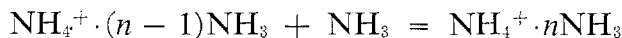


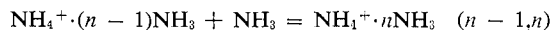
# Ion-Solvent Molecule Interactions Studied in the Gas Phase. Heats and Entropies of Individual Steps.



A. M. Hogg, R. M. Haynes, and P. Kebarle

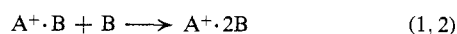
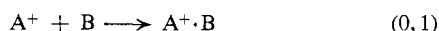
*Contribution from the Chemistry Department, University of Alberta,  
Edmonton, Alberta, Canada. Received June 23, 1965*

**Abstract:** Important and hitherto unavailable information on ion-solvent molecule interactions can be obtained from the study of ion clusters in the gas phase. A new mass spectrometric method is applied to concentration measurements of the clustering reactions ( $n-1, n$ ). Experiments in which the gas sampling is done under near-



molecular flow conditions give good equilibrium constants for ammonia pressure changes by a factor of ten. Determinations of the equilibrium constants at different temperatures lead to the enthalpy and entropy changes. The values obtained are:  $\Delta H_{2,3} = -17.8$ ,  $\Delta H_{3,4} = -15.9$ ,  $\Delta H_{4,5} \sim -9$  kcal./mole,  $\Delta S_{2,3}^\circ = -38$ ,  $\Delta S_{3,4}^\circ = -40.5$  e.u. at 298°K. and atmospheric standard pressure. The numerically much smaller  $\Delta H_{4,5}$  shows that the inner shell is completed with four ammonia molecules. It is shown that the measured thermodynamic values are consistent with estimates based on thermodynamic cycles and calculation.

The study of ions in solution represents a major field of chemical research. It is perhaps not widely realized that a great wealth of significant information on ion-solvent molecule interactions could also be obtained from the study of ion-solvent clusters in the gas phase. Consider the ion  $A^+$  produced in the gas phase by some form of ionizing radiation or thermal means. If the atmosphere surrounding the ion contains the vapor of a polar molecule (solvent B), a number of clustering reactions will occur.



At equilibrium the following relations will hold

$$\Delta F_{0,n}^\circ = \Delta F_{0,1}^\circ + \Delta F_{1,2}^\circ + \dots + \Delta F_{n-1,n}^\circ \quad (\text{I})$$

$$\Delta F_{n-1,n}^\circ = -RT \ln \left\{ \frac{P_{A^+ \cdot nB}}{P_{A^+ \cdot (n-1)B} P_B} \right\} = -RT \ln K_{n-1,n} \quad (\text{II})$$

where  $P_X$  is the partial pressure of X.

Thus knowledge of the equilibrium concentrations of the clustered species  $A^+ \cdot nB$  obtained from experiments at different pressures of B will allow the determination of  $K_{n-1,n}$  and  $\Delta F_{n-1,n}^\circ$ . Such measurements done at different temperatures will lead to the evaluation of  $\Delta H_{n-1,n}$  and  $\Delta S_{n-1,n}^\circ$ . The availability of such detailed information will, for instance, reveal the shell structure, since a discontinuous change of the  $\Delta H_{n-1,n}$  and  $\Delta S_{n-1,n}^\circ$  values will occur whenever a shell is completed. Finally, the total heat of solvation of the ion can also be obtained from the expression III, with

$$\Delta H_{\text{soln}} = \sum_{n=0}^{\infty} [\Delta H_{n-1,n} - \Delta H_{\text{evap}}(\text{B})] \quad (\text{III})$$

equations of the same form holding for the free energy and entropy change of solvation.

The simple relationships just outlined could not be utilized in the past since measurements of equilibrium concentrations of clustered ions were beyond the reach

of the experimentalist. In this paper we wish to show that mass spectrometric techniques can be applied to this problem and lead to solvation-step enthalpies ( $\Delta H_{n-1,n}$ ) and entropies which are in agreement with estimates based on thermodynamic cycles and calculation.

To achieve mass spectrometric measurement of the ion cluster concentrations one must bleed some of the gas from the ion cluster source, through a pinhole, into an evacuated electrode chamber. Here, the gas is pumped away but the ions are captured by electric fields, accelerated, and then magnetically mass analyzed. The measured ion beam intensities are then assumed proportional to the cluster concentrations in the ion cluster-gas source. Utilization is thus made of the fact that eq. II requires only the concentration ratio of an ion cluster pair. The substitution of the ion intensities of course assumes that clustering equilibrium was achieved in the ion source and that the ion intensities faithfully represent the bulk concentrations of the ions. These questions were considered already in two earlier publications<sup>1,2</sup> dealing with clustering of water around  $\text{H}_3\text{O}^+$  and ammonia molecules around  $\text{NH}_4^+$ . It was pointed out<sup>2</sup> that clustering equilibrium is probably achieved since the clustering reactions must be very fast. An experiment supporting the equilibrium assumption is described in the Appendix of the present paper. It is shown there that the ion-intensity ratios remain unchanged when the ionizing  $\alpha$  beam is moved away from the sampling leak. The constancy of relative intensities with increase of reaction time is then interpreted to mean that equilibrium is achieved.

The question whether the ion intensities faithfully represent the bulk concentrations is more complex, since a number of disturbing effects associated with the extraction of the sample from the ion source can cause deviations. These dangers were realized and discussed in the previous work.<sup>2</sup> A very serious source of error can be the growth of the clusters past the sampling

(1) P. Kebarle and A. M. Hogg, *J. Chem. Phys.*, **42**, 798 (1965).

(2) A. M. Hogg and P. Kebarle, *ibid.*, **43**, 449 (1965).

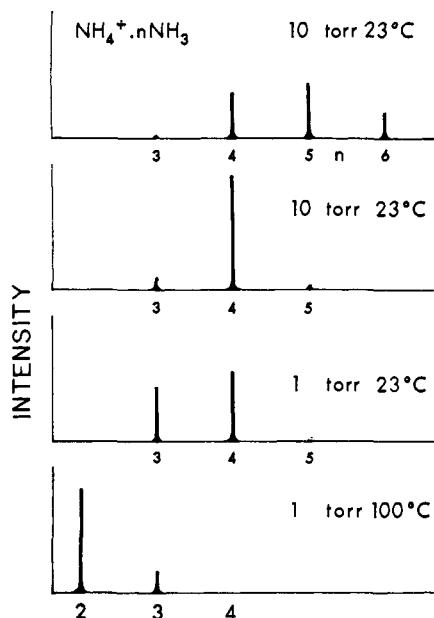


Figure 1. Schematic representation of ion intensities for clustered  $\text{NH}_4^+ \cdot n\text{NH}_3$ . Intensities are expressed as fractions of total ion current. Condition of 1 torr and  $100^\circ$  shows cluster of largest concentration to be  $\text{NH}_4^+ \cdot 2\text{NH}_3$ . Reduction of temperature at constant pressure ( $23^\circ$ , 1 torr) causes clusters to grow. Increase of pressure at constant temperature ( $23^\circ$ , 10 torr) produces further cluster growth. Spectrum at top ( $23^\circ$ , 10 torr) shows effect of using large sampling pinhole ( $70\text{-}\mu$  diameter) producing dynamic flow. The resultant adiabatic cooling causes further nonequilibrium growth of clusters.

leak caused by adiabatic cooling of the dynamically expanding gas. To remove this source of error, a sampling probe with very small orifices was used in the present work so that near-molecular flow was achieved. Expansion under molecular-flow conditions should not lead to decreases of the vibrational and rotational temperature and no further growth of the cluster outside of the ion source.

### Experimental Section

The apparatus used has been described in previous publications<sup>2,3</sup> so that only the general features and some pertinent modifications will be mentioned here.

The gas contained in the ion source is irradiated by a 200-mcurie polonium  $\alpha$  source. The irradiated volume is continually sampled by a cone projecting into it and carrying a leak at its apex. This cone was made removable from the ion source so that the type of sampling leak could be readily changed. All the measurements were done with a laser beam produced leak<sup>4</sup> consisting of 30 holes in  $2.5\text{-}\mu$  thick stainless foil. The  $10\text{-}\mu$  diameter holes were arranged in five rows covering in total an area of less than  $1\text{ mm}^2$ . The mean free path of ammonia at room temperature and 1 torr pressure is  $35\text{ }\mu$ . Thus the diameter of the leaks is smaller than the mean free path up to about 4 torr. One might therefore expect that in the range 0–10 torr molecular flow will be prevailing at least in the sense that the cluster will not grow beyond the leak because of adiabatic cooling in the gas "jet."

The gas was supplied to the ion source from a gas-handling system consisting of two 2-l. storage bulbs and a metal valve manifold. The pressure was measured with an Atlas MCT diaphragm capacity torrmeter. The gas storage bulbs, torrmeter, and ion source were connected by means of short lengths of wide bore tubing (12 mm.) in order to achieve pressure equality throughout the system. The gas-handling system, connecting tubing, and ion source could

(3) P. Kebarle and A. M. Hogg, *J. Chem. Phys.*, **42**, 668 (1965).

(4) This unique leak was generously supplied by Maser Optics Inc., Boston, Mass.

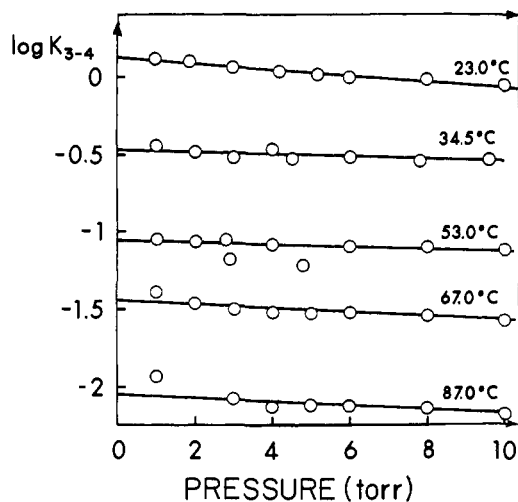


Figure 2. Plot of  $\log K_{3,4}$ , where  $K_{3,4} = I_4/I_3P_{\text{NH}_3}$ , at constant temperatures and variable ammonia pressure (pressure expressed in torr).

be thermostated in the range  $25\text{--}100^\circ$ . The gas-handling system could be baked out at  $150^\circ$ .

### Results and Discussion

Previous work on ammonia<sup>2</sup> has showed that the primary (positive) ions produced by the  $\alpha$  radiation are rapidly converted by ion-molecule reactions to the most stable ion which is  $\text{NH}_4^+$ . Attachment of ammonia molecules then leads to  $\text{NH}_4^+ \cdot n\text{NH}_3$ . A representation of some typical relative ion intensities observed within the experimental range used in the measurements is given in Figure 1. The most abundant species at  $100^\circ$  and 1 torr ammonia pressure is  $\text{NH}_4^+ \cdot 2\text{NH}_3$ . As the temperature is lowered to  $23^\circ$  and 1 torr pressure, the larger clusters,  $n = 3$  and  $n = 4$ , become more stable. Increase of the pressure at constant temperature also increases the cluster size as evident from the increase of the  $n = 4/n = 3$  ratio on going from 1 to 10 torr. The ion intensities given at the top of Figure 1 illustrate the effect of the sampling leak size. In this case a single leak of  $70\text{-}\mu$  diameter was used. The appearance of clusters of higher mass must be due to adiabatic cooling caused by the expansion of the gas jet.

Rewriting eq. II for the ammonia system and with the assumption that the relative ion intensities  $I_n = I(\text{NH}_4^+ \cdot n\text{NH}_3)$  represent adequately the equilibrium concentration ratios, we obtain (IV). Plots of  $\log$

$$RT \log K_{n-1,n} = RT \log \frac{I_n}{I_{n-1}P_{\text{NH}_3}} \quad (\text{IV})$$

$K_{3,4}$  with pressure at different constant temperatures are given in Figure 2. These data show that eq. IV is obeyed to a good approximation for a pressure change by a factor of ten. A plot of  $\log K_{2,3}$  and  $K_{3,4}$  vs.  $1/T$  is shown in Figure 3. The data used for  $K_{2,3}$  were of similar appearance to those in Figure 2. Since there is a small variation of  $\log K$  with pressure, the values used for the enthalpy plots were taken at zero pressure. This was done only for the sake of consistency. Values taken at 5 torr pressure lead to very similar enthalpy data.

The slopes lead to  $\Delta H_{2,3} = -17.8$  and  $\Delta H_{3,4} = -15.9$  kcal./mole. No data could be obtained for the

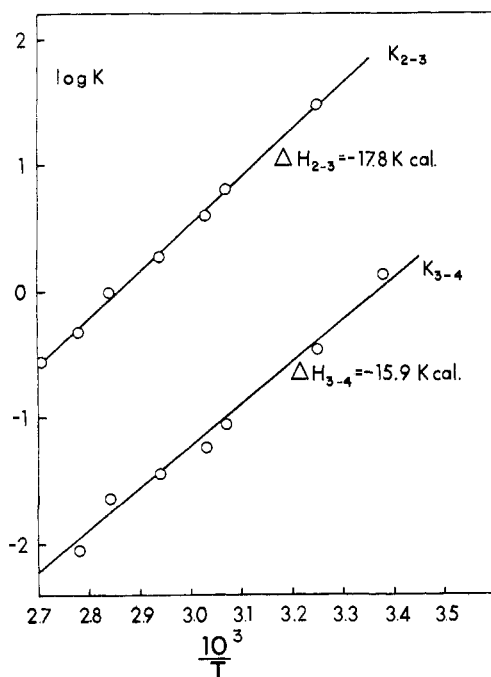


Figure 3. Plots used for the enthalpy determination.

clustering reactions (0.1 and 1.2) which would be observable only at considerably higher temperatures. A  $K_{4,5}$  could still be measured but only at the lowest temperature (25°). It is of interest to point out that the range covered, even though insufficient for the determination of a wider set of reactions, is still quite extensive. Thus the measured ratio  $I_2/I_4$  increases in the range (10 torr at 23° to 1 torr at 100°) by a factor of 100,000.

The thermodynamic data obtained are summarized in Table I. These data will be now compared with predictions from other methods. The total heat of solva-

Table I. Thermodynamic Data on Clustering Reactions



| $n-1,$<br>$n$ | $\Delta F^\circ$<br>(298°K.) <sup>a</sup> | $\Delta H,$<br>kcal./mole | $\Delta S^\circ$<br>(298°K.),<br>e.u. |
|---------------|---|---------------------------|---------------------------------------|
| 2, 3          | -6.4                                      | -17.8                     | -38                                   |
| 3, 4          | -3.8                                      | -15.9                     | -40.5                                 |
| 4, 5          | -0.5                                      | (-9) <sup>b</sup>         | (-33) <sup>c</sup>                    |

<sup>a</sup> Standard state of ammonia, 1 atm. <sup>b</sup> Obtained from  $\Delta F^\circ$  and the estimated entropy loss. <sup>c</sup> Estimated.

tion of the ammonium ion in water has been estimated by several authors. Two more recent references<sup>5,6</sup> give  $\Delta H_{\text{hydr}} = -79$  kcal./mole. However, the value may in fact be numerically somewhat larger. An upper limit is the heat of hydration of sodium which is about -100 kcal./mole. The heat of solvation of ions in liquid ammonia is numerically larger than that in water. The difference for univalent ions appears to be in the range of 5 to 10 kcal.<sup>7,8</sup> Thus the enthalpy of ammoniation of  $\text{NH}_4^+$  may be expected to be

(5) K. P. Mishchenko, *Zh. Fiz. Khim.*, **26**, 1736 (1952).

(6) A. P. Altchuler, *J. Am. Chem. Soc.*, **77**, 3780 (1955).

(7) L. V. Coulter, *J. Phys. Chem.*, **57**, 553 (1953).

(8) W. L. Jolly, *ibid.*, **58**, 250 (1954).

around  $\Delta H_{\text{amm}} = -90$  kcal. The measured  $\Delta H_{2,3}$  and  $\Delta H_{3,4}$  (Table I) add up to  $\Delta H_{2,4} = -33.7$  kcal./mole. Since the initial interactions should be stronger, we (arbitrarily) assume  $\Delta H_{0,2} = -46.3$  kcal./mole so that  $\Delta H_{0,4} = -80$  kcal./mole. Subtracting four times the heat of vaporization of ammonia ( $\Delta H_{\text{evap}} = 5$  kcal.) we obtain  $\Delta H_{0,4} - 4\Delta H_{\text{evap}} = -60$  kcal. From this and the heat of ammoniation of  $\text{NH}_4^+ \cdot 4\text{NH}_3$ . An independent evaluation of this last quantity can be made on basis of the Born equation. The values obtained are in the range -30 to -35 kcal. depending on the assumed radius of the tetraammoniate. Thus these admittedly approximate correlations show that the  $\Delta H_{2,3}$  and  $\Delta H_{3,4}$  are of the correct magnitude.

An approximate evaluation of the entropy changes in the clustering reactions ( $n-1, n$ ) can be made on basis of statistical thermodynamics. The predominant term is due to loss of translational entropy and can be evaluated by the Sackur-Tetrode equation. For the 3,4 reaction this change amounts to 34 e.u. at 258°K. Some rotational loss will also occur. The total rotational entropy of the ammonia molecule is 11 e.u. Once the molecule is attached to the ion only a rotation around the principal axis will be possible. The net rotational loss in reaction 3,4 will be more than half of the rotational entropy of ammonia so that the translational and rotational losses add up to more than 40 e.u. While some vibrational entropy gain will occur, this cannot amount to more than 2 or 3 e.u. Thus the observed value  $\Delta S^\circ_{3,4} = -40.5$  e.u. is of the expected magnitude.

We can use the  $\Delta F^\circ_{4,5}$  obtained at 25° (Table I) to get an estimate for the  $\Delta H_{4,5}$ . Assuming for the moment that  $\Delta S^\circ_{4,5} = \Delta S^\circ_{3,4}$ , we obtain a provisional value  $\Delta H_{4,5} = -11.5$  kcal./mole. This value is numerically considerably lower than the  $\Delta H_{2,3}$  and  $\Delta H_{3,4}$ . This suggests that the inner shell was completed with four molecules. If this is so then the assumed entropy loss was too large since the fifth molecule will have considerably more freedom in the empty and larger outer shell. Taking  $\Delta S^\circ_{4,5} = 33$  e.u.,<sup>9</sup> one obtains a  $\Delta H_{4,5}$  of -9 kcal. The finding that the inner shell contains four molecules is in agreement with our previous work<sup>2</sup> where the same conclusion was reached on the basis of competitive solvation by water and ammonia molecules.

In conclusion, some general remarks about the method might be deemed of interest. An ion source is under construction which will allow the extension of the experimental range to lower temperatures. This will permit the study of reactions leading to larger clusters. An extension of the upper temperature range is being attempted through a replacement of the  $\alpha$  source by an electron gun operating at 30 kev. The electron beam can be passed into the ion source through a thin foil.<sup>11,12</sup>

(9) A rough estimate of the entropy change can be made. Thus following Eley and Evans,<sup>10</sup> one can assign a "two-dimensional" translation in the outer shell. Taking a radius of  $4.5 \times 10^{-8}$  cm. for this shell, one obtains a translational entropy term of 5 e.u. Loosening of the stretching and rocking modes could add about 2 e.u. to this.

(10) D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

(11) J. Seehof, S. Smithberg, and M. Armstrong, *Rev. Sci. Instr.*, **25**, 776 (1958).

(12) F. O. Halliday and A. H. Samuel, Stanford Research Institute, private communication.

The hydration of a number of organic ions can be studied without changes in the method of ion production. We have also observed the hydration of negative ions (*i.e.*,  $\text{Cl}^- \cdot n\text{H}_2\text{O}$ ) on irradiation of suitable (chlorinated) compounds in water vapor. Of the metal ions,  $\text{Na}^+ \cdot n\text{H}_2\text{O}$  was observed several times in high abundance but as an impurity ion. Special methods would seem necessary for the controlled production of metal ions under the mild conditions required for the study of clustering equilibria.

## Appendix

**A Test of the Assumption That Clustering Equilibrium Is Achieved.** In order to test whether clustering equilibrium is achieved in the ion source, a set of experiments was performed in which the reaction time of the ions was increased by moving the  $\alpha$  beam away from the sampling leak. A specially constructed ion source contained a movable collimating slit ( $1 \times 3$  mm., wall thickness 1 mm.) placed 5 mm. in front of the sampling leak, causing the  $\alpha$  beam not to graze the leak but to pass over it. Since a second laser leak was not available, a single 50- $\mu$  diameter leak was used. The experiments were therefore restricted to 1 torr pressure where the disturbance due to cooling of the jet is small. All experiments were done at room temperature. Under these conditions the major ions are  $I_4$  and  $I_3$ . The  $I_4/I_3$  ratio measured previously with the laser leak was 1.3. Measurements with the 50- $\mu$  leak and the slit in the lowest position gave a higher result,  $2.2 \pm$

0.2. The increase of the ratio, which should be due to cooling of the jet, is not too large and should not affect the significance of the results quoted below. When the slit was successively raised by 1, 1.5, and 2 mm. above the plane of the leak, no change in the  $I_4/I_3$  ratio was observed. This result is in agreement with the equilibrium assumption. For comparison, an experiment was done with ethylene. One of the major ionic reactions in ethylene<sup>3,13</sup> is a polymerization started by  $\text{C}_2\text{H}_4^+$  and leading to the ions  $\text{C}_4\text{H}_8^+$ ,  $\text{C}_6\text{H}_{12}^+$ , etc. This is a dynamic system of successive ion molecule reactions and should show intensity changes with movement of the slit. Drastic changes were indeed observed.<sup>13</sup> Thus with ethylene at  $4 \times 10^{-2}$  torr pressure<sup>14</sup> the major ion is  $\text{C}_4\text{H}_8^+$  followed by  $\text{C}_6\text{H}_{12}^+$  and  $\text{C}_8\text{H}_{16}^+$  in decreasing concentrations. A movement of the slit by 1 mm. caused a shift of intensities to higher mass, the  $\text{C}_4\text{H}_8^+$  ion becoming almost extinct. The rate constant for  $\text{C}_4\text{H}_8^+$  reaction with ethylene is very small ( $< 5 \times 10^{-12}$  cc. sec.<sup>-1</sup> molecule<sup>-1</sup>). Considering also that ethylene was present at a concentration 1/25th that of ammonia we see that the rate of the  $\text{C}_4\text{H}_8^+$  reaction is much lower than the rates that could be expected for the ammonia clustering reactions. The constancy of the ammonia intensity ratios thus must be due to the presence of a clustering equilibrium.

(13) P. Kebarle, R. M. Haynes, and S. Searles, *J. Chem. Phys.*, to be published.

(14) The ethylene is mixed with 20 torr of Xe in order to produce only  $\text{C}_2\text{H}_4^+$  as primary ethylene ion; see also ref. 3.

## Phosphines Containing the $\text{CH}_3\text{CF}_3\text{P}$ Group<sup>1</sup>

Anton B. Burg, K. K. Joshi, and John F. Nixon

*Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007. Received August 17, 1965*

**Abstract:** Volatile phosphines of the new general type  $\text{CH}_3\text{CF}_3\text{PX}$  (where X is a functional group) have been made by various methods, including interconversion. The best approach was through addition of  $\text{CH}_3\text{I}$  to  $(\text{CH}_3)_3\text{PPCF}_3$ ; the resulting methiodide  $(\text{CH}_3)_3\text{PPCH}_2\text{CF}_3 + \text{I}^-$  was attacked by HCl to form  $\text{CH}_3\text{CF}_3\text{PCl}$ . This was converted by NaI to  $\text{CH}_3\text{CF}_3\text{PI}$ , and that by  $\text{PH}_3$  to  $\text{CH}_3\text{CF}_3\text{PH}$  or by Hg to  $(\text{CH}_3\text{CF}_3\text{P})_2$ . HCl cleaved the latter to  $\text{CH}_3\text{CF}_3\text{PH}$  and  $\text{CH}_3\text{CF}_3\text{PCl}$ , with reversal by action of  $(\text{CH}_3)_3\text{N}$ . Both  $\text{CH}_3\text{CF}_3\text{PH}$  and  $(\text{CH}_3\text{CF}_3\text{P})_2$  form dissociable  $\text{BH}_3$  complexes, but  $\text{BF}_3$  fails to attach. Ammonolysis or aminolysis of  $\text{CH}_3\text{CF}_3\text{PCl}$  led to  $\text{H}_2\text{NPCH}_2\text{CF}_3$ ,  $\text{HN}(\text{PCH}_2\text{CF}_3)_2$ ,  $\text{CH}_3\text{NHPCH}_2\text{CF}_3$ ,  $\text{CH}_3\text{N}(\text{PCH}_2\text{CF}_3)_2$ , and  $(\text{CH}_3)_2\text{NPCH}_2\text{CF}_3$ , all quantitatively reconvertible by HCl to  $\text{CH}_3\text{CF}_3\text{PCl}$ . The related  $(\text{CH}_3)_2\text{NPCF}_3\text{Cl}$  also was made. Accurate infrared spectra are presented.

The chemistry of phosphine derivatives containing the  $(\text{CH}_3)_2\text{P}-$  and  $(\text{CF}_3)_2\text{P}-$  groups has shown so many interesting contrasts related to the effect of electronegativity upon the base action *vs.* Lewis acid character of phosphorus, as to justify a full study of phosphines based upon the intermediate group  $\text{CH}_3\text{-CF}_3\text{P}-$ . Our syntheses and further studies of a series

of new volatile compounds of the type  $\text{CH}_3\text{CF}_3\text{PX}$  (where X is a chemically active group such as halogen, hydrogen, amino, or phosphino) have shown chemical results mostly confirming the qualitative expectations based upon knowledge of analogous  $(\text{CH}_3)_2\text{PX}$  and  $(\text{CF}_3)_2\text{PX}$  compounds, but unexpected results are possible.

For example, the complex  $\text{CH}_3\text{CF}_3\text{PH} \cdot \text{BH}_3$  showed the expected poor stability, but unlike  $(\text{CH}_3)_2\text{PH} \cdot \text{BH}_3$  or a  $(\text{CF}_3)_2\text{PH} \cdot \text{B}_2\text{H}_6$  mixture, it formed only  $\text{H}_2$  and glassy nonvolatile material on heating in a very small sealed tube; no  $(\text{CH}_3\text{CF}_3\text{PBH}_2)_3$  could be found. Only at low partial pressures and with  $\text{H}_2$  to stabilize the  $\text{B}_2\text{H}_6$  was it possible to obtain this ring trimer, in yields up

(1) Much of this research was supported by the United States Air Force through Contracts AF 33(616)-6913 (KKJ, until Jan. 1961) and AF 33(616)-7810 (JFN, until July 1962), monitored by the Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Later refinements and extensions by ABB were supported by Grants GP-199 and GP-3812 from the National Science Foundation, which also supported the purchase of a Beckman IR7 instrument through Grant G-14665. The contribution of each author is shown by initials.