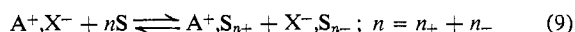


vents shows that EC is 5.7 times more difficult to displace from the cation than is ODCB. This involves the assumption that there is not much difference in the free energy of interaction of TPPO with the solvents EC and ODCB themselves. Grunwald and Miller¹⁷ have recently reported that Henry's law constant, a measure of solute-solvent interaction, for benzyl chloride as solute increased by a factor of 4.6 in going from dioxane as solvent to ethanol. With this in mind, we still believe that the relative magnitudes of the free energies of interaction of solvent and ligand with the cation play the major role in determining the values of K_L we report here. Comparison of these with the ion-pair dissociation constants for methyltri-*n*-butylammonium perchlorate in the two solvents EC and ODCB is instructive in this regard. The ratio, $K(\text{in EC})/K(\text{in ODCB})$, is 15.4 for the perchlorate. Treating the ion-pair dissociation process in a manner analogous to that employed for the cation complex, then we may write



where n is the number of specifically solvating solvent molecules added to the ions in the pair dissociation process. The free ions are more stable in EC by a factor of 15.9. If we assume that the stability of the pairs is the same in the two solvents, and that the relative stability of the cation in EC to that in ODCB is given by the inverse ratio of the K_L values found in this work, then the cation is more stable by a factor of 5.7, leaving a factor of 2.8 for the increase in the stability of the perchlorate anion in EC over that in ODCB. That the cation-solvent interaction should play a greater role in these solvents is reasonable since both solvent molecules have the negative ends of their dipoles more unprotected and available for ion-solvent interaction than are the positive ends of the dipoles. The value of the ratio of the ion-pair dissociation constants in these two solvents, $K(\text{EC})/K(\text{ODCB})$, is very sensitive to the nature of the cation, and less sensitive to the nature of the anion. The ratio for tri-*n*-

(17) W. J. Miller and E. Grunwald, *J. Phys. Chem.*, **68**, 1285 (1964).

butylammonium picrate has been found¹ to be 71, while that for the tetra-*n*-butylammonium picrate has been reported¹⁰ as 13.2. The ratio for tetra-*n*-butylammonium nitrate is¹⁰ 25.6.

Ramsey and co-workers¹³ argue that this effect, the increased dissociation of many salts in EC compared to other solvents having almost the same dielectric constant, is due to an increase in the dielectric constant in the neighborhood of the ions in EC, charged species favoring the *gauche* form of ethylene chloride. Whether one chooses to view the effect in terms of an increased local dielectric constant in EC, or in terms of increased specific ion-solvent interaction, is a matter of taste. We prefer the latter description since it leads¹ to consideration of another solvent parameter, the vapor pressure, in addition to dielectric constant (and dipole moment), which should be of value in accounting for the "solvating power" of a solvent. The greater the escaping tendency (the vapor pressure) of solvent molecules from solvent, the more negative the free energy of specific solvation as in eq. 9. Beard and Plesch recently¹⁸ found that the ion-pair dissociation constant for methyltriethylammonium iodide in methylene chloride did not decrease as much with increasing temperature as would be required by the corresponding decrease in the DT product, eq. 2. They explained their results in terms of a decrease in the distance of closest approach, a , as the temperature increases. The decrease in a is explained as being due to a decrease in pair-solvent interaction as the temperature increases. We offer the alternative explanation that increased specific ion-solvent interaction is occurring upon dissociation of the pair and as the temperature increases, the vapor pressure and thus the solvating power of methylene chloride increases, leading to a smaller decrease in K with rising temperature than one would expect solely from the change in the DT product in eq. 2.

Acknowledgment. This work has been supported in part by a grant from the U. S. Army Research Office, Durham.

(18) J. H. Beard and P. H. Plesch, *J. Chem. Soc.*, 4879 (1964).

Calculation of Chemical Shifts. III. Trivalent Phosphorus¹

H. S. Gutowsky and John Larmann²

Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois. Received April 14, 1965

Expressions are developed for the isotropic, paramagnetic contribution $\sigma_A^{(2)}$ to the magnetic shielding of group V nuclei in AX_3 molecules, and for the anisotropy of the paramagnetic shielding tensor. The localized molecular orbital treatment employs hybridization and ionicity as bond parameters. A comparison of the ^{31}P shifts ob-

served in PH_3 , $\text{P}(\text{CH}_3)_3$, and the phosphorus trihalides with values calculated for $\sigma^{(2)}$ shows that differences in the latter account for the major features of the observed shifts. Also, the calculations indicate that the variations in $\sigma^{(2)}$ do not depend solely upon changes in any one bond parameter.

(1) Supported in part by the U. S. Office of Naval Research and by the National Institutes of Health.

(2) National Institutes of Health postdoctoral fellow.

I. Introduction

Theoretical studies^{3,4} of chemical shifts indicate that for all but the very light nuclei⁴ the dominant contribution to the nuclear shielding tensor is $\sigma^{(2)}$, the second-order paramagnetic term for the atom in question. Expressions for $\sigma^{(2)}$ in terms of orbital populations were developed by Pople⁵ and by Karplus and Das.⁶ More recently, this type of formulation was extended⁴ to include d- as well as p-orbitals, and the results were used to analyze the xenon chemical shifts⁷ observed in some of the new xenon fluorides. The method is limited by its approximate nature and by the fact that there are usually several more adjustable parameters in the theory than there are observable quantities. But its relative simplicity is attractive, so we have explored further the extent to which the differences calculated for $\sigma^{(2)}$ can account for the *general trends* observed in chemical shifts. In particular, we consider here the ³¹P shifts reported some years ago for a variety of trivalent phosphorus compounds.⁸⁻¹⁰

Two attempts have been made to relate the ³¹P chemical shifts in trivalent phosphorus compounds to differences in the second-order paramagnetic term. In the first,⁹ the "p-electron unbalance" at the ³¹P nucleus was expressed simply as the vector sum of contributions from the phosphorus bonding orbitals, each of which was taken to be of the form, including bond ionicity, employed for the ¹⁹F shifts.³ Later, this was modified¹¹ by adjusting the p-electron unbalance to particular values for the limiting cases of p³- and sp³-hybridization. However, neither approach is consistent with the general formulation for $\sigma^{(2)}$. Therefore, we have used the previous derivation⁴⁻⁶ of the components of $\sigma^{(2)}$ to obtain appropriate expressions for the isotropic shielding $\sigma_A^{(2)}$ of the A nucleus in pyramidal, sp³-hybridized, AX₃ compounds as well as for the anisotropy $\eta_\sigma^{(2)}$, in terms of localized bond parameters. These results are then applied to the ³¹P shifts observed in some typical compounds.

II. $\sigma_A^{(2)}$ in AX₃ Pyramidal Compounds

In this section, $\sigma^{(2)}$ is obtained in analytical form applicable to group V elements in trivalent compounds for which π -bonding is negligible. The wave functions of the valence electrons centered on A are assumed to be hybrids, composed of s- and p-orbitals of the following form.

$$\sigma_X = N_X (s + \lambda_X p_i) \quad (1)$$

$$\sigma_{1p} = N_{1p} (s + \lambda_{1p} p_j) \quad (2)$$

Here, σ_X is the hybrid orbital directed toward atom X; N_X is the normalization constant, which is related to the per cent "s" character by $\frac{\sigma}{N_X} = 100N_X^{-2}$; λ_X is the hybridization mixing coefficient; and p_i is a p-orbital directed toward the X atom. Similar definitions apply to the lone-pair hybrid, σ_{1p} . This formulation

(3) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(4) C. J. Jameson and H. S. Gutowsky, *ibid.*, **40**, 1714 (1964).

(5) J. Pople, *Proc. Roy. Soc. (London)*, **A239**, 541, 550 (1957).

(6) M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961).

(7) C. J. Jameson and H. S. Gutowsky, *ibid.*, **40**, 2285 (1964).

(8) H. S. Gutowsky and D. W. McCall, *ibid.*, **22**, 162 (1954).

(9) N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).

(10) J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *ibid.*, **78**, 5715 (1956).

(11) J. R. Parks, *ibid.*, **79**, 757 (1957).

assumes that the internuclear and interorbital angles are identical. Such may not be the case, but in the absence of definitive evidence to the contrary it is a reasonable assumption.

The orbital parameters N_X , λ_X , N_{1p} , and λ_{1p} are then determined by the molecular geometry. A necessary and sufficient condition for the orthogonality of two hybrid orbitals, $s + \lambda p_i$ and $s + \mu p_j$, has been stated by Coulson¹² to be

$$1 + \lambda\mu \cos \theta_{ij} = 0 \quad (3)$$

where θ_{ij} is the interorbital angle. This relationship, along with bond angle data and geometrical considerations, enables one to determine all of the orbital parameters.

The σ_X hybrid on A may be combined with a bonding orbital of the X atom to give a doubly occupied localized molecular orbital of the form

$$\psi_{AX} = \{2[1 + (1 - i_X^2)^{1/2} S_X]\}^{-1/2} [(1 - i_X)^{1/2} \sigma_X + (1 + i_X)^{1/2} \phi_X] \quad (4)$$

for A-X bonds, and

$$\psi_{1p} = \sigma_{1p} \quad (5)$$

for the A atom's lone pair. The parameter i_X , where $0 \leq i_X \leq 1$, is a measure of the ionicity of the A-X bond; ϕ_X is the bonding orbital on atom X and may be a hybrid type; and S_X is the overlap between σ_X and ϕ_X .

For molecules without d-orbital bonding, the diagonal elements $\sigma_{\alpha\alpha}^{(2)}$ of $\sigma^{(2)}$ were found to be of the form⁴⁻⁶

$$\sigma_{\alpha\alpha}^{(2)} = -(e^2 \hbar^2 / \Delta m^2 c^2) \langle 1/r^3 \rangle_p P_{\alpha\alpha} \quad (6)$$

where Δ is the average excitation energy and $\langle 1/r^3 \rangle_p$ is the average value of r^{-3} for the p-electrons in the valence shell of A. The quantity $P_{\alpha\alpha}$ is given in Appendix A of ref. 4 in terms of the orbital populations $p_{\alpha\alpha}$ which are defined in eq. 2 of the same paper. The contribution of $\sigma^{(2)}$ to the isotropic shielding, which governs the high resolution n.m.r. spectra of liquids and gases, is

$$\sigma^{(2)} \equiv \sigma_{av}^{(2)} = \frac{1}{3} \sum_{\alpha} \sigma_{\alpha\alpha}^{(2)} \quad (7)$$

The anisotropy of $\sigma^{(2)}$ may be defined as

$$\eta_\sigma^{(2)} = \sigma_{zz}^{(2)} - \frac{1}{2} (\sigma_{xx}^{(2)} + \sigma_{yy}^{(2)}) \quad (8)$$

when the nucleus in question is on the z axis which is threefold or higher in symmetry.

In order to apply eq. 6-8 to the wave functions in eq. 1-5, we place the A atom at the origin of cartesian coordinates, with σ_{1p} along the z axis and one of the σ_X orbitals in the xz plane. The vectorial nature of p-orbitals is used to express the p_i and p_j of eq. 1 and 2 in terms of the p_x , p_y , and p_z -orbitals. Thereby, the following general equations are obtained for the orbital populations in terms of the bond parameters

$$p_{xx} = p_{yy} = 4N_X^2 \lambda_X^2 I_X^2 \sin^2 \frac{\theta}{2} \quad (9)$$

(12) C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952, p. 194.

Table I. Summary of Structural^a and Bond Parameters Used in Calculating ³¹P Chemical Shifts for PX₃ Molecules

X	r_{P-X} , Å	$\angle XPX$, deg.	N_X	λ_X	N_{1p}	λ_{1p}	i_X	I_X^2	Δ , e.v.
H	1.42	93.3	0.223	4.37	0.923	0.419	0.00	0.309	8
CH ₃	1.87	100	0.385	2.40	0.746	0.893	0.07	0.295	8
F	1.52	104	0.441	2.03	0.645	1.19	0.40	0.288	7.5
Cl	2.00	101	0.400	2.29	0.721	0.962	0.15	0.281	6
Br	2.23	100	0.385	2.40	0.746	0.893	0.10	0.301	6
I	2.47	98	0.349	2.61	0.804	0.740	0.05	0.317	6

^a J. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 181, 222.

$$p_{zz} = 2N_X^2\lambda_X^2I_X^2\left(3 - 4\sin^2\frac{\theta}{2}\right) + 2N_{1p}^2\lambda_{1p}^2 \quad (10)$$

where θ is the X-A-X bond angle, and

$$I_X^2 = \frac{(1 - i_X)}{2[1 + (1 - i_X^2)^{1/2}S_X]} \quad (11)$$

Introduction of eq. 9 and 10 for the orbital populations into the equations⁴ for $\sigma_{\alpha\alpha}^{(2)}$ leads to

$$\sigma^{(2)} = -(2e^2\hbar^2/3\Delta m^2c^2)\langle 1/r^3 \rangle_P \left[6N_X^2\lambda_X^2I_X^2 + 2N_{1p}^2\lambda_{1p}^2 - 24N_X^4\lambda_X^4I_X^4\left(\sin^2\frac{\theta}{2} - \sin^4\frac{\theta}{2}\right) - 8N_X^2\lambda_X^2N_{1p}^2\lambda_{1p}^2\sin^2\frac{\theta}{2} \right] \quad (12)$$

and

$$\eta_{\sigma}^{(2)} = (e^2\hbar^2/\Delta m^2c^2)\langle 1/r^3 \rangle_P \left[6N_X^2\lambda_X^2I_X^2 \times \left(1 - 2\sin^2\frac{\theta}{2}\right) + 2N_{1p}^2\lambda_{1p}^2 + 24N_X^4\lambda_X^4I_X^4 \times \left(2\sin^4\frac{\theta}{2} - \sin^2\frac{\theta}{2}\right) - 8N_X^2\lambda_X^2I_X^2N_{1p}^2\lambda_{1p}^2\sin^2\frac{\theta}{2} \right] \quad (13)$$

It should be noted that as before^{4,6} these expressions neglect contributions from orbitals centered on atoms other than A. Also, eq. 12 and 13 are unlike the analogous results for the xenon fluorides⁷ in that the extent of sp-hybridization is a directly adjustable parameter by means of the X-A-X interorbital angle θ . It has been assumed that the three A-X bonds are equivalent; however, the expressions appropriate for dissimilar substituents are readily obtained though they are algebraically more complex.

III. Application to ³¹P Chemical Shifts in Trivalent Compounds

As noted in the Introduction, several structural and bond parameters appear in eq. 12 and 13 for $\sigma^{(2)}$ and $\eta_{\sigma}^{(2)}$. Some of them are directly measurable and thus are available to good accuracy, but others must be estimated in one way or another. Therefore, quantitative tests of chemical shift theory are seldom possible, and this work is no exception. In Table I the various quantities required to calculate $\sigma^{(2)}$ and $\eta_{\sigma}^{(2)}$ are summarized. We have sought to obtain accurate values of these quantities for the six phosphorus compounds treated, and the results are listed in the table. In Table II, we give the corresponding values for $\sigma^{(2)}$ and $\eta_{\sigma}^{(2)}$, and the differences in $\sigma^{(2)}$ are then compared with the observed ³¹P chemical shifts.

Table II. Summary of Values Calculated for the ³¹P $\sigma^{(2)}$ and $\eta_{\sigma}^{(2)}$ (in p.p.m.) and Comparison with Observed Chemical Shifts for Several Trivalent Phosphorus Compounds

Compound	$\sigma^{(2)}$	$\eta_{\sigma}^{(2)}$	$\Delta\sigma^{(2)}$	δ^a
PH ₃	-570	50	293	465
P(CH ₃) ₃	-630	162	233	289
PF ₃	-709	238	154	130
PI ₃	-823	146	40	49
PCl ₃	-852	254	11	8
PBr ₃	-863	207	0	0

^a From ref. 8 and 9, with the zero of reference changed from H₃PO₄ to PBr₃. A larger positive number corresponds to an upfield shift.

Parameters Required to Evaluate $\sigma^{(2)}$ and $\eta_{\sigma}^{(2)}$. As indicated in II, the interorbital angle θ is taken to be the experimental X-P-X bond angle. Also, this angle establishes the values given in Table I for the N and λ values. The quantity I_X^2 contains the ionic character i_X and the overlap S_X between the bonding orbital on atom X and that on phosphorus. The overlap was evaluated using standard sources of overlap integrals^{13,14} and the experimental P-X bond distance. The factor i_X is more important and more difficult to assess. A simple empirical formula used for diatomic molecules¹⁵ is

$$i_X = 0.16(x_A - x_B) + 0.035(x_A - x_B)^2 \quad (14)$$

where x_A and x_B are the Pauling electronegativities. The values of i_X in Table I were estimated with this formula; they will be somewhat large for the corresponding polyatomic bond. However, the values obtained should be reasonable upper bounds for i_X , and give lower bounds for I_X^2 .

As usual, the average electronic excitation energy Δ presents the most difficulty and probably is the least certain of the required parameters. The ultraviolet spectra of the molecules considered here are of the predissociation type with long ranges of continuous absorption which make it somewhat difficult to assign the appropriate frequencies necessary for determining Δ . The values of Δ were obtained by an arithmetic averaging of the energy bands reported for these molecules and are discussed in detail below. Weaker bands were weighted to a lesser degree based on intensity considerations.

(13) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(14) M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, "Tables of Molecular Integrals," Maruzen and Co., Ltd., Tokyo, 1955.

(15) See ref. 12, p. 134. In ref. 6 it has been suggested that the ionic character scale obtained via quadrupole coupling constants is more appropriate for chemical shift calculations.

The spectra of phosphine¹⁶ and trimethylphosphine^{16a} are similar and $\Delta = 8$ e.v. is assigned to both compounds. Phosphine has a maximum in its lowest energy band at 1910 Å., 6.6 e.v. A predissociation band has a maximum at 1800 Å., 7 e.v., while at shorter wave lengths the bands all overlap into a continuum that extends downward to 1250 Å., 10.1 e.v. Trimethylphosphine has a band similar to phosphine at 2010 Å.; the shorter wave length side to 1850 Å. is continuous.

The spectra of PCl_3 , PBr_3 , and PI_3 are generally similar in appearance and in the positions of maxima; therefore the same Δ , of 6 e.v., is used for all three compounds. As to details, the spectrum of PCl_3 has been measured^{16,17} from about 3000 down to 1200 Å. At long wave lengths, an absorption band occurs at 2800 Å., 4.4 e.v., which is attributed to nonbonding transitions. A second maximum occurs at 2170 Å., 5.6 e.v., in a band of transitions. Another weaker band starting at 1600 Å. with a maximum at 1470 Å., 8.3 e.v., has also been observed. The spectra for phosphorus tribromide¹⁷ and phosphorus triiodide¹⁸ are much less complete. However, the tribromide has two bands at 2635 Å., 4.7 e.v., and 3085 Å., 4.1 e.v., which correspond to the nonbonding transition in the trichloride. Below 2400 Å. the tribromide appears to have a continuous absorption, again similar to the trichloride. Phosphorus triiodide has been measured in solution and has the typical nonbonding band at 2850 Å., 4.3 e.v. Thus, to the extent that they have been investigated, the spectra of PBr_3 and PI_3 are very similar to that of PCl_3 , so the Δ for all three molecules is taken to be the trichloride average of 6 e.v.

Phosphorus trifluoride^{16b} has been measured from 2000 down to 1200 Å., and has a spectrum similar to the trichloride, except that it is displaced to shorter wave lengths. Two bands appear at 1564 and 1515 Å., about 7.8 e.v. A second, weaker band starts at 1405 Å. with a maximum at 1300 Å., 9.2 e.v. The bands then overlap into the typical continuum pattern below 1300 Å. At wave lengths longer than 2000 Å. the nonbonding transition typical of the trihalides would be expected. This would be expected to lower the value of Δ to 7.5 e.v.

Finally, we need a value of $\langle 1/r^3 \rangle$ for the 3p-valence electrons of phosphorus. This may be obtained from experimental values for spin-orbit interactions in the free atom, and in this manner Barnes and Smith¹⁹ calculated $\langle a_0^3/r^3 \rangle_{3p}$ for a series of atoms. Their value for phosphorus is $\langle a_0^3/r^3 \rangle_{3p} = 3.48$ which we used.

IV. Results and Discussion

Table II lists the values for $\sigma^{(2)}$ and $\eta_\sigma^{(2)}$ obtained from eq. 12 and 13 by means of the parameters summarized in Table I. Also, for purposes of comparison with experiment, the differences between the $\sigma^{(2)}$ calculated for each molecule and for PBr_3 are given along with the observed ³¹P chemical shift referred to PBr_3 . These calculated variations in $\sigma^{(2)}$ fall in the

same order as do the observed chemical shifts, and the numerical agreement is reasonably good considering the approximations inherent in the theory. Also, it should be kept in mind that the experimental errors in bond angles and bond lengths are appreciable and that they affect the results of the calculations.

The $\Delta\sigma^{(2)}$ calculated for PH_3 shows the largest deviation from experiment, and that for $\text{P}(\text{CH}_3)_2$ is next. Actually, this could reflect in part our choice of PBr_3 rather than PH_3 as the reference compound for $\Delta\sigma^{(2)}$ and δ . That is, without further data, it is not clear whether the calculations for the phosphorus trihalides or those for PH_3 and $\text{P}(\text{CH}_3)_3$ are in error or whether errors in both contribute to the discrepancies. Measurements of the ³¹P chemical shift anisotropy could be very helpful in this context because, as may be seen in Table II, $\eta_\sigma^{(2)}$ has a substantially different dependence upon the localized bond parameters, hybridization, and ionicity than does $\sigma^{(2)}$. Moreover, the anisotropy does not suffer from the uncertainties in choosing a zero of reference, as must be done for comparisons of $\sigma^{(2)}$. In any event, the ³¹P chemical shifts in these trivalent compounds can be attributed largely to differences in $\sigma^{(2)}$. Also, no single parameter appears to dominate $\Delta\sigma^{(2)}$; instead, differences in ionicity, hybridization, and in Δ all seem to be important.

There are several possible sources of the nonquantitative agreement between the calculations and experiment, with the more obvious ones being errors in Δ , the neglect of the diamagnetic shielding term, and neglect of overlap between the localized molecular orbitals.³⁻⁷ This overlap between two localized molecular orbitals is considered to be small. It should not be confused with the overlap S_X appearing in the formula for the localized molecular orbital. The S_X overlap is between bonding atomic hybrids within a given two-centered molecular orbital and is always sizable. The estimates of the bond ionicity seem to be a less likely source of error; at least the ¹⁹F chemical shift observed in PF_3 is compatible with the i_F of 0.40 used to calculate the ³¹P shift in the compound. The method used to make the check is the same as that applied to the ¹⁹F shifts in the xenon fluorides.⁷ For fluorine, the expression for $\sigma^{(2)}$ is simply

$$\sigma_F^{(2)} = -(2e^2\hbar^2/3\Delta m^2c^2)\langle 1/r^3 \rangle_F [1 - (i_F + s_F)] \quad (15)$$

with symbols as before except for s_F which is the s-character of the bonding orbital centered on F. If the experimental value of 464 p.p.m.²⁰ for $\sigma_F(\text{PF}_3) - \sigma_F(\text{F}_2)$ is attributed to $\Delta\sigma_F^{(2)}$ and the same values are assigned to the other parameters as before,^{6,7} one finds that $i_F \cong 0.40$ which agrees with the value obtained from eq. 14.

The possible effects of π -character have been neglected in our calculations. However, the π -bonding should be nil for PH_3 and $\text{P}(\text{CH}_3)_3$ and could be no more than 10% for the phosphorus trihalides.²¹ This might account for part of the discrepancy between the $\Delta\sigma^{(2)}$ calculated for the two groups of compounds and

(16) (a) M. Halmann, *J. Chem. Soc.*, 2853 (1963); (b) C. M. Humphries, A. D. Walsh, and P. A. Warsop, *Discussions Faraday Soc.*, 35, 148 (1963).

(17) E. Teller and H. Sponer, *Rev. Mod. Phys.*, 13, 75 (1941).

(18) R. Potteril and O. Walker, *Trans. Faraday Soc.*, 33, 363 (1937).

(19) R. G. Barnes and W. V. Smith, *Phys. Rev.*, 93, 95 (1954).

(20) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, 19, 1259 (1951).

(21) See, e.g., T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Academic Press Inc., New York, N. Y., 1958.

the observed $\Delta\sigma$ but it is hardly the main cause.²² Another possibility is the expansion of the phosphorus radial wave function by an amount proportional to the paired-electron density in the phosphorus bonding orbitals. This effect would be greatest for the least ionic P-X bonds, and thus it would tend to decrease $\langle 1/r^3 \rangle_P$ and $\sigma^{(2)}$ for PH_3 and $\text{P}(\text{CH}_3)_3$ as compared to the trihalides, which is in the direction required. The magnitude of the effect is uncertain, but there is some e.s.r. evidence for its existence.²³

A noteworthy feature of the calculations of $\sigma^{(2)}$ and of the experimental shifts for the trihalides is the "reversal" of the trends in the case of PI_3 ; that is, the ordering is PF_3 , PI_3 , PCl_3 , and PBr_3 . This is a consequence of the fact that although the bond parameters such as ionicity and bond hybridization change monotonically in the usual sequence F, Cl, Br, and I, their ef-

(22) Of course one would expect π -bond contributions to be more appreciable in the tetravalent compounds X_3PO and X_3PS .

(23) K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 1019 (1965).

fects upon $\sigma^{(2)}$ are nonlinear and, in some instances opposed, so that $\sigma^{(2)}$ goes through a minimum for PBr_3 . The existence of the minimum is evident also in the ^{31}P shifts found in the series of compounds PCl_3 , PBrCl_2 , PBr_2Cl , and PBr_3 . In observations at 16.2 Mc./sec., their shifts²⁴ were found to be 10.5, 4.3, and 0.6 p.p.m. upfield with respect to PBr_3 . Thus, the change produced in σ by substitution of a Br for a Cl is 6.2, 3.7, and 0.6 p.p.m. for the first, second, and third Br, respectively, which follow the general pattern for the unmixed trihalides themselves.

The formulation given here is applicable in principle to ^{14}N or ^{15}N shifts in trivalent nitrogen compounds. However, few experimental data are available on nitrogen shifts. It would be particularly relevant to the present work if nitrogen shifts could be measured in NH_3 as well as in some of the nitrogen trihalides, to establish whether ammonia has a large upfield shift such as that found for ^{31}P in phosphine.

(24) E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *J. Am. Chem. Soc.*, **81**, 6363 (1959).

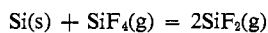
Silicon-Fluorine Chemistry. II. Silicon-Boron Fluorides^{1a}

P. L. Timms,^{1b} T. C. Ehlert,^{1b} J. L. Margrave,^{1b} F. E. Brinckman,^{1c}
T. C. Farrar,^{1c} and T. D. Coyle^{1c}

*Contribution from the Department of Chemistry, Rice University,
Houston, Texas, and the National Bureau of Standards, Washington, D. C.
Received March 16, 1965*

Gaseous SiF_2 and BF_3 are observed to react when condensed together in a trap at liquid nitrogen temperature. Several silicon-boron fluorides have been identified mass spectrometrically, including Si_2BF_7 , Si_3BF_9 , and $\text{Si}_4\text{BF}_{11}$. From n.m.r., infrared, and mass spectral data, one concludes that these molecules are members of the homologous series $\text{SiF}_3-(\text{SiF}_2)_n-\text{BF}_2$. The silicon-boron fluorides are thermally stable to at least 200° as vapors but ignite spontaneously in air. A similar family of mixed fluoro-chloro compounds is obtained by treating BCl_3 with SiF_2 .

It was shown by Pease² that silicon difluoride gas, SiF_2 , can be conveniently prepared from silicon and silicon tetrafluoride at low pressures and temperatures above 1050° .



Studies in this laboratory have shown³ that silicon difluoride is a surprisingly stable gaseous species, although it can be made to react with a wide variety of compounds.

(1) (a) Presented in part before the 148th National Meeting of the American Society, Chicago, Ill., Sept. 1964; (b) Rice University; (c) National Bureau of Standards.

(2) D. C. Pease, U. S. Patents 2,840,588 (June 24, 1958) and 3,032,173 (March 20, 1962) assigned to the Du Pont Co., Wilmington, Del.

(3) (a) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *Nature*, in press; (b) part I: *J. Am. Chem. Soc.*, **87**, 2824 (1965).

The molecule SiF_2 might act either as an electron donor or acceptor. This would be true if the molecule were in either the triplet or singlet state, since, by analogy with difluorocarbene,⁴ these states are likely to be separated by only a small energy barrier. Thus, it was thought that silicon difluoride should be capable of forming adducts of the type $\text{SiF}_2\text{-Y}$ where Y is a strong Lewis acid like boron trifluoride. Difluorocarbene has not been observed to act in this way, probably because the inductive effect of the fluorine limits the availability of the electron pair, but with silicon ($p \rightarrow d$) π -bonding could in part compensate for this.

In addition to being a possible acid-base reaction, the combination of silicon difluoride and boron trifluoride was of interest for two other reasons. First, the B-F and Si-F bond energies are rather similar so that a compound of type $\text{SiF}_2 \cdot \text{BF}_3$ might readily rearrange to SiF_3BF_2 ; and second, it was hoped that this reaction would provide a convenient route to forming simple compounds containing silicon-boron bonds, only a few of which have previously been described (the most recent being SiBCl_5 by Massey⁵).

Experimental

Silicon difluoride was prepared from silicon and silicon tetrafluoride at 0.1-0.2 mm. pressure and a temperature of 1150° as described elsewhere.³ Boron

(4) F. W. Dalby, *J. Chem. Phys.*, **41**, 2297 (1964).

(5) A. G. Massey and D. S. Urch, *Proc. Chem. Soc.*, 284 (1964).