with carbon disulfide in liquid hydrogen sulfide. In amine-containing solutions, however, this relative instability of carbon–sulfur species works in favor of exchange for the present system, where the mechanism is thought to involve reversible thiocarbonate dissociation. The stability and low dissociation rate of bicarbonate would make for a much more limited exchange rate by this type of pathway.

With a view to making the foregoing picture more quantitative, we have tabulated in Table II some analogous rate and equilibrium constants for the carbon dioxide–water and carbon disulfide–hydrogen sulfide systems. The data for the first system are taken from the work by Faurholt,[11] the values being extrapolated either to 25 or $-23°$ and the concentration of water being introduced. (Also the nonliquid nature of the system at $-23°$ is ignored.) The CS_2–H_2S data are derived from the present research and are tabulated in terms of an assumption of the validity of the second (HCS_3^-) exchange model. Any indicated ions in hydrogen sulfide solution would, naturally, occur almost entirely associated in ion pairs with triethylammonium ion. In this table, we see reflected both the lesser stability and the greater dissociation rate of thiocarbonate relative to carbonate, a situation consistent with the preceding qualitative discussion. We further see the thiocarbonate dissociation rate constant, even at $-23°$, to be comparable to the carbon dioxide hydration rate constant (at 25°). In the table we have also given a maximum solvation rate constant for carbon disulfide, calculated from the estimated minimum exchange half-time for nonamine solutions, given in the previous paper.[4] The value is, of course, quite small, much smaller than the carbon dioxide hydration rate constant. Worth noting, however, is the fact that the ratio of these two constants ($\sim 10^6$) is not greatly different from the ratio of the recorded rate constants for reaction of OH^- with CO_2 as compared to SH^- with CS_2 ($\sim 10^4$).

TABLE II

COMPARISON OF RATES AND EQUILIBRIA FOR OXYGEN[a] AND SULFUR COMPOUNDS

$$B + CX_2 \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} BCX_2$$

B	CX_2	t, °C	k_2, M^{-1} sec^{-1}	k_{-1}, sec^{-1}	K, M^{-1}
H_2O	CO_2	25	1.0×10^{-3}	3×10	3×10^{-5}
H_2S	CS_2	25	$<5 \times 10^{-10}$ [b]		
OH^-	CO_2	-23	1.1×10^2	1.6×10^{-7}	7×10^8
SH^-	CS_2	-23	3×10^{-3}	8×10^{-4} [c]	3

[a] Constants for oxygen compounds extrapolated from data in ref 11. Water concentration, included in rate and equilibrium expressions, taken as 55.5 M. [b] Calculated from data in ref 4. H_2S concentration included in rate expression. [b] (Exchange rate constant) × 1.5.

The consistency between previous and present results, especially as reflected in the data tabulation in Table II, appears to support the general interpretation of the latter here presented. It is to be hoped that future work will help to resolve the ambiguity relative to the exact nature of the thiocarbonate species present.

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[11] C. Faurholt, *J. Chim. Phys.*, **21**, 400 (1924).

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Methanol Exchange in Dilute Solutions of Neptunium(V) Ions by Nuclear Magnetic Resonance Spectroscopy

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The relaxation of the methyl and hydroxyl protons of methanol by neptunium(V) has been examined over the temperature range of -80 to $+50°$. The results indicate that the rate of methanol exchange between the coordination sphere of neptunium(V) and the bulk solvent is measurable and has a rate constant of 9.0×10^4 sec^{-1} at 0°. ΔH^* and ΔS^* for this reaction are 7.5 kcal/mole and -8 eu, respectively.

Introduction

For some time it has been known that paramagnetic ions reduce the transverse relaxation time, T_2. McConnell and Berger[1] and Swift and Connick[2] have derived relationships from modified Bloch equations for the determination of the rate of exchange of ligands between the paramagnetic metal ion and the bulk ligand. Representative reactions studied in this way are the exchange of water between the transition elements[2,3] and the exchange of ammonia[4] and thiocyanate[5] ion with nickel(II), as well as the exchange of methanol with the transition metal ions.[6,7]

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[3] R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, *ibid.*, **30**, 950 (1959).

[4] (a) J. P. Hunt, H. W. Dodgen, and F. Klanberg, *Inorg. Chem.*, **2**, 478 (1963); (b) J. P. Hunt, H. W. Dodgen, and F. Klanberg, *ibid.*, **4**, 206 (1965).

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[6] R. G. Pearson, J. Palmer, M. M. Anderson, and A. L. Allred, *Z. Elektrochem.*, **64**, 110 (1960).

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In the present study the temperature dependence of the transverse relaxation time of the hydroxyl and methyl protons of acidified methanol by neptunim(V) was determined. The results of these experiments, which are described subsequently, show that the rate of methanol exchange between neptunium(V) and the bulk solvent is measurable.

Experimental Section

Proton resonance signals were recorded with a Varian Associates DP-60 nmr spectrometer. Chemical shifts and line widths were determined by the usual side band modulation technique. Chemical shifts are reported to within ±1 cps, and line widths are reproducible within ±0.1 cps for methyl and ±0.2 cps for hydroxyl protons. At least six measurements were made for each peak at every temperature. Relatively narrow lines permitted use of the absorption mode. Sweep rates of between 17 and 80 mgauss/min were used. These experiments were performed under conditions where saturation and artificial sweep-broadening effects were minimal.

Transverse relaxation times for the protons were calculated by the use of the relation, $1/T_2 = \pi\Delta\nu$, where $\Delta\nu$ is the full line width in cycles per second at half-maximum intensity.

Temperature control was maintained using a Varian Associates V-4340 variable-temperature probe and accessories and the V-4342 controller. It is estimated that the temperature varied not more than 0.5° for any given experiment although the temperature may be reported only to within ±2°.

Radiochemically pure neptunium(V) was used in these experiments in the following way. Neptunium(VI) in nitric acid was reduced to neptunium(V) with hydroxylamine hydrochloride, and then neptunium(V) hydroxide was precipitated by the addition of ammonium hydroxide. The precipitate was thoroughly washed and then dissolved in hydrochloric acid. Aliquots of this solution were then added to reagent grade methanol along with a few drops of tetramethylsilane and sufficient hydrochloric acid to make the total acid concentration 0.2 M.

Results and Discussion

The theoretical treatment of the data obtained from these experiments is that developed by Swift and Connick.[2] In this treatment changes in $1/T_2$ of the methyl or hydroxyl protons of methanol are due to the presence of the paramagnetic neptunium which shortens their lifetimes through chemical exchange and relaxation effects. More specifically, $1/T_{2P} = 1/T_{2,\mathrm{obsd}} - 1/T_{2,\mathrm{CH_3OH}}$, where $1/T_{2,\mathrm{obsd}}$ is the observed $1/T_2$ for a particular neptunium(V) concentration and $1/T_{2,\mathrm{CH_3OH}}$ is for the acidified methanol. In order to differentiate among possible relaxation mechanisms, T_{2P} must be measured as a function of temperature.

Table I and Figure 1 show the T_{2P} data for the methyl and hydroxyl protons in the presence of neptunium (V) at two different concentrations and cover a temperature range from −80 to +50°. A maximum for $1/T_{2P}$ occurs at 0° and a minimum at at −30°. The features of the curve shown in Figure 1 are quite similar to those found by Luz and Meiboom.[7,8] These workers have shown that the low-temperature "tail" is due to a dipole–dipole interaction between the paramagnetic ion and methanol molecules outside the coordination sphere. An activation energy for the low-temperature region of Figure 1 was found to be −1.5 kcal/mole, which is close to the −1.0 kcal/mole found by Luz and Meiboom[7] in the same temperature range for the cobalt(II)–methanol exchange reaction. Consequently, it was assumed that this contribution could be subtracted from the curves in Figure 1 (see dotted line).

TABLE I

LINE WIDTH DATA FOR NEPTUNIUM(V)–METHANOL EXCHANGE REACTION

$10^3/T$, °K^{-1}	Line width, cps^a		$1/T_{2P}$, sec^{-1}		$1/T'_{2P}$,^{b} sec^{-1}	
	CH$_3$	OH	CH$_3$	OH	CH$_3$	OH
1.98 × 10^{-3} M Np(V), 0.2 M HCl						
3.10	0.8	5.1	2.51	16.0	0.38	9.2
3.20	0.9	6.2	2.82	19.5	0.53	12.0
3.27	...	7.2	...	22.6	...	14.7
3.27	1.2	7.1	3.76	22.3	1.36	14.4
3.27	...	6.0	...	18.8	...	11.3
3.47	1.5	8.8	4.71	27.6	1.95	18.1
3.66	2.3	9.9	7.22	31.1	4.07	19.9
3.80	2.4	9.4	7.54	29.5	4.04	16.7
3.88	2.7	8.9	8.47	27.9	4.76	14.1
3.94	2.5	8.0	7.85	25.1	...	10.6
4.08	3.0	...	9.41	...	5.1	...
4.10	...	7.3	...	22.9	...	6.0
4.10	2.6	7.2	8.16	22.6	3.83	5.7
4.31	2.2	6.6	6.91	20.7	1.90	0
4.49	1.9	7.7	5.96	24.2	0	0
4.63	2.1	...	6.59	...	0	...
4.65	...	9.0	...	28.2	...	0
4.90	2.5	11.3	7.85	35.5	0	0
5.15	2.8	...	8.79	...	0	...
5.18	...	13.9	...	43.6	...	0
4.5 × 10^{-3} M Np(V), 0.2 M HCl						
3.10	2.1	11.7	6.59	36.8	1.65^c	21.8^c
3.20	2.5	13.4	7.85	42.1	2.55^c	25.8^c
3.27	2.8	20.2	8.80	63.5	3.22^c	46.0^c
3.27	2.5	19.1	7.85	60.0	2.27^c	42.5^c
3.30	3.0	15.4	9.42	48.4	3.72^c	30.5^c
3.44	3.3	20.1	10.7	63.1	4.42^c	42.9^c
3.64	4.3	23.1	13.5	72.5	6.26^c	48.0^c
3.69	4.4	20.5	13.8	64.4	6.29^c	38.7^c
3.80	5.2	23.6	16.3	74.0	8.47^c	45.8^c
3.89	6.4	20.1	20.1	63.0	11.4^c	32.2^c
3.97	5.9	18.3	18.5	57.5	9.33^c	24.5^c
4.11	5.3	16.7	16.6	52.5	6.50^c	15.5^c
4.51	...	17.9	...	56.2	...	0^c
4.55	4.5	...	14.1	...	0^c	...
5.26	...	31.0	...	97.4	...	0^c
5.29	7.5	...	23.5	...	0^c	...

[a] The contribution to the observed line width due to the acidified methanol has been subtracted. [b] The contribution of $1/T_{2M}$, the low-temperature "tail," has been subtracted. [c] These values have been normalized to 1.98 × 10^{-3} M neptunium(V).

Results are shown in Figure 2, using the relationship, $1/T'_{2P} = 1/T_{2P} - P_M/T_{2M}$, where $P_M = 4[\mathrm{Np(V)}]/[\mathrm{CH_3OH}]$. This figure clearly shows that there is a temperature region where chemical exchange is important. Furthermore, it is significant that the $1/T'_{2P}$ curves for the hydroxyl and methyl protons merge at about −35° because below this temperature the same value for $1/T'_{2P}$ is obtained from both protons. This is evidence that an actual exchange reaction is being measured and that the lifetime of the methanol–neptunium(V) complex may be obtained as a function of temperature.

In the temperature range where $1/T'_{2P}$ decreases with decreasing temperature (0 to −30°), condition

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(8) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 1058 (1964).

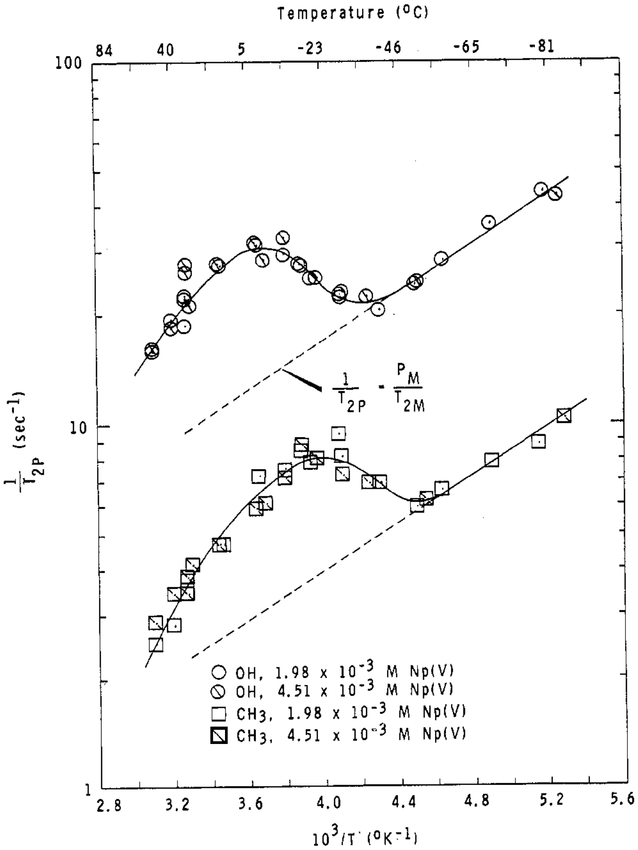

Figure 1.—Proton relaxation rates, $1/T_{2P}$, for methanol with neptunium(V) as a function of temperature. These solutions were 0.2 *M* in hydrochloric acid.

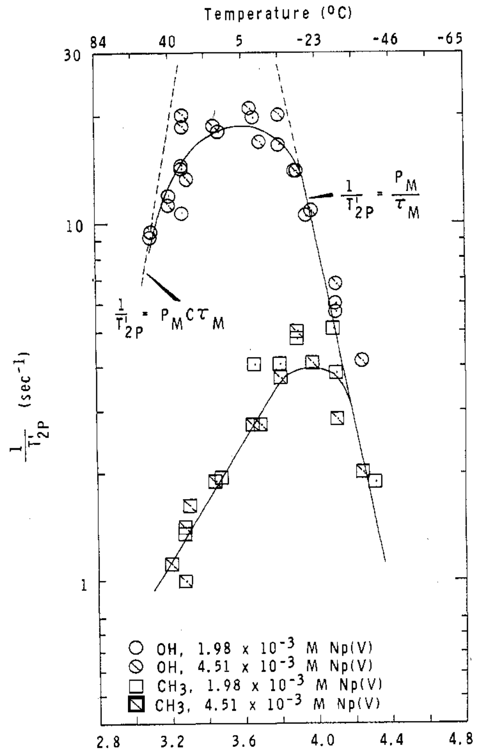

Figure 2.—Proton relaxation rates, $1/T'_{2P}$, for methanol with neptunium(V) as a function of temperature. These solutions were 0.2 *M* in hydrochloric acid.

10c of Swift and Connick[2] holds; *i.e.*, $1/T_{2M}^2 >> \Delta\omega_M^2$, $1/\tau_M^2$. The rate constant for the exchange, $1/\tau_M$, is given by the equation

$$\frac{1}{\tau_M} = \frac{1}{P_M T_{2P}} \tag{1}$$

where the data fit the Arrhenius equation

$$\frac{1}{\tau_M} = 1.8 \times 10^{11} \exp\left(\frac{-7900}{RT}\right) \tag{2}$$

In the neptunium(V)–methanol complex it is assumed that four methanol molecules are coordinated to the equatorial position of the linear NpO_2^+ ion. Values for ΔH^* and ΔS^* were calculated from the equation

$$\frac{1}{\tau_M} = \frac{kT}{h} \exp\frac{T\Delta S^* - \Delta H^*}{RT} \tag{3}$$

and Table II is a summary of the rate constant and activation parameters thus obtained.

TABLE II

SUMMARY OF RATE DATA FOR THE NEPTUNIUM(V)–METHANOL EXCHANGE REACTION

Quantity	Value
$1/\tau_M$, sec^{-1} at 0°	$(9.1 \pm 0.8) \times 10^4$
E_a, kcal/mole	7.9 ± 0.4
ΔH^*, kcal/mole	7.5 ± 0.4
ΔS^*, eu	-8.8 ± 0.6

For that region of the curve in Figure 2 between 0 and +50°, either condition 10b or 10d of Swift and Connick[2] may apply. Although the features of the curve are similar to those found for water[2] or ammonia exchange[4] with nickel(II) ion (condition 10b), this possibility was eliminated for the following reasons. The assumption, $1/\tau_M^2 >> \Delta\omega_M^2 >> 1/T_{2M}\tau_M$, is not satisfied. Furthermore, it was found that the $\Delta\omega_M$ obtained from the equation

$$\frac{1}{T_{2P}} = P_M \Delta\omega_M^2 \tau_M \tag{4}$$

differed by an order of magnitude from that found by the direct measurement of the chemical shift. $\Delta\omega_M$ is defined as the difference between the resonance frequencies of the bound and unbound methanol protons. Therefore, another mechanism had to be considered.

Condition 10d assumes $(1/T_{2M}\tau_M) >> 1/T_{2M}^2$, $\Delta\omega_M^2$ and is given by

$$\frac{1}{T_{2P}} = \frac{P_M}{T_{2M}} \tag{5}$$

In this case the temperature dependence of T_{2M} must be known in order to analyze the data. Bernheim, *et al.*,[3] have shown that the equation for T_{2M} has the form

$$T_{2M} = C^{-1}\tau_e^{-1} \tag{6}$$

and that the correlation time τ_e is given by the equation

$$\frac{1}{\tau_e} = \frac{1}{T_{1e}} + \frac{1}{\tau_M} \tag{7}$$

where T_{1e} is the electronic T_1 and τ_M is the lifetime of the complex. If the experimentally observed T_{2P} is a function of T_{2M} and τ_M, then

$$\frac{1}{T_{2P}} = \frac{P_M}{T_{2M} + \tau_M} = \frac{P_M}{\tau_M + C^{-1}(1/T_{1e} + 1/\tau_M)} \qquad (8)$$

where C is the constant in eq 6 which is assumed to be temperature independent. This assumption may not be true as will be shown below.

At relatively high temperatures (30-50°) eq 8 reduces to

$$\frac{1}{T_{2P}} = \frac{CP_M}{(1/T_{1e} + 1/\tau_M)} \qquad (9)$$

Using eq 9 at two different temperatures, a value of $\sim 3 \times 10^{-6}$ sec was found for T_{1e}. C was then calculated to be $\sim 5 \times 10^{10}$ using the same equation at a high temperature. However, some caution should be attached to the significance of these values. Since $\Delta\omega_M$ and consequently A/h are temperature dependent, C will also be temperature dependent and can no longer be considered a constant as some authors[2] have assumed. The value of T_{1e} is orders of magnitude larger than those found for other elements.[9] It would be more desirable to use values of T_{1e} obtained by independent means (esr) for the purpose of fitting these data. Unfortunately, it has not been determined in such a way.

Chemical shifts of the hydroxyl and methyl protons were determined as a function of temperature in order to establish the limiting conditions for T_{2P}, and these data are shown in Figure 3. Since condition 10d holds for the high-temperature region, then the equation which relates the observed chemical shift, $\Delta\omega_{obsd}$, to $\Delta\omega_M$ is given by $\Delta\omega_{obsd} = -P_M\Delta\omega_M$. Now $\Delta\omega_M$ and A/h, the scalar coupling constant, can be calculated.

After correction for "background" shift due to the free methanol, $\Delta\omega_M$ for the hydroxyl protons was found to be 9×10^4 cps at 40°. In view of the small and uncertain observed shift for the methyl protons, $\Delta\omega_M$ was not calculated for these protons.

Calculation of A/h for the hydroxyl protons was made by use of the equation

$$\frac{A}{h} = \frac{\Delta\omega_M}{\omega_0}\frac{3kT\gamma}{J(J+1)h\gamma_e} \qquad (10)$$

which was developed by Bloembergen.[10] In this equation k is Boltzmann's constant, ω_0 is the resonance frequency, γ is the proton magnetogyric ratio, J is the total angular momentum of neptunium(V), and γ_e is the electron magnetogyric ratio. At 40° A/h for the hydroxyl proton was calculated to be 9.5×10^5 and is comparable to those found for the transition elements.[3-7] So, the 5f electrons of neptunium(V) must be sufficiently unshielded to extend significantly into the region of the proton, and this is consistent with other observations that the 5f orbitals participate in chemical bonding.[11-15]

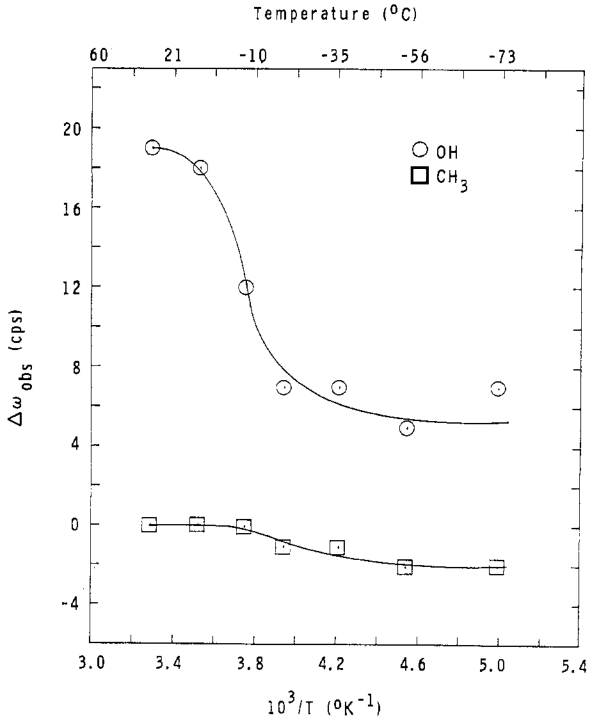

Figure 3.—Frequency shift of methanol protons for a solution containing 7.5×10^{-3} M neptunium(V) as a function of temperature. This solution was 0.2 M in hydrochloric acid.

Probably the most significant aspect of this study is that it demonstrates that ligand exchange reactions of the actinide elements may be measured by the nmr line-broadening technique. This is certainly true for neptunium(V), and it should be possible to examine the reactions of the other oxidation states of neptunium as well as uranium.

It should be noted that these measurements were made in the presence of a very low concentration of free radicals owing to the α radiolysis of methanol. Assuming a G value of 2 for the radiolysis of methanol the free-radical concentration for a 4×10^{-3} M neptunium(V) solution is estimated to be less than 10^{-8} M. This concentration of free radicals is not expected to contribute significantly to the relaxation of the methanol protons relative to that of neptunium.

The rate constant for methanol exchange is considerably larger for neptunium(V) than those for comparable reactions involving nickel(II) and cobalt(II).[7,8] In addition, the ΔH^* for the neptunium(V) reaction is about half that observed for the nickel(II) and cobalt(II) reactions.[7,8] Excluding possible crystal-field effects which may alter the mechanism of exchange, the differences in rate of exchange and ΔH^* may be naively explained on the basis of a simple electrostatic model where the free energy of activation is due to an ion–

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dipole interaction. It would be expected that the neptunium(V)–methanol interaction would be less than that for a 2+ ion–methanol interaction and result in a lower ΔF^*.

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The Reaction of Ammonia–Chloramine Mixtures with Phosphorus–Phosphorus Bonds

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The reactions of ammonia–chloramine mixtures with tetramethyldiphosphine, tetraethyldiphosphine, tetraphenyldiphosphine, and tetraphenylcyclotetraphosphine have been shown to result in the fission of the phosphorus–phosphorus bonds and in the formation of the same products as would be expected from the reaction of ammonia–chloramine mixtures with the corresponding mono- or dihalophosphines. The previously postulated but not isolated compounds $[(C_6H_5)_2P(NH_2)_2]Cl$ and $[(C_6H_5)P(NH_2)_3]Cl$ were obtained. It is postulated that the initial products of the P–P bond fission are R_2PCl and R_2PNH_2. It was also shown that dimethyldiaminophosphonium chloride reacts with PCl_5 to yield $(CH_3)_2Cl_4P_3N_3$. The mode of formation and the infrared spectrum indicate that this product is a phosphonitrilic cyclic trimer in which both methyl groups are on the same phosphorus atom.

It has recently been reported[1-3] that the reaction of ammonia–chloramine mixtures with monochlorophosphines produces diaminophosphonium chlorides which undergo self-condensation reactions giving phosphonitrilic polymers. Since halophosphines are formed by cleavage of diphosphines and polyphosphines with free halogens,[4,5] it was interesting to determine if phosphorus–phosphorus bonds would be cleaved by reaction with chloramine. Thus, the reaction of ammonia–chloramine mixtures with substituted diphosphines, for example, might give the same products which are obtained from the analogous reaction with monochlorophosphines.

We now are reporting the results of a study of the reactions of gaseous chloramine and ammonia with tetramethyldiphosphine, tetraethyldiphosphine, tetraphenyldiphosphine, and tetraphenylcyclotetraphosphine. The reaction of dimethyldiaminophosphonium chloride with phosphorus(V) chloride was also studied.

Experimental Section

Materials.—The gaseous mixture of chloramine and ammonia was produced by the gas phase reaction of chlorine with ammonia in a generator similar to that described by Sisler, *et al.*[6] The gas flow rates were such that the mole ratio of ammonia to nitrogen to chlorine was approximately 12:3:1, and the production rate of chloramine was approximately 0.1 mole/hr.

All solvents used were reagent grade. Benzene, diethyl ether, and petroleum ether were dried and stored over calcium hydride. Phenyldichlorophosphine and diphenylchlorophosphine were provided by Victor Chemical Works. Tri-*n*-butylphosphine was otained from Food Machinery and Chemical Corp. Dimethyldiaminophosphonium chloride for the reaction with phosphorus(V) chloride was synthesized from dimethylchlorophosphine.

Manipulative Methods.—Liquid reagents and solvents were transferred by pipet to minimize exposure to atmospheric oxygen and water vapor. The substituted diphosphines and tetraphenylcyclotetraphosphine were stored and transferred in an inert-atmosphere box containing dry nitrogen. Hygroscopic reaction products were also stored and handled in the drybox.

Analyses.—Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Several nitrogen analyses were obtained in these laboratories using a Coleman Model 29 nitrogen analyzer. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

The infrared spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrometer and on a Beckman Model IR10 spectrophotometer. Solid samples were examined between KBr disks as Nujol mulls. In certain instances thin films could be obtained by carefully evaporating a chloroform solution of the sample on a KBr disk. The infrared spectral absorptions are listed in Table I. Sections of the infrared spectrum of $[(C_6H_5)_2P(NH_2)_2]Cl$ are shown in Figure 1.

Preparation of Substituted Diphosphines and Tetraphenylcyclotetraphosphine.—Tetramethyldiphosphine and tetraethyldiphosphine were prepared by the method of Maier.[7] The observed boiling point of tetramethyldiphosphine was 36° (16 mm) [lit.[7] bp 38–40° (16 mm)]. The observed boiling point of tetraethyldiphosphine was 67° (1.7 mm) [lit.[7] bp 220–223° (740 mm)]. Both liquids are spontaneously flammable in air.

Tetraphenyldiphosphine was synthesized by the reaction of diphenylchlorophosphine with tri-*n*-butylphosphine.[8] The material used in this study melted at 118–121° (lit.[5] mp 120.5). Although strict precautions against oxidation of the diphosphine

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