crystal specimen ($a = 5.7634$ Å), was similar to that of NiP_2, being nearly independent of temperature from 4.2 to 298°K with a value of 3×10^{-4} ohm cm at room temperature. This behavior indicates that $NiAs_2$ is a metallic conductor analogous to $PdAs_2$.

C. FeP_2, $FeAs_2$, CoP_3, $CoAs_2$, CuP_2, and PdP_2.—The diphosphides of iron and palladium (quenched from 1100°), as well as the diarsenides of iron and cobalt (quenched from 400°), occurred in their respective low-pressure forms. In the case of cobalt, CoP_3 with the skutterudite-type structure and a small amount of an unidentified phase were formed.

The failure of these compounds to form the pyrite-type structure may be related to the density and electronic configurations of their low-pressure forms. Both FeP_2 and $FeAs_2$ belong to that class of marcasite-type compounds having the diamagnetic, low-spin d^4 electronic configuration and a small c/a ratio.[15] The density is already high ($FeAs_2$, 7.7 g/cm^3) and the structure is stabilized by metal–metal bonding. In the arsenopyrite-type structure of cobalt diarsenide, cobalt is formally tetravalent and occurs in pairs of edge-sharing octahedra. It is also diamagnetic[19] and stabilized by metal–metal bonding. In cobalt phosphide, the skutterudite-type structure was observed. This compound should also be diamagnetic, as is isotypic $CoAs_3$[20] with cobalt formally trivalent in an octahedral low-spin d^6 configuration.

Copper diphosphide retained the low-pressure form in which the divalent cation is found in pairs[11] and is also diamagnetic. Reaction of Cu + 2As gave a product admixed with As. The X-ray pattern matched that reported[21] for the mineral-phase Cu_2As, koutekite.

If pyrite-type dipnictides of Fe, Co, and Cu were formed, the electronic configuration of these cations would have unpaired electrons. It appears that the low-spin, diamagnetic state has the greater stability in the higher phosphides and arsenides of these elements, and consequently no transformation is observed.

Transformation of the PdP_2 structure to the pyrite-type structure would involve a change in formal oxidation state from divalent to tetravalent for the Pd and a change of configuration of the P from infinite chains to tetravalent dianions. Since pyrite-type phases of $PdAs_2$ and $PdSb_2$, as well as of PtP_2, $PtAs_2$, and $PtSb_2$, form readily, formation of a PdP_2 pyrite phase under appropriately high pressure seems likely.

Acknowledgments.—The authors wish to thank C. L. Hoover for supervision of the high-pressure experiments, J. L. Gillson for the electrical measurements, R. B. Flippen for the magnetic susceptibility data, and L. J. Guggenberger for helpful discussions.

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[19] F. Hulliger, *Phys. Letters*, **4**, 282 (1963).

[20] F. Hulliger, *Helv. Phys. Acta*, **34**, 782 (1961).

[21] ASTM X-Ray Powder Diffraction File Card 13-581.

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Studies on the Chemistry of Halogens and of Polyhalides. XXVIII. Complexes of Iodine with Substituted Pyridines in Carbon Tetrachloride Solutions

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Formation constants of the complexes formed by pyridine and 14 substituted pyridines with iodine have been determined spectrophotometrically in carbon tetrachloride solutions at 25°. A plot of Hammett σ constants *vs.* K_f yields a straight line given by the equation: $\log K_f = -2.25\sigma + 2.11$. Likewise a plot of $\log K_f$ *vs.* pK_a of the respective pyridines follows a linear relationship with the exception of cases where steric hindrance becomes an important factor. If the substituent groups are electron donors themselves (phenyl or nitrile), a simple spectrophotometric technique fails to give the formation constant of the complex, presumably owing to the stepwise formation of two complexes.

Introduction

Since the publication of the classical paper by Benesi and Hildebrand[1] in 1949 numerous papers have appeared in the chemical literature on the spectrophotometric studies of charge-transfer complexes. The seeming simplicity of the experimental techniques contributed heavily to the widespread use of this type of investigation. It is unfortunate, however, that all too frequently the limitations of this technique have been largely ignored and it is only relatively recently that a detailed analysis of possible experimental errors allows one to evaluate the significance of the experimental results. A recent paper by Person[2] clearly shows the limited validity of experimental results when the Benesi–Hildebrand technique is used to study very weak complexes. Likewise it has been shown that the linearity of the Benesi–Hildebrand plot by itself is not a sufficient criterion for assuming a simple 1:1

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[1] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

[2] W. B. Person, *ibid.*, **87**, 167 (1965).

interaction between the donor and the acceptor molecules,[3] but that it is quite imperative to check the constancy of the data by doing the measurements at several wavelengths. It is rather unfortunate that too often measurements are reported only at a single wavelength.

Pyridine complexes with halogens and particularly with iodine both in the solid state and in solution have been studied by a number of investigators. It is interesting to note, however, that the stability of the pyridine–iodine complex is still a matter of dispute. Spectrophotometric measurements on the pyridine–iodine system in heptane by Reid and Mulliken[4] gave the following values for the formation constants: 2°, $K_f = 649$; 16.7°, 290; 41°, 101 M^{-1}. The interpolated value for 25° is $\approx 200\ M^{-1}$. Popov and Rygg, using a similar technique but carbon tetrachloride as solvent,[5] reported a formation constant of $102 \pm 5\ M^{-1}$. Maki and Plyler studied the far-infrared band of the N–I stretch of the $Py \cdot I_2$ complex at 184 cm^{-1} and have obtained a similar value of $107 \pm 25\ M^{-1}$.[6] Likewise Alosi, *et al.*, reported a value of 106 M^{-1} for the formation constant.[7] On the other hand, Chaudhuri and Basu reported a much lower value of 43.74 M^{-1} [8] in chloroform solutions and the value went up to 183 M^{-1} in a recent paper by Sobczyk, *et al.*[9] The latter work was carried out in carbon tetrachloride. Shortly after the completion of this work a report of Bhaskar and Singh[10] appeared in the literature which described studies on a number of identical complexes in chloroform solutions. The experimental results are, however, somewhat different from ours. It should be noted that very little attention has been paid by most investigators to the role of the solvent in these reactions. In most cases it has been assumed that the solvent behaves as an inert medium for the complexation reaction.

It was of interest to us to do a rather detailed study of the iodine-substituted pyridine complexes in carbon tetrachloride solutions with proper regard for the limitations of the experimental techniques. Consequently, every precaution was taken to check the validity of our data.

Experimental Part

Chemicals.—Technical grade pyridine was refluxed for 2 hr over granulated barium oxide and then slowly distilled through a column packed with 100-cm helices. The middle fraction of the distillate was used; $n^{24}{}_D$ 1.5062; lit.[11] $n^{25}{}_D$ 1.5044.

With two exceptions all of the substituted pyridines used in the investigation were obtained from the Aldrich Chemical Co. They were dried over granulated barium oxide and then fractionally distilled. The 2,6-dichloropyridine, a solid at room temperature, was recrystallized twice from water–ethanol mixtures. The 4-*t*-butylpyridine and 3-ethylpyridine were gifts of the Reilly Tar and Chemical Co. The list of compounds is given in Table I. In all cases at least one physical property was compared with what seems to be the best literature value.

The purifications of carbon tetrachloride and of iodine have been described in previous publications.[12]

Solutions.—Solutions of iodine in carbon tetrachloride were prepared by the standard techniques. Although their concentrations could be determined by iodometric titrations, it was found that equal accuracy was obtained by measuring the absorption of the solution at 517 mμ and calculating the concentration from the value of the molar absorptivity at this wavelength (ϵ_{517} 927). Stock solutions of the respective pyridines were made by weighing the respective compound into a volumetric flask and diluting with purified solvent.

Mixed solutions of iodine and of the respective pyridine were prepared just before each measurement. Contact of solutions with the atmosphere was kept to a minimum but no attempt was made to do all of the transfers in a completely inert atmosphere. Preliminary results have indicated that brief contacts of the solution with the atmosphere did not alter the experimental data. Likewise it was found that solutions of iodine and the pyridines were stable for *at least* 1 hr after mixing, and, in general, spectral measurements were completed within 5–10 min of the initial mixing.

Absorption Spectra.—Absorption spectra were obtained on a Cary Model 14 spectrophotometer. Either 1- or 5-cm path length cells were used. All measurements were carried out at a room temperature of ≈25°. The ratio of donor to acceptor was varied within such limits so as to give a good spread of experimental points.

Spectral data obtained on the donor–iodine mixtures were used to calculate the formation constant of the complex using the method described by Ketelaar, *et al.*[13] In Ketelaar's equation

$$\frac{1}{\epsilon_t - \epsilon_{I_2}} = \frac{1}{C_D}\,\frac{1}{K_f(\epsilon_c - \epsilon_{I_2})} + \frac{1}{\epsilon_c - \epsilon_{I_2}}$$

ϵ_t is the apparent molar absorptivity of I_2 (*i.e.*, the measured absorbance of the solution divided by the total I_2 concentration), ϵ_c and ϵ_{I_2} are the molar absorptivities of the complex and I_2, respectively, K_f is the formation constant of the complex, and C_D is the concentration of base. A plot of $1/(\epsilon_t - \epsilon_{I_2})$ *vs.* $1/C_D$ should give a straight line. From the slope and intercept of this line the formation constant and the molar absorptivity of the complex can be determined. It should be noted that this method is likely to give better results than the treatment of Benesi and Hildebrand since measurements had to be made at wavelengths at which both the complex and iodine absorb.

Spectra of iodine–amine solutions containing a fixed amount of iodine and a variable amount of the amine were obtained in the 530–390-mμ spectral range. A typical set of spectral curves is illustrated in Figure 1. All pyridine derivatives listed in Table I gave essentially ideal isosbestic points. In the case of 4-phenylpyridine and of 4-cyanopyridine, a marked shift in the isosbestic point was observed with a change in the amine:iodine ratio. It seems quite likely that this behavior may be due to the formation of weak $py \cdot 2I_2$ complexes since a second molecule of iodine may form a weak bond with the phenyl or the cyano group, respectively.

Calculations.—A regression analysis of the data was performed on a CDC 3600 computer with points over three standard deviations off the line being rejected. Large excesses of pyridines were found to cause a shift in the isosbestic point due to an increase in the polarity of the solvent which favors the formation of triiodide ion. Thus, it was necessary in most cases to use base concentrations too small to allow direct use of Ketelaar's

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(3) K. Conrow, G. D. Johnson, and R. E. Bowen, *J. Am. Chem. Soc.*, **86**, 1025 (1964); G. D. Johnson and R. E. Bowen, *ibid.*, **87**, 1655 (1965).

(4) C. Reid and R. S. Mulliken, *ibid.*, **76**, 3869 (1954).

(5) A. I. Popov and R. H. Rygg, *ibid.*, **79**, 4622 (1957).

(6) A. G. Maki and E. K. Plyler, *J. Phys. Chem.*, **66**, 766 (1962).

(7) G. Alosi, G. Gauzzo, G. Giacometti, and U. Mazzucato, *Trans. Faraday Soc.*, **61**, 1406 (1965).

(8) J. N. Chaudhuri and S. Basu, *ibid.*, **55**, 898 (1959).

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(13) J. A. A. Ketelaar, C. van der Stolpe, A. Goudsmit, and W. Dzcubas, *Rec. Trav. Chim.*, **71**, 1104 (1952).

TABLE I

FORMATION CONSTANTS OF IODINE COMPLEXES WITH PYRIDINE AND SUBSTITUTED PYRIDINES IN CARBON TETRACHLORIDE SOLUTIONS AT ≈25°

Base	$10^4[I_2]$, M	K_f, M^{-1}	Acidity constant,[a] pK_a	Range of base concn, M	λ_{max}, mμ
2,6-Dichloropyridine	7.99	$\ll 1$	?		
2-Fluoropyridine	1.64	1.4 ± 0.4	−0.44	0.0274–0.2085	*b*
2-Chloropyridine	2.20	3.3 ± 0.15	0.72	0.02132–0.1279	*b*
2-Bromopyridine	2.23	4.4 ± 0.22	0.90	0.02465–0.09861	*b*
3-Chloropyridine	2.19	16.6 ± 0.30	2.84	0.02126–0.09870	430
3-Bromopyridine	1.10	17.2 ± 0.20	2.84	0.01615–0.09142	428
Pyridine	0.650	109 ± 1.3	5.21	0.0105–0.1700	415
3-Methylpyridine	5.83	207 ± 3.0	5.63	0.00378–0.01890	412
4-Methylpyridine	4.50	216 ± 3.5	5.98	0.00289–0.03072	411
4-*t*-Butylpyridine	5.86	300 ± 4.3	5.99	0.001464–0.009324	410
2,5-Dimethylpyridine	0.650	304 ± 2.2	6.40	0.00398–0.02602	413
4-Ethylpyridine	0.650	248 ± 1.7	5.99	0.00364–0.08390	410
3,5-Dimethylpyridine	5.81	379 ± 3.3	6.15	0.000817–0.01677	408
3,4-Dimethylpyridine	6.54	421 ± 12.0	6.46	0.00162–0.00669	408
3-Ethylpyridine	6.59	244 ± 1.0	5.56	0.00208–0.02246	412

[a] D. D. Perrin, Ed., "Dissociation Constants of Organic Bases in Aqueous Solutions," International Union of Pure and Applied Chemistry, London, 1965. Best values were selected (25°) whenever possible. [b] An absorption maxima was not discernible at the concentrations used.

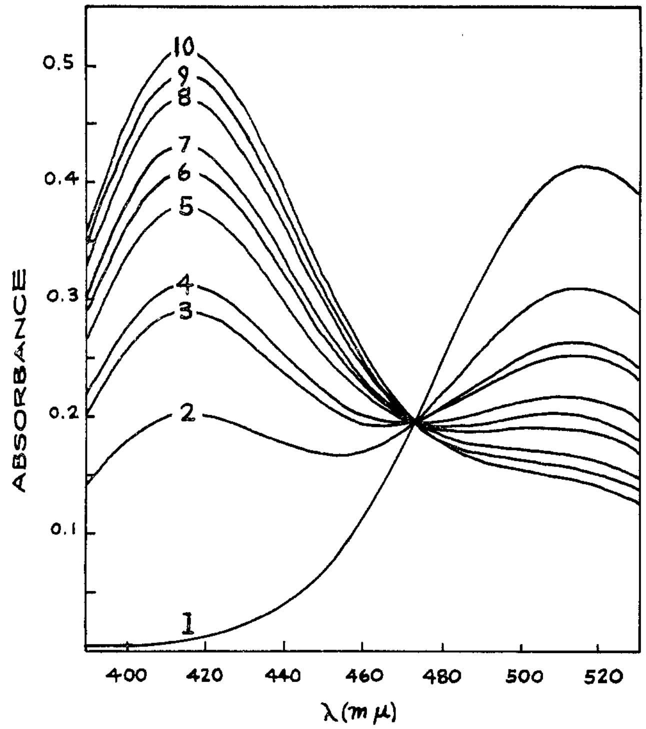

Figure 1.—Absorption spectra of the pyridine–iodine system in carbon tetrachloride solutions; $C_{I_2} = 4.44 \times 10^{-4}$ M; C_{Py} (M): (1) 0.0, (2) 0.00581, (3) 0.00762, (4) 0.00834, (5) 0.01143, (6) 0.01524, (7) 0.01669, (8) 0.02286, (9) 0.02503; (10) 0.03338.

equation. To overcome this difficulty an iteration was performed on the equation in the following manner. The experimental values of $1/C_D$ and $1/(\epsilon_t - \epsilon_{I_2})$ were used in Ketelaar's equation to calculate a value for K_f. This value for K_f was then used to calculate a value for the concentration of the complex which was subtracted from each value of C_D to give a new array. The process was then repeated until successive values for K_f agreed within 0.1%.

In performing this type of mathematical analysis a great deal of caution must be exercised since relatively small errors in certain experimental parameters can cause large errors in the evaluation of the formation constant. A good illustration of such an error is the extreme sensitivity of K_f to the iodine concentration for complexes where $K_f < 10$. In this study it was found that a change of 2.0% in the iodine concentration caused a 50% change in the value for K_f of the 2-fluoropyridine complex. This uncertainty is evident in the large standard deviation for the K_f of the complex.

The iteration procedure for solving Ketelaar's equation offers a distinct advantage in the evaluation of formation constants from experimental data. The values converged rapidly and reproducibly at all wavelengths. This method makes it possible to use lower concentrations of the donors, and thus it avoids the possibility of a change in the physical properties of the solvent in solutions with high concentrations of the base. It also makes it unnecessary to use a complex iterative procedure such as the one reported by Conrow, *et al.*[3]

As in all calculations of this type, we assumed that activity coefficients are equal to unity; *i.e.*, the values of K_f are expressed in concentration units. It should be noted that this assumption may be rather dangerous especially in the case of weak complexes where a large excess of donor (or acceptor) has to be added in order to produce a measurable change in the absorption spectrum. The concentration of the component in excess may be as high as 2–4 M, and under these conditions it would be unreasonable to expect that activity coefficients, even of uncharged species, can be ignored.

Calculations were carried out at least at three different wavelengths at at least 10-mμ intervals.

Results and Discussion

The results of our measurements are shown in Table I. The values of the formation constants vary from $\ll 1$ for the 2,6-dichloropyridine complex to 421 M^{-1} for the strongest complex, $3,4\text{-}(CH_3)_2\text{-py} \cdot I_2$. A comparison of our values for the formation constant of the pyridine–iodine complex with those reported in a previous publication, as well as the values of Maki and Plyler[6] and of Alosi, *et al.*,[7] shows a satisfactory agreement (109 ± 1.3 *vs.* 101, 107, and 106, M^{-1} respectively). The higher value of Mulliken and Reid[4] is probably due to the difference in solvent. The values of 43.74 M^{-1} of Chaudhuri and Basu[8] and 183 M^{-1} reported by Sobczyk, *et al.*,[9] seem to be less reliable, as well as their value of 358 M^{-1} for the formation constant of the 4-methylpyridine–iodine complex. On the other hand, Alosi and coworkers[7] report formation constants of 223 and 230 M^{-1} for 3- and 4-methylpyridine, respectively, which are in good agreement with our data.

There is a considerable amount of disagreement between our data and those of Bhaskar and Singh.[10] In general, their values of the formation constants are about 50% smaller than the values listed in Table I. It should be noted that Bhaskar and Singh carried out their measurements in chloroform solutions. Chloroform, besides being more polar than carbon tetrachloride, is also a notoriously poor solvent for the study of halogen complexes due to the ease with which it is oxidized by air to give HCl as one of the products. Hydrochloric acid easily reacts with halogens to give polyhalide ions and this reaction, obviously, can introduce a large error in the spectrophotometric study of iodine complexes. Chloroform can only be used as a solvent for such studies if it is very carefully purified just prior to use. It also appears that the spectral measurements of Bhaskar and Singh[10] were carried out only at a single wavelength.

It has been shown in a previous publication that it is possible to correlate the formation constants of halogen complexes with acetonitrile and chlorinated acetonitrile with the Taft σ^* constant,[14] where σ^* is a measure of only the inductive effect in a rigid aliphatic compound. Since in the case of substituted pyridines the resonance and the steric effects would likewise be important, it seemed more reasonable to investigate the possible correlation between the Hammett σ function and the log of the formation constant of the respective complexes. A plot of σ *vs.* log K_f is shown in Figure 2. It is seen that a reasonably straight line is obtained. The equation of the line is given by

$$\log K_f = -2.25\sigma + 2.11 \qquad (1)$$

The standard deviation of the slope is 0.16 and the value of r, Jaffé's correlation coefficient,[15] is 0.98.

According to Jaffé's criteria[15] for the magnitude of the correlation coefficient, the value of ρ is in good agreement with the Hammett equation. A similar study of iodine complexes of substituted styrylpyridines by Mazzucato, *et al.*,[16] gave values of $\rho = -2.1$ with $r = 0.93$ (values for pyridine, 4-methylpyridine, and 3-methylpyridine were also included in the calculation). Rather poor correlation as shown by the low value of r may be due to the interaction of the halogen with the delocalized electrons of the stilbene ring (*cf.* our results with 4-phenylpyridine and 4-cyanopyridine described above).

There are some rather minor discrepancies which illustrate the limitations of the theory. For example, one would expect the value of σ for 3-chloropyridine to be greater than that of 3-bromopyridine which would imply that the K_f value for the corresponding 3-bromopyridine complex would be the larger of the two. Experimentally the values for K_f follow the expected order; however, the σ values do not.

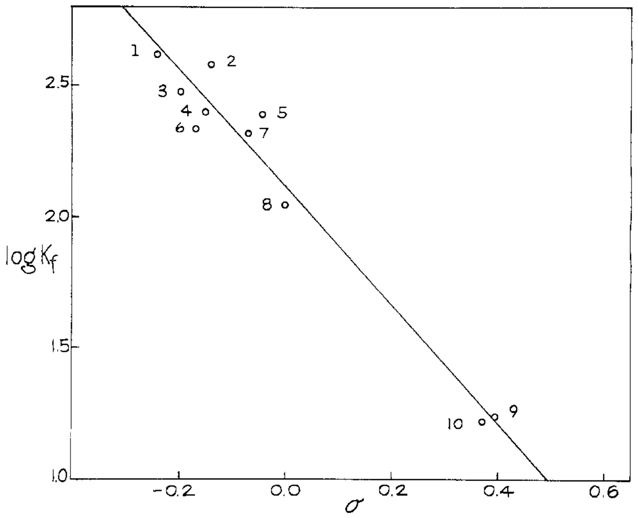

Figure 2.—Relationship between log K_f and the Hammett σ function for the pyridine–iodine complexes in carbon tetrachloride solutions: (1) 3,4-CH_3, (2) 3,5-CH_3, (3) 4-*t*-C_4H_9, (4) 4-C_2H_5, (5) 3-C_2H_5, (6) 4-CH_3, (7) 3-CH_3, (8) Py, (9) 3-Br, and (10) 3-Cl.

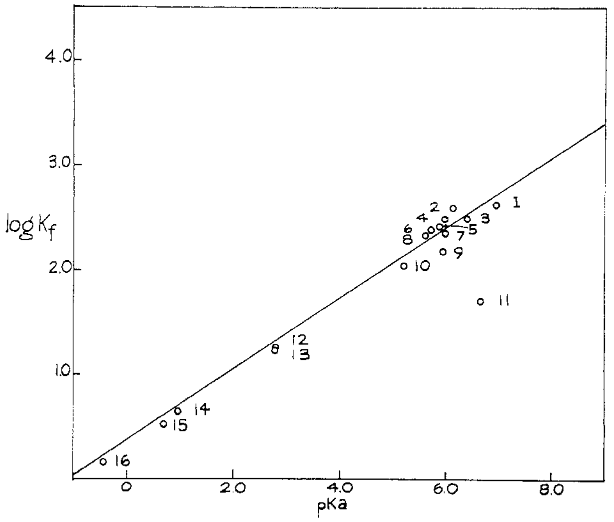

Figure 3.—Relationship between the acidity constant of the pyridines in aqueous solutions and the formation constants of the pyridine–iodine complexes in carbon tetrachloride solutions: (1) 3,4-CH_3, (2) 3,5-CH_3, (3) 2,5-CH_3, (4) 4-*t*-C_4H_9, (5) 4-C_2H_5, (6) 3-C_2H_5, (7) 4-CH_3, (8) 3-CH_3, (9) 2-CH_3, (10) Py, (11) 2,6-CH_3, (12) 3-Br, (13) 3-Cl, (14) 2-Br, (15) 2-Cl, and (16) 2-F.

It was also of interest to us to determine if there is a correlation between the acid dissociation constants of the pyridines and the iodine complex formation constant. Chaudhuri and Basu[8] claim that their results did not indicate any parallelism between the basicity of the pyridines and their ability to form halogen complexes. On the other hand, as seen from Figure 3, a plot of pK_a *vs.* log K_f does indeed yield a fairly straight line although there is some scatter of the experimental points. This is implied from the combination of our results in Figure 2 and those of Jaffé and Doak[17] in which they obtained a linear

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(14) W. B. Person, W. C. Golton, and A. I. Popov, *J. Am. Chem. Soc.*, **85**, 891 (1963).

(15) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

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(17) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 4441 (1955).

plot between the pK_a's of several substituted pyridines and the Hammett σ constant.

A number of investigators have studied the relationship between the basicity of pyridines and their ability to form various types of complexes. A comprehensive study of the relationship between the pK_f values of silver complexes of amines with their pK_a values by Bruehlman and Verhoek[18] has shown that plots of pK_f *vs.* pK_a fall on two straight lines, one for the pyridines and primary aliphatic amines and one for secondary amines. Recently Cattalini and coworkers[19] have shown that the plot of log K for the reaction $AuCl_4^- + py \rightleftarrows Au(py)Cl_3 + Cl^-$ gave three straight lines, one for pyridines without steric hindrance, one for pyridines with one methyl group in the 2 position, and a third one for pyridines with methyl groups in the 2 and 6 positions.

It can be concluded, therefore, that in pyridine and in substituted pyridines, in the absence of steric effects, there is a definite parallelism between the complexing abilities of the amines and their basicities. Such correlation, of course, would be expected if one adopts Lewis' definition of acids and bases since both H^+ and I_2 are Lewis acids. It should be noted, however, that such generalizations are only applicable to cases where the reference bases do not differ appreciably in structure.

Acknowledgment.—The authors gratefully acknowledge the support of this work by the U. S. Army Research Office (Durham).

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Fluorophosphine Ligands. V. Reactions of μ-Oxo-bis(difluorophosphine), F_2POPF_2, with Acids

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The compound F_2POPF_2 adds one and only one BH_3 group when brought into contact with B_2H_6 at a pressure of 1 atm and a temperature of 25°. Dissociation of $F_2POPF_2 \cdot BH_3$ is favored by higher temperatures and reduced pressures; the immediate products are F_2POPF_2 and B_2H_6. Analyses of the ^{19}F, ^{11}B, and ^1H nmr spectra prove that the BH_3 is bound to one of the phosphorus atoms. No reaction is observed with BF_3 and F_2POPF_2. The addition of HBr to F_2POPF_2 leads to the cleaving of the P–O–P bond with the formation of F_2HPO and PF_2Br. The structure of F_2HPO has been established by means of the ^{31}P, ^{19}F, and ^1H nmr spectra. The compound F_2HPO has also been observed in the reaction of PF_3 with small amounts of H_2O at 150° and in the reaction of $(CH_3)_3SnOH$ with PF_2Br. When F_2HPO is maintained as a liquid at room temperature, disproportionation to give PF_3 and the previously unreported $FHPO_2H$ occurs. The ^{31}P, ^1H, and ^{19}F nmr spectra were used to identify monofluorophosphorous acid, $FHPO_2H$.

The recently reported[1] compound F_2POPF_2 has three potentially basic sites; hence, a number of possible reactions with acids might be anticipated. Transformations resulting from reactions with both Brønsted and Lewis acids are described herein.

The Reaction of F_2POPF_2 with Lewis Acids

(1) **With Diborane.** Diborane reacts with F_2POPF_2 as indicated by the equation

$$^1/_2B_2H_6(g) + F_2POPF_2(g) \xrightarrow{25°} F_2POPF_2 \cdot BH_3(g)$$

Yields of 85% were obtained. No evidence for a double or triple adduct was obtained under the conditions used here. The boron-11 nmr spectrum of $F_2POPF_2 \cdot BH_3$ was obtained at 32.1 Mc using a Varian HR-100; the expected borane quartet was observed. (J_{BH} = 104 cps; δ relative to $B(CH_3)_3$ = 130 ppm). Each member of the quartet was split into a doublet by direct coupling with phosphorus (J_{BP} = 55.8 cps). The B–P coupling constant of 55.8 is comparable to the value of J_{BP} (54.3 cps) in $(CH_3)_2HPBH_3$ where direct B–P bonding is mandatory. Thus, bonding of a BH_3 unit to one of the phosphorus atoms is clearly indicated. Boron–phosphorus coupling in $F_2POPF_2 \cdot BH_3$ contrasts sharply with a lack of such coupling in $F_2PPF_2 \cdot BH_3$. A rapid intramolecular exchange of BH_3 between P atoms was postulated to explain the lack of coupling in $F_2PPF_2BH_3$.[2] Such rapid exchange between coordination sites is definitely not taking place in $F_2POPF_2BH_3$.

The phosphorus-31 nmr spectrum was obtained at 40.4 Mc on a Varian HR-100 spectrometer. The spectrum confirms the fact that a borane group is directly bonded to only one of the two phosphorus atoms. Three sets of triplets were observed; the first was that for the free F_2POPF_2 in the system[3] (δ relative to

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[1] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

[2] K. W. Morse and R. W. Parry, *ibid.*, **89**, 172 (1967).

[3] Some difficulty was experienced in separating small amounts of F_2POPF_2 from $F_2POPF_2 \cdot BH_3$. Slow decomposition to give F_2POPF_2 and B_2H_6 at reduced pressures and low temperatures would explain the observation. Thermodynamic quantities for the system F_2POPF_2–B_2H_6 are being obtained.