

value throughout the run. Such errors would lead to internal inconsistencies in data taken at different concentrations and/or current densities. Except in cases where specific adsorption of the electroactive ion is important in determining effective capacitance, these errors could be avoided by calculating a capacitance

at each potential from experimental observation of  $d\epsilon/dt$  at the same charging currents in the absence of the electroactive species.

A subsequent communication will illustrate the application of these results to experimental studies of  $\text{Ag}^+$  in molten  $\text{NaNO}_3$ .

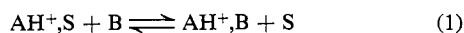
## Ion-Solvent Interaction. The Interaction of a Phosphine Oxide and a Quaternary Ammonium Ion

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Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina. Received April 29, 1965

*The effect of added triphenylphosphine oxide on the conductances of methyltri-*n*-butylammonium perchlorate and iodide in *o*-dichlorobenzene and of the perchlorate in ethylene chloride has been investigated at 25°. The results are interpreted in terms of cation-phosphine oxide complex formation. The addition of the phosphine oxide to the cation lowers the limiting equivalent conductance of the salts 15–17%. Viewing the addition of phosphine oxide to the cation as involving a displacement of a solvating solvent molecule from the cation, the association constants for the complex in the two solvents are used as measures of specific cation-solvent interaction to account for the differences observed for ion-pair dissociation constants in the two almost isodielectric solvents.*

Previous reports<sup>1,2</sup> from this laboratory represented studies of the effects of addends such as amines on the conductances of tertiary ammonium salts in *o*-dichlorobenzene (ODCB) and chlorobenzene. These effects were interpreted in terms of nucleophilic displacement of S by B, from the cation,  $\text{AH}^+$  (eq. 1), where S



represents a solvating solvent molecule and B represents a molecule of addend. We assumed that the limiting equivalent conductance,  $\Lambda_B^0$ , of the hypothetical salt,  $\text{AH}^+\text{B}, \text{X}^-$ , where  $\text{X}^-$  is the corresponding anion, was approximately equal to  $\Lambda_0^0$ , the limiting equivalent conductance of the salt,  $\text{AH}^+\text{X}^-$ , in the solvent in question. This assumption was forced upon us since the salt, tri-*n*-butylammonium picrate typically, was such a weak electrolyte in the solvents used that independent values of limiting equivalent conductances could not be obtained by the usual extrapolation procedures.

The present work was initiated to test the validity of the foregoing assumption. The salts chosen, methyltri-*n*-butylammonium perchlorate and iodide, were selected because they are strong enough electrolytes in ethylene chloride,<sup>3</sup> and thus presumably in ODCB,

that good values of  $\Lambda^0$  can be obtained by extrapolation. The addend, triphenylphosphine oxide (TPPO), was chosen by trial. The amines used in prior work had little or no effect on the conductance of the fully quaternized salt. A clue pointing to the associating capabilities of phosphoryl compounds was furnished principally by the observation of Elliott and Fuoss<sup>4</sup> that in tricresyl phosphate as solvent, the ion-pair dissociation constant of tri-*n*-butylammonium picrate was almost as large as that for the tetrasalt. Further, similar compounds are used extensively as solvent extraction agents for salts and acids,<sup>5</sup> presumably through strong interaction of the phosphoryl oxygen group and the cation.

Our choice of ODCB and ethylene chloride (EC) as solvents was based on prior work<sup>1,2</sup> in these media in this laboratory.

### Experimental

Methyltri-*n*-butylammonium perchlorate was prepared from the iodide by metathesis with silver perchlorate in alcohol solution. The product was recrystallized from alcohol, m.p. 169° (lit.<sup>3</sup> m.p. 159°). The salt was dried *in vacuo* at room temperature for 24 hr. prior to use. The iodide was prepared as previously.<sup>1</sup> Triphenylphosphine oxide (Columbia Organic Chemicals Co.) was dissolved in benzene, extracted with aqueous sodium bicarbonate, and washed with distilled water. The benzene was evaporated and the recovered TPPO was recrystallized from a benzene-hexane mixture. The TPPO was dried *in vacuo* at 90° for 24 hr., m.p. 154–155°. ODCB (Allied Chemical Co., Solvay Process Division) and EC (Columbia Organic Chemicals Co.) were treated as described previously.<sup>1</sup> The specific conductance of the ODCB was  $1-2 \times 10^{-11}$  mho/cm., while that of EC was  $1 \times 10^{-10}$  mho/cm. The conductance bridge, cells, and experimental procedure have been described elsewhere.<sup>1</sup> All measurements were carried out at 25.00°.

(1) E. K. Ralph, III, and W. R. Gilkerson, *J. Am. Chem. Soc.*, **86**, 4783 (1964).

(2) W. R. Gilkerson and E. K. Ralph, III, *ibid.*, **87**, 175 (1965).

(3) L. F. Gleysteen and C. A. Kraus, *ibid.*, **69**, 451 (1947).

(4) M. A. Elliott and R. M. Fuoss, *ibid.*, **61**, 294 (1939).

(5) See R. M. Diamond and D. G. Tuck in "Progress in Inorganic Chemistry," Vol. 2, F. A. Cotton, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 171 ff.

## Results

The effects of added TPPO on the density, viscosity, and dielectric constant of ODCB and on the dielectric constant of EC appear in Figure 1. The partial molar volume of TPPO in ODCB, calculated from the slope of the  $d$  vs.  $C$  curve, is 230 cc. This compares well with the value 235 cc., which one obtains from similar data in *p*-xylene.<sup>6</sup> The dielectric incre-

**Table I.** Equivalent Conductances with and without Added TPPO at 25°

| $10^5 C$                                    | $\Lambda$ | $10^5 C$        | $\Lambda$ |
|---|-----------|-----------------|-----------|
| Bu <sub>3</sub> MeNClO <sub>4</sub> in ODCB |           |                 |           |
| 0.957                                       | 23.25     | 1.676           | 19.26     |
| 1.633                                       | 19.55     | 2.691           | 16.27     |
| 2.546                                       | 16.70     | 3.962           | 14.06     |
| 3.427                                       | 14.94     | 5.183           | 12.65     |
| 4.347                                       | 13.63     | 6.638           | 11.46     |
| 5.432                                       | 12.49     | 7.734           | 10.77     |
| 6.853                                       | 11.37     | 8.950           | 10.14     |
| 8.011                                       | 10.67     | 10.273          | 9.58      |
| +0.01357 M TPPO                             |           | +0.02698 M TPPO |           |
| 1.486                                       | 21.98     | 0.863           | 26.70     |
| 2.721                                       | 18.05     | 1.644           | 22.56     |
| 4.162                                       | 15.53     | 2.627           | 19.56     |
| 5.346                                       | 14.15     | 3.603           | 17.63     |
| 6.765                                       | 12.93     | 4.568           | 16.24     |
| 8.217                                       | 11.99     | 5.678           | 15.02     |
| 9.466                                       | 11.34     |                 |           |
| 10.647                                      | 10.82     |                 |           |
| Bu <sub>3</sub> MeNI in ODCB                |           |                 |           |
|   |           | +0.01208 M TPPO |           |
| 1.545                                       | 14.53     | 1.462           | 16.47     |
| 3.359                                       | 10.66     | 3.323           | 12.08     |
| 4.900                                       | 9.103     | 4.948           | 10.28     |
| 7.134                                       | 7.749     | 6.728           | 9.055     |
| 9.926                                       | 6.713     | 10.33           | 7.551     |
| 13.02                                       | 5.958     | 12.58           | 6.939     |
| 17.48                                       | 5.231     | 15.13           | 6.409     |
| +0.01878 M TPPO                             |           | +0.03062 M TPPO |           |
| 1.655                                       | 16.32     | 1.385           | 18.51     |
| 3.498                                       | 12.37     | 3.002           | 14.17     |
| 5.319                                       | 10.47     | 5.028           | 11.64     |
| 7.162                                       | 9.272     | 6.590           | 10.46     |
| 10.23                                       | 7.984     | 8.863           | 9.268     |
| 13.63                                       | 7.069     | 11.69           | 8.267     |
| 18.50                                       | 6.201     | 14.93           | 7.462     |
| Bu <sub>3</sub> MeNClO <sub>4</sub> in EC   |           |                 |           |
|   |           | +0.01407 M TPPO |           |
| 1.686                                       | 57.38     | 1.498           | 57.90     |
| 3.084                                       | 52.92     | 3.035           | 53.05     |
| 4.621                                       | 49.39     | 4.809           | 49.20     |
| 6.224                                       | 46.59     | 6.529           | 46.41     |
| 7.612                                       | 44.61     | 8.427           | 43.97     |
| 10.12                                       | 41.74     | 10.06           | 42.23     |
| 13.10                                       | 39.15     |                 |           |
| +0.02623 M TPPO                             |           | +0.03440 M TPPO |           |
| 1.594                                       | 57.19     | 1.521           | 56.84     |
| 2.894                                       | 53.32     | 3.746           | 51.00     |
| 4.538                                       | 49.78     | 5.012           | 48.64     |
| 6.262                                       | 46.96     | 7.236           | 45.47     |
| 8.270                                       | 44.36     | 9.248           | 43.22     |
| 10.15                                       | 42.40     | 11.11           | 41.50     |
|   |           | 13.23           | 39.84     |

ments were calculated from capacitance readings on the conductance bridge, obtained in the course of the determination of solvent conductance corrections for

(6) E. Fischer, I. Lauicht, and S. Pinchas, *J. Phys. Chem.*, **66**, 2708 (1962).

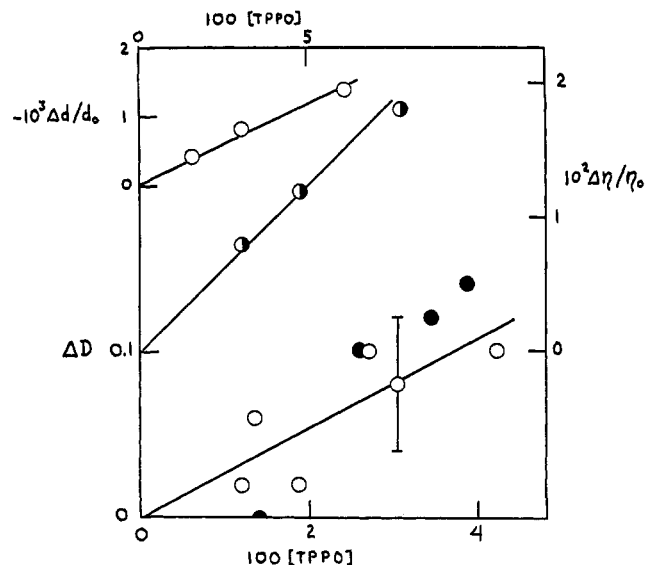


Figure 1. Relative decrease in density of solutions of TPPO in ODCB: upper set of open circles, upper left-hand ordinate, upper abscissa. Relative increase in viscosity of TPPO in ODCB: right half-filled circles, right-hand ordinate, upper abscissa. Increase in dielectric constant of TPPO in ODCB (open circles) and EC (closed circles): lower left-hand ordinate, lower abscissa. Uncertainty in  $\Delta D$  is indicated by the height of the error bar.

the TPPO solutions. The air capacity of the cell, 4.91 pf., was too small for precise work. However, the straight line drawn through the points in Figure 1 represents the dielectric increments one calculates using Onsager's equation,<sup>7</sup> a dipole moment of TPPO of 4.4 D.,<sup>6</sup> the same as in *p*-xylene, and a value for atomic plus electronic polarization of 96 cc.<sup>8</sup>

The equivalent conductances,  $\Lambda$ , of the salts at various concentrations (molarities) in the two solvents with and without added TPPO appear in Table I. In each case, the specific conductance of the solvent, 1% or less of the total, was subtracted from the observed specific conductance of the solution to yield the specific conductance presumed due to the salt. The conductance data in each solvent-addend system were treated by the method of Shedlovsky<sup>9</sup>

$$1/(\Lambda S) = 1/\Lambda^0 + \Lambda C S y_{\pm}^2 / K(\Lambda^0)^2$$

where  $S$  is the Shedlovsky function and  $y_{\pm}^2$  is calculated from the Debye-Hückel theory.  $\Lambda_0^0$  is the limiting equivalent conductance in pure solvent, while  $\Lambda_a^0$  will be used to designate those obtained in solvent-TPPO mixtures.  $K_0$  is the ion-pair dissociation constant for salt in pure solvent, while  $K$  is that in the presence of added TPPO. The data were analyzed on an IBM 1620 computer using a program written for us by Dr. S. M. Katz. The physical constants used in the calculations are given in the order ODCB, EC: viscosity (cp.), 1.272,<sup>10</sup> 0.785<sup>11</sup>; density (g./cc.), 1.3007,<sup>1</sup> 1.2455<sup>11</sup>; dielectric constant, 10.06,<sup>12</sup> 10.23.<sup>11</sup>

(7) (a) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936); (b) T. Gammann, *Helv. Chim. Acta*, **41**, 1956 (1958); (c) W. R. Gilkerson and K. K. Srivastava, *J. Phys. Chem.*, **64**, 1458 (1960); **65**, 272 (1961).

(8) G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 146 (1945).

(9) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(10) F. Accascina, E. L. Swartz, P. L. Mercier, and C. A. Kraus, *Proc. Natl. Acad. Sci. U. S. A.*, **39**, 917 (1953).

(11) D. L. Fowler and C. A. Kraus, *J. Am. Chem. Soc.*, **62**, 2237 (1940).

(12) P. H. Flaherty and K. H. Stern, *ibid.*, **80**, 1034 (1958).

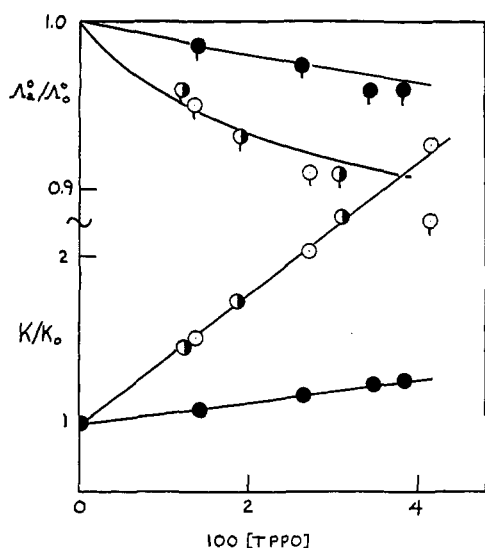


Figure 2. Effect of added TPPO on conductance parameters. Methyltri-*n*-butylammonium perchlorate in ODCB (open circles), in EC (closed circles), and the iodide in ODCB (right half-filled circles). Flagged points represent values of  $\Lambda_a^0/\Lambda_0^0$ .

In pure ODCB at 25°, we find  $\Lambda_0^0$  to be 43.87 for the perchlorate and 42.25 for the iodide.  $K_0$  is found to be  $5.36 \times 10^{-6}$  and  $2.59 \times 10^{-6}$  for these two salts, respectively. These dissociation constants are comparable to those found by Kraus and co-workers<sup>10</sup> for trimethyloctadecylammonium picrate ( $1.9 \times 10^{-6}$ ) and tri-*n*-butyloctadecylammonium iodide ( $6.3 \times 10^{-6}$ ) in ODCB at 25°. In pure EC at 25°, we find  $\Lambda_0^0$  to be 67.55 and  $K_0$  to be  $8.52 \times 10^{-5}$  for the perchlorate. For the same system, Gleysteen and Kraus<sup>3</sup> reported these to be 68.30 and  $8.0 \times 10^{-5}$ , respectively. The conductances of solutions of the iodide in EC changed with time, implying some decomposition, so that further study of this salt-solvent system was abandoned.

The ratios,  $\Lambda_a^0/\Lambda_0^0$  and  $K/K_0$ , are plotted vs. TPPO concentration in Figure 2. The latter plots are observed to be linear. The results for both the iodide and perchlorate salts in ODCB fall on the same line. The limiting equivalent conductances are seen to decrease with increasing TPPO concentration.

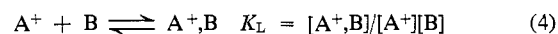
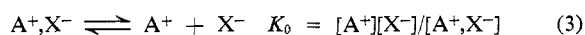
### Discussion

The 2% increase in viscosity of 0.03 *M* TPPO in ODCB (Figure 1) is not enough to account for the 10% decrease in  $\Lambda^0$  for both salts in ODCB at the same concentration of TPPO (Figure 2). The linear increase of the ion-pair dissociation constants with increasing TPPO concentration is far greater than can be reasonably accounted for by the increase in dielectric constant. If the effect of the latter is taken<sup>13,14</sup> to be given by eq. 2, then an apparent distance of closest approach,  $a$ ,

$$\ln K = \text{constant} - z^2 e^2 / akDT \quad (2)$$

is found to be 0.75 Å., an unrealistically small value. Formation of a complex between the highly polar TPPO molecule and the cation,  $\text{Bu}_3\text{MeN}^+$ , can explain both the decrease in  $\Lambda_a^0$  and the increase in  $K$ . Equilibrium

4 would then be added to the usual ion-pair dissociation equilibrium 3 where  $\text{A}^+$  represents the methyltri-*n*-



butylammonium cation,  $\text{X}^-$  represents the anion, perchlorate or iodide, B represents the TPPO molecule, and  $\text{A}^+, \text{B}$  represents the cation-TPPO complex. It has been shown<sup>15</sup> that the conductance in such a case should follow the form of eq. 2, but with the apparent limiting equivalent conductance being given by

$$\Lambda_a^0 = \Lambda_0^0(1 + \Lambda_B^0 K_L [\text{B}]/\Lambda_0^0)/(1 + K_L [\text{B}]) \quad (5)$$

and the apparent dissociation constant by

$$K = K_0(1 + K_L [\text{B}]) \quad (6)$$

From the slope of the plot of  $K/K_0$  vs. [TPPO] in Figure 2, we find  $K_L$  to be 39.0 in ODCB and 6.8 in EC.

Equation 5 may be rearranged to give

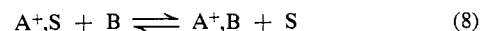
$$\Lambda_a^0 K/K_0 = \Lambda_0^0 + \Lambda_B^0 K_L [\text{B}] \quad (7)$$

so that from a plot of  $\Lambda_a^0 K/K_0$  vs. [TPPO], we obtain values of  $\Lambda_B^0$  of 37.1 for the perchlorate and 35.7 for the iodide in ODCB and 56.0 for the perchlorate in EC. These values of  $\Lambda_B^0$  and  $K_L$  were used to calculate the points through which the smooth curves were drawn in Figure 2.

The values of  $\Lambda_B^0$  for the complexed salts are seen to be some 15% lower than  $\Lambda^0$  for the uncomplexed salts in ODCB, while that in EC is 17% lower. The TPPO molecule is so bulky that one would expect the drag it exerts on a cation to which it is attached to be greater than that for, say, a pyridine molecule. We thus conclude that the ratio  $\Lambda_B^0/\Lambda_0^0$  is unity within 10% for the systems  $\text{Bu}_3\text{NHX}$ -pyridine, -tributylamine, -acetonitrile, etc., and that our prior assumption of this was correct within experimental error.

Replacement of the hydrogen atom by a methyl group, in going from the tri-*n*-butylammonium ion to the methyltri-*n*-butylammonium ion, results in an increase in the distance of closest approach of the negative end of the dipolar ligand to the positive nitrogen in the cation as well as eliminating the possibility of hydrogen bonding contributing to the stability of the complex. The ligand association constants for TPPO with the methyltri-*n*-butylammonium cation in ODCB are of respectable magnitude, in view of the foregoing, when compared to the tri-*n*-butylammonium-acetonitrile system in ODCB.  $K_L$  for the latter was found<sup>1</sup> to be 212. We have, in TPPO complex formation, an unambiguous case of ion-dipole interaction such as Fuoss and D'Aprano<sup>16</sup> discussed in connection with observations of decreases of the order of 1% in the conductances of quaternary ammonium bromides in acetonitrile in the presence of 0.008 *M* *p*-nitroaniline.

The interaction of TPPO and the cation may profitably be viewed<sup>1,16</sup> as a displacement of at least one solvating solvent molecule, S, from the cation,  $\text{A}^+$ , by the incoming TPPO molecule, represented by B in eq. 8. Inspection of the values of  $K_L$  in the two sol-



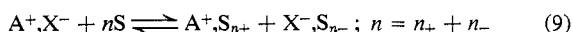
(13) H. Y. Inami, H. K. Bodenseh, and J. B. Ramsey, *J. Am. Chem. Soc.*, **83**, 4745 (1961).

(14) R. M. Fuoss, *Proc. Natl. Acad. Sci. U. S. A.*, **45**, 807 (1959).

(15) See eq. 9 of ref. 1.

(16) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **67**, 1722 (1963).

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 Miller<sup>17</sup> 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 found<sup>1</sup> to be 71, while that for the tetra-*n*-butylammonium picrate has been reported<sup>10</sup> as 13.2. The ratio for tetra-*n*-butylammonium nitrate is<sup>10</sup> 25.6.

Ramsey and co-workers<sup>13</sup> 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 leads<sup>1</sup> 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 recently<sup>18</sup> 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 Phosphorus<sup>1</sup>

H. S. Gutowsky and John Larmann<sup>2</sup>

*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  $^{31}\text{P}$  shifts ob-*

*served in  $\text{PH}_3$ ,  $\text{P}(\text{CH}_3)_3$ , 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.