particular series. In view of the demonstrated importance of π-bonding in boron trifluoride, it has been suggested[23] that the latter is the case in interpreting F^{19} chemical shifts in the series[24] RBF_2 and R_2BF (R = Cl, Br). Lack of adequate evidence regarding the changes in π-bonding for the series under consideration prevents a definite correlation with the negative slopes in Fig. 2.

Furthermore, closer examination of the F^{19} shifts in Fig. 2 indicates a more complicated situation. The trend in F^{19} shift in the phosphorus(III) chlorofluorides opposite to that in the phosphorus(V) chlorofluorides is particularly puzzling. If it is assumed that changes in π-bonding predominate in the PCl_xF_{5-x} and $POCl_xF_{3-x}$ series, it might be expected that this effect should be important in the PCl_xF_{3-x} series also. One might make the additional speculation that the presence of a readily available source of electrons, the lone electron pair, in the latter series may be "influential" in accounting for the opposite trends.

Explanations used in attempting to account for F^{19} shifts in fluorocarbon derivatives of metals[25] and organic fluorine compounds[26] have little applicability in accounting for the trends in the phosphorus chlorofluorides.

Additional studies of F^{19} shifts in series involving other central atoms should prove helpful in allowing more definitive correlations.

Acknowledgment.—Appreciation is expressed to the National Science Foundation for a grant supporting this work.

[23] T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6223 (1960).

[24] T. D. Coyle and F. G. A. Stone, *J. Chem. Phys.*, **32**, 1892 (1960).

[25] E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *ibid.*, **36**, 124 (1962), recently made calculations on the availability of low-lying excited states and concluded that the paramagnetic term should increase in the order $H < F < Cl$. This agrees qualitatively with the trend in F^{19} shifts in the series, CH_xF_{4-x} and CCl_xF_{4-x}, but does not predict the opposite trends in F^{19} shift in the PCl_xF_{3-x} series compared to the PCl_xF_{5-x} series.

[26] G. V. D. Tiers, *J. Am. Chem. Soc.*, **78**, 2914 (1956), invoked a "repulsive unshielding" effect attributed to the presence of bulky groups in causing a downfield shift in F^{19} resonance. While steric effects in a trigonal bipyramidal model (PCl_xF_{5-x} series) might be slightly greater than those in a pyramidal model (PCl_xF_{3-x} series), no appreciable change in steric requirements is expected for the series $POCl_xF_{3-x}$ compared to the series PCl_xF_{3-x} with increasing chlorine substitution. In both series, $POCl_xF_{3-x}$ and PCl_xF_{5-x}, the F^{19} shift trends downfield with similar slopes as x increases.

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The Relative Acceptor Properties of Phosphorus(V) Chlorofluorides and Antimony Pentachloride. A Calorimetric Investigation[1,2]

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The heats of solution of phosphorus trichlorodifluoride, phosphorus tetrachloromonofluoride, and antimony pentachloride in nitrobenzene were determined calorimetrically. The heats of reaction of these halides and phosphorus pentachloride with pyridine in nitrobenzene were measured calorimetrically. Comparing these values with similar data on the boron halides, the ordering of Lewis acid strengths toward pyridine obtained was: $BBr_3 > BCl_3 \sim SbCl_5 > PCl_3F_2 > BF_3 \overline{>} PCl_4F > PCl_5$. Heats of reaction of $SbCl_5$ with monoalkylpyridines were determined. Substitution of a methyl group in the 2-position of pyridine reduced the stability of the complex. Substitution in the 4-position enhanced the stability. Changes in structure of the alkyl group (ethyl or isopropyl) in the 4-position had little further effect on the stability of the complexes. The result of such changes in the 2-position suggested the presence of reactions other than simple complex formation. The 1:1 complexes of antimony pentachloride and alkylpyridines were prepared and characterized.

Introduction

Previous literature[1,5–7] shows that the pentahalides of phosphorus and antimony exhibit acceptor properties in that they form 1:1 complexes with a variety of Lewis bases. In the case of PF_5·base complexes a F^{19} n.m.r. study[7] supports an octahedral model with no observable dissociation occurring except in the case of complexes containing weak or hindered bases such as 2,4,6-trimethylpyridine.

In a continuation of our study of pentacoördinated molecules[1] it was decided to investigate the coördination tendencies of members of group V and if possible compare such data with the coördination tendencies of the boron halides reported[8] earlier.

Since the relative acceptor strengths of the boron halides were determined calorimetrically by measuring their heats of reaction with pyridine in nitrobenzene solution, a direct comparison would be possible only if

[1] Pentacoördinated Molecules. II. Previous paper: R. R. Holmes and W. P. Gallagher, *Inorg. Chem.*, **2**, 433 (1963).

[2] Abstracted from theses submitted by W. Patrick Gallagher and Richard P. Carter in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology. Presented before the Inorganic Division at the 144th National Meeting of the American Chemical Society, Los Angeles, California, April, 1963.

[3] Bell Telephone Laboratories, Incorporated, Murray Hill, N. J.

[4] National Science Foundation Predoctoral Fellow, 1959–1961.

[5] R. R. Holmes and E. F. Bertaut, *J. Am. Chem. Soc.*, **80**, 2980 (1958).

[6] (a) S. Johnson, Ph.D. Thesis, Purdue University, 1953; (b) R. R. Holmes, Ph.D. Thesis, Purdue University, 1953.

[7] E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1960).

[8] H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **78**, 2173 (1956).

analogous measurements could be performed with pentahalide members of group V.

The phosphorus(V) chlorofluorides discussed in the preceding paper[1] seemed suitable in that at least the members, PCl_4F and PCl_3F_2, possessed relatively low volatility, formed 1:1 complexes with pyridine, and were found to be sufficiently soluble in the calorimetric solvent, nitrobenzene. In addition, both phosphorus and antimony pentachloride were found convenient to work with.

Experimental

Materials.—Nitrobenzene (Fisher reagent grade) was distilled and stored over calcium hydride in sealed ampoules: b.p., 209.0–209.2° at 736 mm. Phosphorus pentachloride (Baker and Adamson) was purified by sublimation, similar to an earlier procedure.[5] The purification of pyridine and antimony pentachloride as well as the preparation and purification of phosphorus tetrachloromonofluoride and phosphorus trichlorodifluoride were described in the preceding paper.[1]

2-Isopropylpyridine was synthesized and purified according to a procedure by Brown and Murphey,[9] b.p. 157.6–158.4° at 740.7 mm. (lit.[9] 159.8° at 753 mm.). The other alkylpyridine compounds used were available from Eastman (practical grade) except 4-isopropylpyridine (K and K) and 2,6-lutidine (Matheson). All the pyridine compounds were dried with barium oxide, distilled, and the middle fractions stored over barium oxide. Boiling points are recorded in Table I.

TABLE I

BOILING POINTS OF ALKYLPYRIDINES

Alkylpyridine RC_5H_4N, R–	B.p., °C., obsd.	p, mm.	B.p., °C., lit.	p, mm.
2-Methyl	129.1	740	129.4[10]	760
2-Ethyl	146.5–147.4	742.6	148.7[9]	746
2,6-Lutidine	143.1	741.1	144.0[10]	760
4-Methyl	142.9	739.0	145.4[10]	760
4-Ethyl	165.5	741.1	167.8[10]	760
4-Isopropyl	181.6	739.8	181.5[9]	743

The purity was checked by gas–liquid chromatography using a procedure designed specifically for pyridines by Decora and Dinneen.[10] A series arrangement of columns was used. The first 10 ft. of a 20 ft. section (0.25 in. diameter copper tubing) was packed with Tide, treated as previously described.[10] The next 10 ft. contained silicone high vacuum grease supported on Tide. The analyses were performed with a Perkin–Elmer vapor fractometer. Qualitative results showed a purity of 97% for 4-picoline and closer to 95% for the 2- and 4-isopropyl derivatives. All the other pyridines exhibited one peak and hence a minimum purity of 98%.

Apparatus and Procedure.—The calorimeters used in this work were identical with those used in a calorimetric study involving the boron halides. They were constructed by the Ace Glass Company from a copy of the original design. A diagram of the apparatus, the method of the preparation of the solutions, and the general operational procedure have appeared elsewhere.[8,11] The constant temperature bath remained at 30.00° ± 0.005° over the time period of the measurements. Brooklyn calorimeter thermometers, 17 to 34°, graduated in 0.01° division were used to measure the temperature rise. Details of the electrical calibration are available elsewhere.[12]

The only significant change in procedure involved minimizing the length of time either PCl_4F or PCl_3F_2 were at room temperature so that disproportionation of the liquids and their nitrobenzene solutions would be negligible. Accordingly, small crushable glass ampoules containing weighed amounts of halide were prepared as described previously[8] using freshly synthesized phosphorus(V) chlorofluorides. The ampoules were stored at −78° until just before use. The nitrobenzene for the heat of solution determinations was brought to equilibrium temperature in a 500-ml. volumetric flask immersed, except for the upper part of the neck, in the constant temperature bath. Soon after the ampoule had been placed in the calorimeter and the nitrobenzene pipetted over it, the dewar jacket was evacuated. These procedures enabled runs to be made with the phosphorus(V) chlorofluorides at room temperature for less than 1 hr.

For the determinations of the heat of reaction of PCl_4F and PCl_3F_2 with pyridine in nitrobenzene solution, the pyridine solution for each determination was added to the calorimeter at least 8 hr. before the run was carried out. The nitrobenzene solutions of the phosphorus halides were made up by breaking ampoules containing known amounts of the halides beneath the surface of the nitrobenzene which had been equilibrated by several hours immersion of the volumetric flask in the constant temperature bath. After this solution was added to the calorimeter, thermal equilibrium was established and the determination made. The halides were always in excess so that if any disproportionation should occur, it would not limit the amount of reaction taking place. Since PCl_2F_3 did not form a 1:1 complex with pyridine, it was not investigated calorimetrically.

Known quantities of $SbCl_5$ contained in crushable glass ampoules were used in determining its heat of solution in nitrobenzene following the normal procedure.[8] The determination of the heat of solution of PCl_5 was prevented, however, due to the very slow rate of solution in nitrobenzene.

During all runs the contents of the calorimeters were examined through the unsilvered strip of the jacket to see if any solid was being formed. The contents also were checked directly after each run. No solids were observed; although some of the solutions would yield solids on standing for a day or so.

Results

In order that the calorimetric measurements have significance, it was necessary to characterize the products of the reaction of the various halides with pyridine bases. In the preceding paper[1] the adducts $C_5H_5N \cdot PCl_4F$ and $C_5H_5N \cdot PCl_3F_2$ were reported. Both $C_5H_5N \cdot PCl_5$[6b,13] and $C_5H_5N \cdot SbCl_5$[14] have been prepared previously. In addition the composition $3C_5H_5N \cdot 2SbCl_5$ has been reported.[14] Using an excess of $SbCl_5$ the remaining adducts were synthesized by mixing the components in carbon tetrachloride solution inside a nitrogen-filled drybox. A white solid formed in each case. The solutions were filtered, washed with dry carbon tetrachloride, and the resulting solids analyzed. The analyses and melting points are reported in Table II. Only 1:1 compounds were obtained. The adduct $C_5H_5N \cdot SbCl_5$ also was prepared in this way. In the case of 2,6-lutidine and $SbCl_5$ a white solid formed but decomposed on attempted sublimation. Elemental analyses did not show a simple adduct.

In order to gain assurance that the 1:1 adducts were present in nitrobenzene solution at the end of a calorimetric determination, cryoscopic measurements of molecular weights were carried out on the following ad-

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[9] H. C. Brown and W. A. Murphey, *J. Am. Chem. Soc.*, **73**, 3308 (1951).

[10] A. W. Decora and G. U. Dinneen, *Anal. Chem.*, **32**, 164 (1960).

[11] H. C. Brown and R. H. Horowitz, *J. Am. Chem. Soc.*, **77**, 1730 (1955).

[12] W. P. Gallagher, Ph.D. Thesis, Carnegie Institute of Technology, 1961.

[13] I. R. Beattie and M. Webster, *J. Chem. Soc.*, 1730 (1961).

[14] J. C. Hutton and H. W. Webb, *ibid.*, 1518 (1931).

TABLE II

ANALYSES OF 1:1 COMPLEXES OF ANTIMONY PENTACHLORIDE WITH PYRIDINE COMPOUNDS

Pyridine base·$SbCl_5$[a] $RC_5H_4N\cdot SbCl_5$, R–	M.p., °C., with dec.		Analyses N	Cl
Hydrogen	218		3.43	46.67
		Calcd.	3.70	46.94
2-Methyl	93		3.31	45.50
4-Methyl	107		3.28	45.41
		Calcd.	3.57	45.26
2-Ethyl[b]	113		3.28	43.96
4-Ethyl	106		3.19	43.92
		Calcd.	3.45	43.70
2-Isopropyl	130		3.13	42.23
4-Isoprypyl	150		3.22	42.32
		Calcd.	3.33	42.24

[a] A chlorine analysis of a representative sample of $SbCl_5$ used in adduct preparation and calorimetry showed 59.41% (calcd., 59.36%). [b] Carbon and hydrogen analyses for the 2-ethylpyridine·$SbCl_5$ adduct are: Calcd.: C, 20.70; H, 2.22. Found: C, 20.91; H, 2.33.

ducts dissolved in nitrobenzene solution: $C_5H_5N\cdot PCl_5$, mol. wt. 288 at 0.00831 *m* (*m* = molality), 294 at 0.0250 *m* (calcd., 287); $C_5H_5N\cdot SbCl_5$, mol. wt. 351 at 0.0226 *m* (calcd., 378); 4-isopropylpyridine·$SbCl_5$, mol. wt. 427 at 0.0157 *m* (calcd., 420). The low specific conductances of these solutions (for example, 6.7×10^{-5} mho/cm. for a 0.00831 *m* solution of $C_5H_5N\cdot PCl_5$ in nitrobenzene) agreed with conductance measurements on solutions obtained after a calorimetric determination. The conductance showed no change over 1 day for the $C_5H_5N\cdot PCl_5$ solutions but small changes were observed for the $C_5H_5N\cdot SbCl_5$ solutions. Further, conductance measurements of PCl_5 dissolved in nitrobenzene showed that ionization was occurring only to a minor extent, in agreement with a study by Payne.[15] Solutions of $SbCl_5$ in nitrobenzene behaved similarly.

Table III lists average values for the heats of solution of the liquids $SbCl_5$, PCl_4F, and PCl_3F_2 in dilute nitrobenzene solution. No variation in value with concentration was detected in the case of $SbCl_5$. For PCl_4F and PCl_3F_2 the heats of solution were determined at the same concentrations used in the measurement of their heats of reaction with pyridine.

TABLE III

HEATS OF SOLUTION OF $SbCl_5$, PCl_4F, AND PCl_3F_2 IN NITROBENZENE AT 30.0°

Halide	Heat of soln., $-\Delta H$, kcal./mole
PCl_4F	3.1 ± 0.1
PCl_3F_2	2.0 ± 0.1
$SbCl_5$	10.4 ± 0.4

The results of the calorimetric determinations of the heats of reaction of $SbCl_5$, PCl_5, PCl_4F, and PCl_3F_2 (each in nitrobenzene solution) with pyridine (in nitrobenzene solution) are summarized in Table IV. In the case of $SbCl_5$ heats of reaction with other pyridine compounds are listed as well (all in nitrobenzene solution). Neither variation of the concentration of the reactant present in lowest molarity nor variation in the concentration ratio, halide to base, exerted any noticeable effect on the heats of reaction. Consequently, average values of all determinations for each reaction are reported.

TABLE IV

HEATS OF REACTION OF ANTIMONY PENTACHLORIDE AND PHOSPHORUS(V) CHLOROFLUORIDES WITH PYRIDINE COMPOUNDS IN NITROBENZENE SOLUTION AT 30.0°

Halide	Pyridine base RC_5H_4N, R–	Heat of reaction, $-\Delta H$, kcal./mole
PCl_5	Hydrogen	22.0 ± 0.2
PCl_4F	Hydrogen	27.0 ± 0.2
PCl_3F_2	Hydrogen	35.3 ± 0.3
$SbCl_5$	Hydrogen	28.3 ± 0.4
$SbCl_5$	2-Methyl	26.2 ± 0.6
$SbCl_5$	4-Methyl	31.0 ± 0.6
$SbCl_5$	4-Ethyl	30.7 ± 0.5
$SbCl_5$	4-Isopropyl	30.1 ± 0.5

In most determinations the halide concentration was in excess because the pyridine solutions could be prepared more accurately. As a check, in several cases pyridine solutions in nitrobenzene were titrated with perchloric acid (acetic acid solvent).[16] The concentrations were found to agree to within one part in 500 with the concentrations determined by direct weighing. In the $SbCl_5$–pyridine reaction excess pyridine served to increase the observed heat of reaction significantly. These values were not included in the average reported in Table IV. The latter effect may be associated with the formation of the higher adduct $2SbCl_5\cdot 3C_5H_5N$ previously mentioned.

Discussion

In view of the rather substantial heats of reaction of the various pentahalides with pyridine compounds in nitrobenzene solution reported in Table IV and the observed invariance of the values to concentration changes of the components, the pentahalides must be present essentially in the form of their undissociated adducts, $RC_5H_4N\cdot MX_5$. Further evidence is provided by the cryoscopic measurements in nitrobenzene showing expected molecular weights for the presence of 1:1 adduct formation. The presence of only one sharp doublet in the F^{19} n.m.r. spectra[1] of the adducts $C_5H_5N\cdot PCl_4F$ and $C_5H_5N\cdot PCl_3F_2$ dissolved in nitrobenzene solution argues against the presence of an ionization equilibrium involving fluorine and the F^{19} shifts of the adducts relative to the pure liquid chlorofluorides are in the direction expected for complex formation.[1] Finally, the low conductance of nitrobenzene solutions of the adducts $C_5H_5N\cdot PCl_5$ and $C_5H_5N\cdot SbCl_5$ indicates the lack of appreciable ionization.

Accordingly, the sums of the heats of solution of the various halides in nitrobenzene (Table III)

$$MX_5(l) + C_6H_5NO_2(l) = MX_5(soln.) \qquad (1)$$

and the heats of reaction of the various halides with

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(15) D. S. Payne, *J. Chem. Soc.*, 1052 (1953).

(16) H. C. Brown and A. Cahn, *J. Am. Chem. Soc.*, **77**, 1715 (1955).

pyridine compounds in nitrobenzene solution (Table IV)

$$\mathrm{MX_5(soln.)} + \mathrm{RC_5H_4N(soln.)} = \mathrm{RC_5H_4N{\cdot}MX_5(soln.)} \quad (2)$$

give the heats of reaction for the process

$$\mathrm{MX_5(l)} + \mathrm{RC_5H_4N(soln.)} = \mathrm{RC_5H_4N{\cdot}MX_5(soln.)} \quad (3)$$

Values for the latter reactions are summarized in Table V along with the corresponding values for eq. 2 and 3 for the boron halides.[8] An estimated value of 2.5 to 4.5 kcal./mole was used for the heat of solution of the hypothetical liquid phase of PCl_5 in nitrobenzene derived from a consideration of the $-\Delta H$ values for the same reaction of the two following members of the series, PCl_4F and PCl_3F_2.

Table V

Heats of Reaction of Boron, Antimony, and Phosphorus Halides with Pyridine Compounds

Halide	Pyridine base RC_5H_4N, R–	Heat of reaction, $-\Delta H^a$ kcal./mole
PCl_5(l)	Hydrogen	(24.5–26.5)
PCl_4F(l)	Hydrogen	30.1 ± 0.3
PCl_3F_2(l)	Hydrogen	37.3 ± 0.4
$SbCl_5$(l)	Hydrogen	38.7 ± 0.8
BF_3(l)	Hydrogen	31.7 ± 1.5
BCl_3(l)	Hydrogen	39.5 ± 0.4
BBr_3(l)	Hydrogen	44.5 ± 0.4
BF_3(soln.)	Hydrogen	25.0 ± 1.0
BCl_3(soln.)	Hydrogen	30.8 ± 0.2
BBr_3(soln.)	Hydrogen	32.0 ± 0.2
$SbCl_5$(l)	2-Methyl	36.6 ± 1.0
$SbCl_5$(l)	4-Methyl	41.4 ± 1.0
$SbCl_5$(l)	4-Ethyl	41.1 ± 0.9
$SbCl_5$(l)	4-Isopropyl	40.5 ± 0.9

[a] The heats of reaction for the boron halides were determined at 25°.

Making the reasonable assumption that the amount of association in the liquid phase of the pentahalides is small,[17] then the heats of reaction in Table V provide a measure of the relative Lewis acid strengths of the various halides.

Whereas the acid strengths of the boron halides toward pyridine are in the order $BBr_3 > BCl_3 > BF_3$, opposite to that predicted on the basis of electronegativity considerations,[8] the order of acid strengths of the phosphorus(V) chlorofluorides toward pyridine parallel expectations based on the relative electronegativities of the halogens, $PCl_3F_2 > PCl_4F > PCl_5$.

The latter order is also that expected on the basis of a steric effect. The introduction of larger chlorine atoms in place of fluorine atoms may serve to decrease the stability of the adduct. However, in view of the approximately 20% increase in covalent radius of phosphorus compared to boron (somewhat nullified by the greater coördination number of phosphorus) and, moreover, the lack of any noticeable steric effect in the corresponding boron halide series with pyridine, one would not predict that such an effect would control the order of acid strengths in the phosphorus series. Earlier work[18] had established the order of acid strength of phosphorus halides with trimethylamine, $PCl_3 > PBr_3 \sim CH_3PCl_2 > (CH_3)_3P$, indicating that electronegativity is an important factor in controlling acceptor strength in the tricoördinated state. Even so, not a great deal of information regarding the magnitudes of various factors influencing adduct stability in hexacoördinated phosphorus compounds has been accumulated at present. Hence a definite assignment must be postponed.

The order opposite to trends in electronegativity appearing in the boron halide series had been attributed to the increasing degree of π-bonding on going from the bromide to the fluoride.[8] Later a similar order of acid strength toward pyridine was observed in the gallium halides[19] and Cotton and Leto,[20] using LCAO methods, calculated that the decrease in reorganization energies in going from the fluoride to the iodide was sufficient to account for the established order of acid strengths.

The apparent unimportance of π-bonding in determining relative acid strengths in the phosphorus(V) chlorofluorides may very likely be due to the fact that of the four empty 3d orbitals available in pentacoordinated phosphorus for π-bonding with filled fluorine orbitals, three still remain in hexacoördinated phosphorus after the σ-bonding hybridization has changed from sp^3d to sp^3d^2. Of the four 3d orbitals available before coördination, two should be capable of forming strong π-bonds, while after coördination, all three remaining 3d orbitals should be capable of forming relatively strong π-bonds[21] (provided that the ligands wish to participate). However, it is not certain to what degree π-bonding exists in these molecules but on the basis of the above reasoning whatever the amount present in the chlorofluorides, the amount need not decrease appreciably on adduct formation.

In the boron halides, on the other hand, the one boron atom p orbital available for π-bonding becomes totally unavailable for such bonding or nearly so when the boron atom changes its σ-bonding orbitals from sp^2 hybridization in the tricoördinated compound to the sp^3 hybridization in the tetracoördinated adducts.

Comparison of the values of the heats of reaction (Table V) yields this order of acid strengths toward pyridine: $BBr_3 > BCl_3 \sim SbCl_5 > PCl_3F_2 > BF_3 \overline{>} PCl_4F > PCl_5$. It is noted that the heat of reaction increases approximately 6 kcal./mole each time a fluorine atom replaces a chlorine atom in the series PCl_xF_{5-x}. If the incremental change continued uniformly PF_5 would be an acceptor molecule of considerable strength, at least toward pyridine. In any event the data show that PCl_3F_2 is a stronger acid than BF_3 toward pyridine.[22] Recently, Clifford and Kongpricha[23] found that PF_5 and SbF_5 were stronger acids

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(17) D. S. Payne, *Quart. Rev.* (London), **15**, 173 (1961).

(18) R. R. Holmes and R. P. Wagner, *Inorg. Chem.*, **2**, 384 (1963).

(19) N. N. Greenwood and P. G. Perkins, *J. Chem. Soc.*, 1145 (1960).

(20) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

(21) H. Eyring, J. Walter, and G. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 231.

(22) The observation that PF_5 complexes react with water or alcohols more rapidly than analogous BF_3 complexes has been cited as evidence that PF_5 complexes are much less stable than BF_3 complexes.[7] In the absence of more quantitative information, it is assumed that the term "stable" was not used in the thermodynamic sense.

(23) A. F. Clifford and S. Kongpricha, *J. Inorg. Nucl. Chem.*, **20**, 147 (1961).

than BF_3 in liquid hydrogen fluoride, using fluoride ion as the reference base.

The heat of solution of $SbCl_5$ in nitrobenzene (10.4 kcal./mole) approximates the corresponding value[8] for BCl_3 (8.7 kcal./mole). In view of their similar acid strength in pyridine, $SbCl_5$ most likely is present in the form of its adduct, $C_6H_5NO_2 \cdot SbCl_5$, similar to that postulated for BCl_3 in nitrobenzene.[24]

The heats of solution of PCl_4F and PCl_3F_2 in nitrobenzene (Table III) are lower than expected if a parallel in acid strength with the two bases, nitrobenzene and pyridine, is assumed. A value near 7 kcal./mole would be expected instead of the observed 2–3 kcal./mole. Hence, if adduct formation is taking place with the weak base, nitrobenzene, it must be doing so to a limited extent. Further, there is the possibility of the presence of an equilibrium ionization in the case of PCl_4F and PCl_3F_2 in nitrobenzene; however, further work is necessary to resolve the situation. In any case the over-all heat of reaction of the pure liquid halides with pyridine in nitrobenzene is independent of the state of the halide in nitrobenzene solution.

Considering the heats of reaction of $SbCl_5$ with alkylpyridine compounds in nitrobenzene, it is seen (Table V) that 2-methylpyridine produces a lower value than that obtained with pyridine. Such a lowering may serve to show the operation of a steric effect between the methyl group and neighboring chlorine atoms attached to antimony, especially since substitution of a methyl, ethyl, or isopropyl group in the 4 position gave similar heats of reaction, approximately 2 to 2.5 kcal./mole higher than the value observed with pyridine. The higher values found for alkyl substitution in the 4-position indicate the presence of an inductive effect. These changes parallel those observed[25] with BF_3 and monoalkyl pyridines studied by analogous methods.

Although it was possible to characterize 1:1 adducts containing $SbCl_5$ and either 2-ethyl or 2-isopropylpyridine, the heats of reactions involving these systems in nitrobenzene were not reproducible, suggesting the presence of competing reactions. $SbCl_5$ reacted with 2,6-lutidine but no characterizable product was isolated.

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(24) R. F. Grossman, *J. Org. Chem.*, **22**, 581 (1957), reported the isolation of $C_6H_5NO_2 \cdot SbCl_5$. We confirmed the preparation by precipitating it out of nitrobenzene solution by the addition of excess $SbCl_5$. *Anal.* Calcd. for $C_6H_5NO_2 \cdot SbCl_5$: C, 17.16; H, 1.19; N, 3.39; Cl, 41.99; Sb, 28.84. Found: C, 16.91; H, 1.39; N, 3.30; Cl, 41.89; Sb, 29.01. From infrared data, Grossman concluded that the structure was a simple addition compound involving Sb–O coördination.

(25) H. C. Brown and R. H. Horowitz, *J. Am. Chem. Soc.*, **77**, 1733 (1955).

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Zinc Phosphide Iodide (Zn_3PI_3) and Zinc Arsenide Iodide (Zn_3AsI_3): New Compounds with Disordered Defect Zincblende Structure

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New compounds, Zn_3PI_3 and Zn_3AsI_3, have been synthesized by the reaction of Zn_3P_2 or Zn_3As_2 with ZnI_2 in evacuated sealed quartz tubes at 475°. They have disordered defect zincblende structures (space group F$\bar{4}$3m) in which three zinc atoms and one vacancy are disordered over four cation sites, and three iodine atoms and one phosphorus (or arsenic) atom are disordered over four anion sites. A high Debye parameter for the zinc atoms is attributed to vibrations in the direction of the vacancies. The lattice constants compare favorably with values calculated from atomic radii. Relationships among this new modification of the zincblende structure and other structures are discussed. The compounds reported are the only ones found in the pseudobinary systems studied; compounds with the antichalcopyrite structure have not been observed. Some chemical and physical properties of the new compounds are given.

Introduction

The chalcopyrite ($CuFeS_2$) structure (space group I$\bar{4}$2d) is related to the zincblende (cubic ZnS) structure (space group F$\bar{4}$3m) in that the metal atoms of the former are so ordered in the zincblende-type structure that zinc atoms are alternately replaced by copper and iron atoms. This results in tetragonal symmetry with a doubling of the number of formula weights per unit cell but with the *c*/*a* ratio of the unit cell slightly less than two.

In addition to $CuFeS_2$, chalcopyrite structures are found in many other compounds of the type $A^{I}B^{III}C_2^{VI}$[1] as well as of the type $A^{II}B^{IV}C_2^{V}$[2] (*e.g.*, $ZnGeP_2$). On the other hand, $MgGeP_2$ has been reported[3] to crystallize with the cubic zincblende structure wherein the metal ions are totally disordered on the site corresponding to that of Zn in zincblende.

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(1) See, for instance, H. Hahn, G. Frank, W. Klingler, A. D. Meyer, and G. Störger, *Z. anorg. allgem. Chem.*, **271**, 153 (1953).

(2) See, for instance, H. Pfister, *Acta Cryst.*, **11**, 221 (1958).

(3) O. G. Folberth and H. Pfister, *ibid.*, **14**, 325 (1961).