then the basic assumption of invariance of ΔH with temperature is false and only an approximate value for the midpoint of the temperature range could be obtained.

The decrease in the magnitude of $\Delta H_n°$ with increasing complexity of α-amino acid in the formation of metal complexes is much more pronounced for nickel than for copper.[2,3] Seven of the nine $\Delta H_2°$ values determined were more negative than were the corresponding $\Delta H_1°$ values, probably indicating differences in solvation of the NiL^+ ions. It is noteworthy that the values of $\Delta S_1°$ for Cu^{2+} and Ni^{2+} complexes and of $\Delta S_2°$ for Cu^{2+} complexes were more positive for alanine complexes than for either glycine or phenylalanine complexes, while the value of $\Delta S_2°$ for Ni^{2+} complexes increased from glycine to alanine to phenylalanine.

As one might expect, the formation constants for ML^+ decrease with increasing ligand complexity. This trend is not so pronounced for the formation of NiL_2 complexes.

Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida

The Reactions of Dimethylaminophosphines with Dimethylchloramine

By S. R. Jain, L. K. Krannich, R. E. Highsmith,
and Harry H. Sisler

Received November 7, 1966

It has been well established that the chloramination of tertiary phosphines in the presence of ammonia yields aminophosphonium chlorides.[1-4] Several tertiary phosphines, including some dialkylaminophosphines,[2-4] were chloraminated in our laboratory and invariably analogous results were obtained. It was of interest to know whether dimethylchloramine also behaves toward the dimethylaminophosphines in an analogous way giving phosphonium salts according to the equations

$$(CH_3)_2NP(CH_3)_2 + (CH_3)_2NCl \longrightarrow [\{(CH_3)_2N\}_2P(CH_3)_2]Cl \quad (1)$$

$$[(CH_3)_2N]_2P(CH_3) + (CH_3)_2NCl \longrightarrow [\{(CH_3)_2N\}_3P(CH_3)]Cl \quad (2)$$

If so, it was thought that the proton magnetic resonance spectra of the reaction products of eq 1 and 2 might provide a further proof of the chloramination occurring on the phosphorus atom as has been observed in the earlier studies.[2-4]

The results of the present investigation show that except in the case of tris(dimethylamino)phosphine, the reactions of dimethylchloramine with dimethylaminophosphines yield the expected phosphonium salts, the chloramination occurring on the phosphorus atom of the aminophosphines. The analogous reactions of tris(dimethylamino)phosphine with ammonia plus chloramine and with ammonia-free chloramine were carried out. A different result was obtained for the reaction of tris(dimethylamino)phosphine with dimethylchloramine, and a mechanism for this reaction has been suggested.

Experimental Section

All operations were conducted in a moisture-free nitrogen atmosphere.

Materials.—Solvents were dried over calcium hydride. Dimethylamine used in the preparation of aminophosphines was obtained from the Matheson Co. Phosphorus trichloride, obtained from J. T. Baker Co., was redistilled before use. The aminophosphines[5,6] and dimethylchloramine[7] were synthesized by previously reported procedures.

Analyses.—Elemental analyses were carried out by the Galbraith Microanalytical Laboratories. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus.

Infrared Spectra.—Infrared spectra were recorded with a Beckman Model IR-10 grating infrared spectrophotometer. The spectra of solids were taken in the form of Kel-F mulls for the range 2.5–7.5 μ and as Nujol mulls for the range 7.5–20 μ using KBr plates. A summary of spectral bands is presented in Table I.

Table I[a]

Infrared Data (cm^{-1})

$[\{(CH_3)_2N\}_3PCH_3]Cl$

2940–2800 b, s, 2620 w, 2425 w, 2240 w, 1600 w, 1450 s, 1420 m, 1327 s, 1315 s, 1280 sh, 1185 s, 1165 sh, 1155 sh, 1115 w, 1080 sh, 1060 s, 990 b, vs, 922 m, 810 vs, 735 vs, 615 w, 450 m

$[\{(CH_3)_2N\}_2P(CH_3)_2]Cl$

2925 s, 2800 s, 2800 s, 2310 vw, 1440 s, 1420 m, 1410 m, 1320 m, 1305 s, 1288 m, 1178 s, 1110 vw, 1068 s, 995 b, vs, 970 m, 952 m, 898 s, 775 m, 770 s, 720 m

$[\{(CH_3)_2N\}_3PNH_2]Cl$

3175–2800 b, vs, 2550 b, w, 2320 b, vw, 1565 s, 1540 sh, 1480 sh, 1450 vs, 1410 sh, 1300 vs, 1176 vs, 1166 sh, 1114 w, 1066 vs, 993 m, 758 s, 745 s, 626 m, 470 m

$[\{(CH_3)_2N\}_3PNH_2]PF_6$

3470 s, 3300 s, 3045 m, 3025 m, 2995 m, 2940 w, 2820 w, 1575 w, 1530 w, 1478 s, 1460 w, 1425 m, 1312 s, 1176 s, 1076 s, 1000 vs, 937 m, 833 b, s, 758 s, 741 s, 625 w, 557 vs, 465 b, w

$[\{(CH_3)_2N\}_3PNH_2]B(C_6H_5)_4$

3450 vs, 3360 vs, 3000 sh, 2945 sh, 2920 s, 2865 m, 2830 m, 1565 vs, 1485 s, 1460 b, s, 1418 w, 1302 s, 1266 w, 1167 s, 1147 m, 1144 sh, 1064 m, 1027 m, 1000 vs, 951 m, 858 w, 846 m, 758 m, 743 vs, 735 vs, 717 m, 708 vs, 625 w, 615 m, 605 s

[a] s, strong; m, medium; w, weak; sh, shoulder; b, broad.

Nuclear Magnetic Resonance Spectra.—Nuclear magnetic resonance spectra for protons were recorded with a Varian Associates A-60A spectrometer at 60 Mcps. The spectra were run in $CDCl_3$ solutions with tetramethylsilane as external standard. ^{31}P chemical shifts were determined with respect to H_3PO_4 (85%) as external standard using a Varian Model V-4300-2 high-resolution spectrometer at 19.3 Mcps in chloroform solution. A summary of the nmr data is given in Table II.

Reaction of Dimethylaminodimethylphosphine with Dimethyl-

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TABLE II

NMR PARAMETERS FOR PHOSPHONIUM SALTS

Compound	τ_{NCH_3}	τ_{CH_3}	J_{PNCH}, cps	J_{PCH}, cps	$\delta^{31}P$, ±2.5 ppm
$[\{(CH_3)_2N\}_2P(CH_3)_2]Cl$	7.08	7.58	10.5	13.8	−68.4
$[\{(CH_3)_2N\}_3P(CH_3)]Cl$	7.08	7.63	10.0	14.2	−54.4
$[\{(CH_3)_2N\}_3PNH_2]Cl$[a]	7.11		9.5		−42.6
$[\{(CH_3)_2N\}_3PCl]Cl$	6.9		13.0		−50.3
$[\{(CH_3)_2N\}_3PBr]Br$[b]	6.96		13.5		

[a] Data reported previously, see ref 4. [b] Data reported previously, see ref H. Nöth and H. J. Vetter, *Ber.*, **98**, 1981 (1965).

chloramine.—In a typical experiment 1.6 g of freshly prepared dimethylchloramine (0.02 mole) in 25 ml of dry ether was added dropwise to an ice-cooled, well-stirred solution of dimethylaminodimethylphosphine (0.017 mole) in 25 ml of ether. A white precipitate formed immediately. The reaction mixture was stirred for 4 hr after bringing it to room temperature. The solid reaction product was filtered, washed with acetone, then with ether, and dried under vacuum. On heating, the white, hygroscopic, solid material turned gray, but it did not melt below 300°; yield 65%.

Anal. Calcd for $[\{(CH_3)_2N\}_2P(CH_3)_2]Cl$: C, 39.02; H, 9.82; N, 15.17; P, 16.78; Cl, 19.20. Found: C, 38.63; H, 10.58; N, 14.90; P, 16.74; Cl, 19.13.

Reaction of Bis(dimethylamino)methylphosphine with Dimethylchloramine.—Dimethylchloramine (1.8 g, 0.0225 mole) in 50 ml of dry ether was added dropwise to an ice-cooled solution of bis(dimethylamino)methylphosphine (0.022 mole) in 80 ml of ether. A white precipitate formed immediately. After the reaction was complete, the reaction mixture was brought to room temperature. The solid reaction product was filtered, washed with ether, and dried under vacuum. The white, hygroscopic compound turned brown and started to decompose at about 250°; yield 68%.

Anal. Calcd for $[\{(CH_3)_2N\}_3P(CH_3)]Cl$: C, 39.34; H, 9.90; N, 19.67; P, 14.50; Cl, 16.59. Found: C, 39.17; H, 10.08; N, 19.44; P, 14.37; Cl, 16.87.

Reaction of Tris(dimethylamino)phosphine with Dimethylchloramine.—In a typical experiment 2.02 ml of dimethylchloramine (0.0246 mole) in 5 ml of ether was slowly added to a solution of 2.0 g of tris(dimethylamino)phosphine (0.0123 mole) in 10 ml of ether in a flask equipped with a filter and an overhead stirrer. A white powdery precipitate was observed shortly after the addition was complete. The powder assumes a yellowish tint after about 3 hr and becomes a yellowish tacky mass after 24 hr. The above reaction mixture was filtered after 1.5 hr, washed with ether, and dried under vacuum; mp 252–254°. The yield after a reaction time of 1.5 hr was about 15%. Longer reaction time resulted in a larger yield (up to 80%) but the product obtained was less pure.

Anal. Calcd for $[\{(CH_3)_2N\}_3PCl]Cl$: N, 17.95; Cl, 30.30. Found: N, 17.8; Cl, 30.96.

The same reaction product is obtained when dimethylchloramine and tris(dimethylamino)phosphine are mixed in a 1:1 mole ratio. This compound, on recrystallization from tetrachloroethane, forms an adduct with the solvent, decomposing at 145–150°.

Anal. Calcd for $[\{(CH_3)_2N\}_3PCl]Cl \cdot C_2H_2Cl_4$: C, 23.90; H, 5.01; N, 10.45; P, 7.70; Cl, 52.92. Found: C, 24.82; H, 5.76; N, 10.99; P, 8.13; Cl, 51.00.

Reaction of Tris(dimethylamino)phosphine with Ammonia and Chloramine and with Ammonia-Free Chloramine.—Tris(dimethylamino)phosphine (0.01 mole) was pipetted into 75 ml of petroleum ether and chloraminated in the presence of ammonia on the chloramine generator for 6 min (0.01 mole of chloramine). The chloramine generator used in this study is similar to that described previously.[8] A white precipitate formed immediately. At the completion of the reaction, the solution was filtered and the white, solid product was recrystallized from a chloroform–diethyl ether mixture. The white, needlelike crystals obtained melted at 146–149°; yield 80%.

Anal. Calcd for $[\{(CH_3)_2N\}_3PNH_2]Cl$: C, 33.57; H, 9.39; N, 26.10; P, 14.43; Cl, 16.52. Found: C, 32.17; H, 9.51; N, 24.88; P, 14.40; Cl, 16.52.

In another experiment, 0.006 mole of tris(dimethylamino)phosphine in 10 ml of ether was mixed with 0.0066 mole of ammonia-free chloramine in 60 ml of ether. Ammonia-free chloramine was prepared as described in an earlier report from this laboratory.[9] After the completion of the reaction, the ether was filtered off and the remaining solid was crystallized from a chloroform–ether mixture. White crystals obtained; mp 145–149°; yield 82%.

Anal. Calcd for $[\{(CH_3)_2N\}_3PNH_2]Cl$: N, 26.10; Cl, 16.52. Found: N, 26.5; Cl, 14.8. The infrared and nmr spectra of this sample and the one obtained by chloramination in the presence of ammonia were found to be identical.

Tris(dimethylamino)aminophosphonium Salts. (a) Hexafluorophosphate.—An aqueous solution of tris(dimethylamino)aminophosphonium chloride was added dropwise to a saturated aqueous solution of potassium hexafluorophosphate in equimolar ratio. A white solid formed immediately and was recrystallized from 1-propanol. The melting point of the recrystallized material was 269–272°; yield 95%.

Anal. Calcd for $[\{(CH_3)_2N\}_3PNH_2]PF_6$: N, 17.28. Found: N, 17.19.

(b) **Tetraphenylborate.**—The tetraphenylborate derivative was prepared by mixing aqueous solutions of tris(dimethylamino)aminophosphonium chloride and sodium tetraphenylborate in equimolar quantities. A white solid formed immediately and was recrystallized from boiling chloroform; mp 265–266°; yield 90%.

Anal. Calcd for $[\{(CH_3)_2N\}_3PNH_2]B(C_6H_5)_4$: N, 11.24. Found: N, 11.46.

Discussion

The results of the present investigation show that the reactions of dimethylaminodimethylphosphine and bis(dimethylamino)methylphosphine with dimethylchloramine give the corresponding phosphonium chlorides as expected. Evidence concerning their structures and a proof that the chloramination occurs on the phosphorus atom of the aminophosphine is provided by a proton magnetic resonance study of these salts. In the first place, if the chloramination occurs on the nitrogen atom of the aminophosphines, $[(CH_3)_2N]_2P(CH_3)$ or $(CH_3)_2NP(CH_3)_2$, more than two doublets would be observed in the proton magnetic resonance spectra. The presence of only two doublets (as shown in Figure 1) indicates that the added dimethylamino group in the phosphonium salts is indistinguishable from the other dimethylamino groups attached to the phosphorus atom. Furthermore, the 6:1 and 2:1 area ratio observed for the dimethylamino and methyl proton peaks in the nmr spectra of the chloramination products of bis(dimethylamino)methylphosphine and dimethylaminodimethylphosphine, respectively, definitely show that the incoming dimethylamino group is attached to the phosphorus atom. Similar results have been obtained on the methyl iodide adducts of these phosphines by Cowley and Pinnell.[10]

The reaction of tris(dimethylamino)phosphine with

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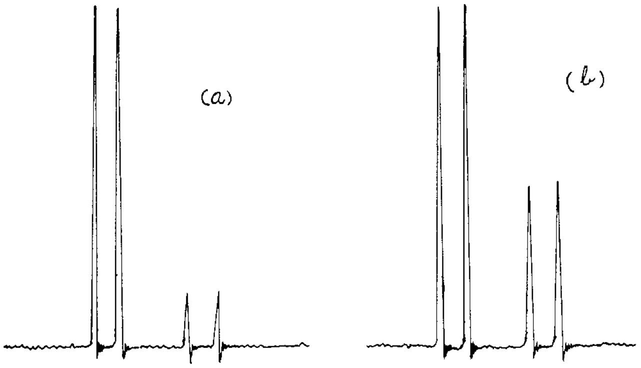

Figure 1.—The proton nmr spectra of (a) $[\{(CH_3)_2N\}_3PCH_3]Cl$ and (b) $[\{(CH_3)_2N\}_2P(CH_3)_2]Cl$. The ratios of the areas under the doublets are 6:1 in (a) and 2:1 in (b).

ammonia plus chloramine and with ammonia-free chloramine yields the expected aminophosphonium chloride. However, the reaction of tris(dimethylamino)phosphine with dimethylchloramine is unusual in the sense that the expected tetrakis(dimethylamino)phosphonium salt is not obtained. Analytical and infrared data for this reaction product are identical with those for tris(dimethylamino) chlorophosphonium chloride, reported earlier by Nöth and Vetter (see Table II). These authors established the phosphonium-salt-like nature of this substance by measuring its equivalent conductivity and by preparing various derivatives. The proton nmr spectrum of this compound is comparable to that of the corresponding bromophosphonium bromide and so is the chemical shift of phosphorus comparable to that of other phosphonium salts as shown in Table II. It is interesting to note that the analogous reaction of the tris(dimethylamino)arsine with dimethylchloramine yields the tetrakis(dimethylamino)arsonium salt.[11] The tetrakis(dimethylamino)phosphonium salt is not obtained, perhaps because of the steric hindrance resulting from the interaction of four dimethylamino groups. The reaction probably occurs in accordance with the equation

$$[(CH_3)_2N]_3P + 2(CH_3)_2NCl \longrightarrow [\{(CH_3)_2N\}_3PCl]Cl + (CH_3)_2NN(CH_3)_2$$

Evidence of the presence of tetramethylhydrazine in the reaction mixture is provided by the strong reducing properties of the supernatant liquid.

Infrared data for the new phosphonium salts are presented in Table I. Some of the characteristic bands can be readily identified, *e.g.*, C–H stretch at 2940–2800 cm^{-1}, C–H deformation at 1450 cm^{-1}, $P–CH_3$ or $P–N(CH_3)_2$ vibration at 1315–1300 cm^{-1}, and $P–N(CH_3)_2$ at 1000–990 cm^{-1}. These spectra are similar to those of other phosphonium salts reported earlier[2,4] and can be assigned accordingly.

Acknowledgment.—The authors are pleased to acknowledge the partial support of this research by the National Science Foundation through project No. GP4505, and by the National Institutes of Health through grant No. CA08263-02, both with the University of Florida.

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Contribution from Argonne National Laboratory,
Argonne, Illinois 60439

The Melting-Point Diagram for the System Uranium Hexafluoride–Plutonium Hexafluoride

By L. E. Trevorrow, M. J. Steindler, D. V. Steidl,
and J. T. Savage

Received November 10, 1966

In order to obtain information on condensed-phase equilibria in the system UF_6–PuF_6, a thermal analysis study was carried out, yielding a temperature–composition phase diagram. The only other literature reference[1] to condensed-phase equilibria in a binary mixture of actinide hexafluorides indicates that solid solutions are formed in the system UF_6–NpF_6.

Experimental Section

Materials.—The materials, UF_6 and PuF_6, were manipulated by vacuum distillation in apparatus constructed of nickel tubing and fittings and Monel diaphragm valves. The manifold was located in a glove box to contain the α hazard.

Emission-spectrographic analysis of the UF_6 indicated that the predominant impurities were P, at a concentration of <400 ppm, and As, B, Cs, Pd, Re, Sb, Sn, and Th, each present at concentrations of <100 ppm. Two determinations of the triple point of a sample of the UF_6 yielded values of 64.1 and 64.2°. The best literature value[2] for the triple point of UF_6 is 64.05°.

The PuF_6 was prepared by reaction of fluorine with PuF_4 at 550°; it was purified by a trap-to-trap distillation similar to that described by Weinstock and Malm.[3] The purity of the PuF_6 product was indicated by the triple point and also by an emission-spectrographic analysis of the PuF_4 used in its preparation. The PuF_4 contained Ca (<25 ppm), Fe (<20 ppm), and Sb (<20 ppm) as predominant impurities. Two determinations of the triple point of a sample of purified PuF_6 yielded values of 51.5 and 51.3°. The best literature value[2] for the triple point of pure PuF_6 is 51.59° obtained by extrapolation of vapor pressure data.

Thermal Analysis.—For thermal analysis, mixtures were contained in a nickel sample tube which could be closed by a bellows valve assembly with a Teflon seat. The temperature of a mixture was measured by a thermocouple positioned within a well in the bottom of the tube.

For either thermal analysis or differential thermal analysis, sample tubes were positioned in cavities within a cylindrical nickel block, the temperatures of which could be varied as a linear function of time by the aid of a program controller. Most of the analyses were performed at a heating rate of 0.3°/min; some were performed at 0.6°/min. The signal of the thermocouple in the sample tube was measured by a recording potentiometer, which was periodically calibrated against a Leeds and Northrup Type K-3 potentiometer.

The composition of each mixture was determined by weighing the sample tube after each component had been added to it by vacuum distillation. Small samples (1–4 g) were used to promote homogeneity in the absence of stirring.

Results and Discussion

The shapes of the melting curves were characteristic of those exhibited by solid solutions, and the solidus and liquidus points were determined by intersections

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