and R. E. Connick, *ibid.*, **78**, 5785 (1956).