Evaluation of the Basicity of Phosphine Oxides and Phosphine Sulfides by Measurements of Chemical Shift in Sulfuric Acid Solutions[1]

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Abstract: The pK_{BH^+} values of $(CH_3)_2PO_2H$, $CH_3P(O)(OCH_3)_2$, $(C_6H_5)_2P(O)CH_3$, $C_6H_5P(O)(CH_3)_2$, $(C_6H_5)_2P(S)CH_3$, $C_6H_5P(S)(CH_3)_2$, and $(CH_3)_2PS_2H$ have been determined by measurements of chemical shift of methyl groups bonded to phosphorus as a function of sulfuric acid concentration. The data indicate considerable π bonding in PS and PO bonds. Phosphine oxides are about 10^6 less basic than amine oxides, arsine oxides, and stibine oxides. Previous reports of the basicity of phosphine oxides are misleading. The method used here has been validated by study of acetophenone and N,N-dimethylacetamide; pK's of these compounds are known from other methods.

There has been considerable interest in the nature of the P–O bond in phosphine oxides especially in regard to the role of d orbitals in π bonding.[3] Bond energies,[4] bond lengths,[3,5] infrared spectra,[3,7] C^{13}–H coupling constants,[8] and hydrogen bonding[9] all indicate considerable P–O π bonding in phosphine oxides. The N–O bond in trimethylamine oxide, on the other hand, appears to be a single bond.[3,8]

There has been little work on the basicity of phosphine oxides and sulfides, and this might be expected to give indications concerning P–O and P–S bonding in both neutral and protonated forms. N Oxides are sufficiently basic to be measured by potentiometric titration; the pK_{BH^+}[10] of $(CH_3)_3NO$ is 4.7.[11] The pK_{BH^+} of $(CH_3)_3PO$ has been listed in a table as 0,[11] but this was on the basis of titration and evaluation of its effect on HBr-catalyzed hydrolysis of methyl acetate which indicated basicity immeasurably small by these techniques. This estimate for the basicity of $(CH_3)_3PO$ has been quoted in a review on the base strength of weak organic bases.[12] By measurements of proton chemical shifts as a function of sulfuric acid concentrations, we had determined the basicity of a phosphinic acid, $(CH_3)_2PO_2H$, and a phosphinate ester, $(C_6H_5)_2PO_2CH_3$,

in connection with a study of the acid-catalyzed hydrolysis of phosphinates.[13] We have now confirmed the validity of this method and studied a more complete set of compounds which may be classed as phosphine oxides and sulfides.

Results

In the compounds studied, chemical shifts for CH_3 hydrogens were measured relative to $(CH_3)_3N^+H$; a sample plot of the data for dimethylphenylphosphine oxide is shown in Figure 1. Trimethylammonium ion was used as a standard to minimize changes in chemical shifts due only to changes in solvation. The large solvation effects should be in the media with high $[H_2SO_4]$ where most or all of the water will be involved in solvating protons. This would probably decrease solvation of the protonated phosphine oxide and lead to a change in chemical shift relative to an uncharged and/or unprotonated standard. By using $(CH_3)_3N^+H$ as a standard we should minimize this problem, since both BH^+ and $(CH_3)_3N^+H$ have one acidic hydrogen for interaction with solvent and solvation effects should, therefore, be similar.

The data are plotted against the H_0 scale[14] since this is a scale conveniently available as a standard. Although there are problems with the H_0 scale based on primary anilines serving as a measure of acidity when studying other bases or substrates,[13] this can be considered by use of eq 1[15] where the M value is a measure

$$\log [BH^+]/[B] = M(pK_{BH^+} - H_0) \qquad (1)$$

of the protonation behavior of B relative to Hammett bases (primary anilines).[17] If $M = 1$, B is a Hammett

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(3) For a recent summary see (a) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter 3. See also (b) R. F. Hudson, *Pure Appl. Chem.*, **9**, 371 (1964); (c) L. Larsson, *Svensk Kem. Tidskr.*, **71**, 336 (1959).

(4) S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole, and J. C. McCoubrey, *Quart. Rev.* (London), **17**, 204 (1963).

(5) A recent, accurate determination [H. K. Wang, *Acta Chem. Scand.*, **19**, 879 (1965)] of the P–O bond length in trimethylphosphine oxide, r(P–O) = 1.48 A, can be compared with the sum of single bond covalent radii[6] P + O = 1.10 + 0.66 = 1.76 A.

(6) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 224.

(7) (a) E. A. Robinson, *Can. J. Chem.*, **41**, 3021 (1963); (b) H. Gerding, J. W. Maarsen, and D. H. Zijp, *Rec. Trav. Chem.*, **77**, 361 (1958).

(8) P. Haake, W. B. Miller, and D. A. Tyssee, *J. Am. Chem. Soc.*, **86**, 3577 (1964).

(9) (a) T. Kubota, *ibid.*, **88**, 211 (1966); (b) G. Aksnes, *Acta Chem. Scand.*, **14**, 1475 (1960).

(10) We use the symbol pK_{BH^+} rather than pK_a for clarity; pK_{BH^+} specifically refers to the equilibrium $BH^+ \rightleftharpoons B + H^+$, but pK_a also could refer to $HA \rightleftharpoons H^+ + A^-$ since the protons of the methyl groups of $(CH_3)_3PO$ and $(CH_3)_3NO$ should be somewhat acidic.

(11) P. Nylen, *Z. Anorg. Allgem. Chem.*, **246**, 227 (1941).

(12) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 325, 392 (1963).

(13) P. Haake and G. Hurst, *J. Am. Chem. Soc.*, **88**, 2544 (1966).

(14) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter IX. (b) The scale used here is Hammett's with the corrections above 60% H_2SO_4 given by M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963). This scale is internally consistent since it is based on primary anilines and seems to be a reasonable one to adopt as a standard. It appears to be finding general acceptance; see, for example, K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965).

(15) We use eq 1 with M as a measure of the effect of medium relative to the effect on Hammett bases. Other forms of this equation have been used[13,16] with a rather than M, but use of M should lead to less confusion. Equation 1 is discussed in more detail in ref 13.

(16) A. R. Katritzky, A. J. Waring, and K. Yates, *Tetrahedron*, **19**, 465 (1963).

(17) This seems preferable to development of a new scale for each substrate, as has been done: for amides, the H_a scale.[18]

Table I. Acidity Constants and H_0 Dependences for Protonated Phosphine Oxides and Phosphine Sulfides

Compd[a]	H_0 at half-protonation[b]	$\log [BH^+]/[B] = M(pK_{BH^+} - H_0)$		Δ_{BH^+}[d]	Δ_B[d]	No. of pts between 5 and 95% proton-ation[e]
		pK_{BH^+}[c]	M			
Dimethylphosphinic acid (A)	−4.3	−4.07 (−1.25 ± 0.07)	0.308 ± 0.016	119.4	78.6	7
Dimethyl methylphos-phonate (B)	−5.5	−5.22 (−2.48 ± 0.16)	0.475 ± 0.027	48.2	67.6	8
Diphenylmethylphosphine oxide (C)	−3.3	−3.20 (−2.23 ± 0.25)	0.697 ± 0.065	29.2	44.4	7
Dimethylphenylphosphine oxide (D)	−2.2	−2.09 (−0.946 ± 0.063)	0.453 ± 0.023	33.2	55.7	10
Diphenylmethylphosphine sulfide (E)	−4.5	−4.75 (−12.76 ± 5.16)	2.69 ± 0.64	15.0	30.5	3
Dimethylphenylphosphine sulfide (F)	−4.5	−4.58 (−8.31 ± 0.15)	1.82 ± 0.02	18.9	41.6	3
Dimethyldithiophosphinic acid (G)	−5.6	−5.72 (−5.57 ± 2.18)	0.974 ± 0.24	14.2	32.5	3
	−1.1	−1.07 (−1.54 ± 0.07)	1.43 ± 0.05	32.5	44.9	7

[a] Chemical shifts of underlined CH_3 groups were measured. [b] This is equal to pK; from sigmoid graph of Δ against H_0. [c] The values in parentheses are intercepts (and their standard deviations) determined by least squares. [d] Values of chemical shifts are relative to $(CH_3)_3N^+H$; positive indicates upfield shift. [e] This is number of points used to determine M and pK_{BH^+} by least squares on eq 2. More data were obtained and used to get H_0 at half-protonation, Δ_B, and Δ_{BH^+}.

base.[13] All the data we obtained could be plotted according to eq 1 and gave straight lines, from which M and pK_{BH^+} values could be obtained: M = slope, pK_{BH^+} = intercept/M.

A, R = R′ = CH_3; R″ = OH E, R = R′ = C_6H_5; R″ = CH_3
B, R = CH_3; R′ = R″ = OCH_3 F, R = C_6H_5; R′ = R″ = CH_3
C, R = R′ = C_6H_5; R″ = CH_3 G, R = R′ = CH_3; R″ = SH
D, R = C_6H_5; R′ = R″ = CH_3

The pK_a's can also be obtained by evaluation of the point where [BH$^+$] = [B]. This is the halfway point on the sigmoid curves (e.g., Figure 1), i.e., the point where Δ = (Δ_B + Δ_{BH^+})/2. Table I gives all our data for phosphine oxides including pK's determined by this method and pK and M values from a least-squares calculation using eq 1. The chemical shifts found for B and BH$^+$ relative to $(CH_3)_3N^+H$ are also given in Table I. It can be seen that (Δ_B − Δ_{BH^+}) is large enough to give reliable results. Determination of pK's by either method depends on the values of these chemical shifts, but it turns out that application of eq 1 to determination of pK's is not as sensitive to slope as one might expect from the fact that the pK is determined by the intercept. Since a lowering of slope lowers the absolute value of the intercept (the intercepts in these plots are negative), there is a compensating effect since pK = intercept/slope. Consequently, although some standard deviations are large in Table I, the pK_{BH^+} values from eq 1 and from half-protonation agree well. The larger standard deviations come from those compounds where only a few points were obtained between 5 and 95% protonation due to a steep dependence of protonation on H_0, which results in a high M value.

Another argument for standard use of the H_0 scale in studies of basicity relates to the M values. It seems

likely that these M values may be quite useful in evaluation of solvation effects on the protonation of weak bases when there is a large enough body of these data available.
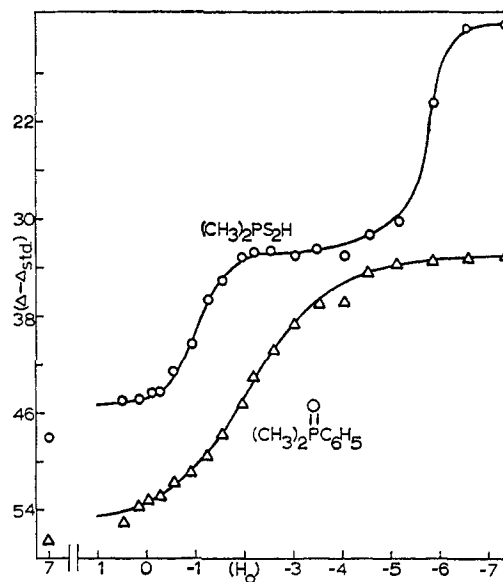

Figure 1. Dependence of chemical shift of methyl groups of dimethylphenylphosphine oxide and dimethyldithiophosphinic acid on H_0 in aqueous sulfuric acid.

Perhaps the most important question in this study has to do with the reliability of this method. Despite the use of $(CH_3)_3N^+H$ as a standard it could be argued that all the data observed here could be largely medium effects so that the apparent titration curves observed (e.g., Figure 1) could have little relation to basicity. We have several pieces of evidence which refute this line of devil's advocacy. First, we used this method to determine the pK values for N,N-dimethylacetamide (H) and acetophenone (I); the chemical shifts of the

(18) K. Yates, J. Stevens, and A. R. Katritzky, Can. J. Chem., 42, 1957 (1964).

Table II. Basicity of N,N-Dimethylacetamide and Acetophenone by Nmr and Other Methods

Compound	H_0 at half-protonation	Nmr pK_{BH^+}[a]	Nmr M[a]	Nmr Δ_B[b]	Nmr Δ_{BH^+}[b]	Lit. pK_{BH^+}	No. of p between 5 and 95% protonation
$CH_3CON(CH_3)_2$	−0.34	−0.39 (−0.376 ± 0.049)	0.97 ±0.04	48.1	28.0	−0.19[c]	9
$CH_3COC_6H_5$	−6.45	−6.51 (−3.37 ± 0.39)	0.52 ± 0.05	21.6	−14.8	−6.45[d]	5

[a] By least squares using log $([BH^+]/[B]) = M(pK − H_0)$. Values in parentheses under pK_{BH^+} are the values of the intercepts and their standard deviations as determined by least squares. The ± values under M are standard deviations of the slope by the same method. [b] Chemical shift in cps from the methyl hydrogens of $(CH_3)_3N^+H$. [c] Reference 12. [d] K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965).

underlined methyl groups were evaluated as a function of acidity. The pK_{BH^+} values obtained by the nmr method are in good agreement with those previously observed (Table II). Secondly, dimethyl sulfone is known to be very weakly basic and is only partially protonated in concentrated sulfuric acid.[12,19] We observe no titration curve of chemical shifts for dimethyl sulfone in the region of acidity where titration curves are observed for the compounds in Table I. Finally, we have studied trimethylamine oxide (J) by this method. This amine oxide has a pK in the range

H   I   J
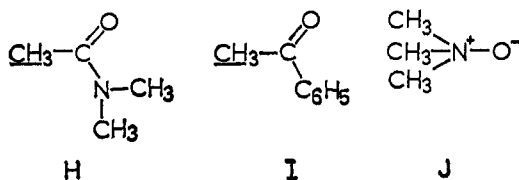
measurable by potentiometric methods: $pK_{BH^+} = 4.65$.[11] We find less than 3-cps change in chemical shift between $H_0 = 0$ and $H_0 = −7$ for this compound. Since protonation of J is essentially complete throughout this range, this result further supports the validity of our method.

Two pK values are listed in Table I for dimethyldithiophosphinic acid, $(CH_3)_2PS_2H$. The titration cruve for this compound is shown in Figure 1; two inflections are clearly present. These are probably due to: (1) protonation of the anion, $H^+ + Me_2PS_2^- \rightleftharpoons Me_2PS_2H$, $pK_{AH} = −1.07$; (2) protonation of the acid, $H^+ + Me_2PS_2H \rightleftharpoons (CH_3)_2PS_2H_2^+$, $pK_{BH^+} = −5.72$. The pK_{AH} is inconsistent with the results of Kabachnik, *et al.*,[20] on other dithiophosphinic acids. The pK_{AH} values they found by potentiometric titration might be in error due to problems with false pK's of strong acids.[21] Alternatively, the two inflection points we observed here could be due to (1) protonation of the neutral acid and (2) another phenomenon. Since $(CH_3)_2PO_2H$ is about 1 to 2 powers of 10 less basic than phosphine oxides and phosphine sulfides have $pK_{BH^+} = −4.5$, it does seem very likely that pK_{BH^+} is −5.6 for $(CH_3)_2PS_2H$. It then is difficult to attribute $pK = −1.1$ to anything other than $(CH_3)_2PS_2H \rightleftharpoons (CH_3)_2PS_2^- + H^+$.

Discussion

Basicity of Phosphine Oxides. The pK_{BH^+} of trimethylphosphine oxide was reported[11,12] as 0; on the basis of our results (Table I), it seems likely that this is in error. Certainly phosphine oxides (K) are generally protonated (eq 2) to only a small extent in 1 M acid.

$$\text{>P=O+H}^+ \rightleftharpoons \text{>P}^{\pm}\text{OH} \qquad (2)$$

K   L

The basicities we have measured for phosphine oxides are compared with other oxides in Table III. Therefore, in basicity phosphine oxides resemble carbonyl

Table III. Comparison of Basicities of Some Oxides

Compound	pK_{BH^+}
$CH_3C(O)C_6H_5$	−6.5[a,b]
$(CH_3)_3NO$	4.7[c]
$(CH_3)_2P(O)C_6H_5$	−2.4[b]
$CH_3P(O)(C_6H_5)_2$	−3.2[b]
$(CH_3)_3AsO$	3.8[c]
$(CH_3)_3SbO$	5.4[c]

[a] Footnote d, Table II. [b] This work. [c] Reference 11.

compounds more than the oxides of other group Va elements; the oxides of nitrogen, arsenic, and antimony are 10^6–10^8 times more basic than phosphine oxides. Amine oxides can have no N–O π bonding, and carbonyl groups are known to have considerable double bond character.

Although C and D do not have C_{3v} symmetry, it is probable that these phosphine oxides have two nearly equivalent π orbitals[3a,22] so that K might be better written as $\text{>P}{\stackrel{\cdot\cdot}{=}}\text{O}$. The short P=O bond length[6] and the radial density distributions of the phosphorus and oxygen orbitals probably contribute to the strength of π bonding in K.[25] The longer As–O and Sb–O bonds would cause weaker π bonding in arsine and stibine oxides.

(22) The interaction of the phenyl substituents with the P–O π system is probably small since there is little difference in the length of $C(sp^2)$–P and $C(sp^3)$–P bonds.[23] Therefore, in C and D there should be little perturbation of a symmetrical π(P–O) system with two π orbitals.

(23) In $(CH_3)_3PO$, r(P–C) = 1.81 A;[6] in $(C_6H_5)_2PO_2H$, r(P–C) = 1.81 A.[24]

(24) T-T. Liang and K-C. Chi, *Acta Chim. Sinica*, **31** (2), 155 (1965).

(25) Related discussions of d–p π bonding: D. W. J. Cruickshank, *J. Chem. Soc.*, 5846 (1961); D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *ibid.*, 332 (1954). The simple view of π bonding in K and L would involve d–p, P–O overlap. However, to mention two possible perturbations, there might be mixing of phosphorus orbitals resulting in stronger π and/or σ bonds and π bonding involving hybrid oxygen orbitals, such as sp^2, would be possible.
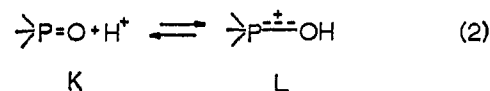
(19) R. J. Gillespie and J. A. Leisten, *Quart. Rev.* (London), **8**, 40 (1954).

(20) M. I. Kabachnik, T. A. Mastrukova, A. E. Shipov, and T. A. Melentyeva, *Tetrahedron*, **9**, 10 (1960).

(21) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962.

There have been no structural reports on a protonated (L) or alkylated phosphine oxide, but the structures of several phosphate esters are known and indicate $r(P-OR) \sim 1.55$ A and $\angle(POR) \sim 120°$.[26] Using these parameters, a reasonable model for the structure of L would involve an sp^2 oxygen atom. It is impossible to intuitively predict exactly what oxygen orbitals are involved in π bonding in L, but it is clear that the longer P–OR bond length and the use of some oxygen p orbital character in σ bonding should lead to a reduction in P–O π bonding.[25] In addition, the presence of a charge on L and the consequent orbital contractions might be detrimental to strong π bonding.

The large bond energies of P–O bonds in $(CH_3)_3PO$ and $(C_6H_5)_3PO$ (139 and 128 kcal/mole, respectively)[4] are consistent with strong π bonding in K. The bond strength of the P–O bonds of $(CH_3O)_3P$ (91 kcal/mole)[4] indicates the kind of decrease which might be expected on protonation.

Therefore, although many factors can affect pK's, including stability of both acid and basic forms, solvation effects, etc., the large differences in basicity shown in Table III and consideration of bonding and bond energies certainly suggest that π bonding in phosphine oxides makes an important contribution to the structure. On the other hand, it appears that π bonding is quite weak in arsine and stibine oxides.

Substitution of CH_3O or HO for C_6H_5 in phosphine oxides reduces the basicity considerably (Table I). It thus appears that the inductive effect of the CH_3O and HO groups are predominant over resonance effects. In A and B there is probably a more complex π system than in C and D, but resonance effects might be quite different from carboxylates and other systems involving only p orbitals. We assume that in A and B, protonation is on the P=O oxygen, but protonation on the POR oxygen has not been excluded.

Phosphine Sulfides. The difference of basicity of $(CH_3)_2O$ (pK_{BH^+} = −3.8) and $(CH_3)_2S$ (pK_{BH^+} = −5.4)[12] indicates that the differences between phosphine sulfides and phosphine oxides in Table I are due largely to the substitution of sulfur for oxygen. Therefore, P–S π bonding must also be important. However, Hudson has concluded there is less P–S than P–O π bonding,[3a] and our basicity data are only suggestive. Other data related to P–S π bonding are needed.

M Values. The M values for phosphine oxides are all less than 1 by a considerable amount, indicating that these bases are not behaving as Hammett bases. Using the symbols B′ for Hammett base and B for the bases under study[13]

$$\log f_B f_{B'H^+}/f_{BH^+} f_{B'} = (1 - M)(H_0 - pK_{BH^+}) \quad (3)$$

We have previously[13] discussed the relation of a low M value to acid-inhibited hydrolysis of p-nitrophenyl diphenylphosphinate and proposed that an important factor was a decrease in f_B with increasing acidity.[27] The tendency of phosphine oxides to form hydrogen bonds may be an important factor in this effect, and the M values (Table I) can be explained in this framework. The important interaction of a neutral base with sulfuric acid solvent should be by hydrogen bonding. Oxygen should normally form stronger hydrogen

bonds than nitrogen and nitrogen stronger than sulfur. Since the Hammett bases are anilines, the oxygen base should be salted in more strongly and $f_B/f_{B'}$ should decrease for phosphine oxides as acid concentration increases. The sulfur bases should be salted in less strongly than anilines and $f_B/f_{B'}$ should increase with increasing acid concentration. Both of these effects would explain the M values observed. This hypothesis also explains the M values for $(CH_3)_2PO_2H$ and $(CH_3)_2PS_2H$ compared to the other phosphine oxides and phosphine sulfides. These bases have two oxygens or sulfurs which can form hydrogen bonds and therefore ought to show lower M values than $(CH_3)_2$-$P(O)C_6H_5$ and $(CH_3)_2P(S)C_6H_5$, as they do.

Experimental Section

Melting points were taken with a calibrated Mel-Temp block. Analyses were performed by Miss Heather King, UCLA microanalytical laboratory. Nuclear magnetic resonance spectra were taken on a Varian Model A-60 instrument; tetramethylsilane was used as a standard. Infrared spectra were taken on a Perkin-Elmer Model 421 spectrophotometer.

Diphenylmethylphosphine Oxide. The oxide was prepared from diphenylmethylphosphine by oxidation with oxygen. The phosphine was prepared from diphenylchlorophosphine (Columbia Chemical Co.) in ether by addition of methyllithium in ether (Alfa Inorganics Inc.), followed by distillation. The oxide was recrystallized from benzene, mp 109–110° (lit.[28] mp 110–111°). The infrared spectrum in KBr included absorptions at 1430 (aromatic) and 1293 cm^{-1} (P=O). The nmr spectrum shows a doublet at τ 8.0 with J_{PCH} = 13 cps and two multiplets with centers at τ 2.2 and 2.5 integrating as expected.

Anal. Calcd for $C_{13}H_{13}PO$: C, 72.21; H, 6.06. Found: C, 72.30; H, 6.24.

Dimethylphenylphosphine Oxide. This oxide was prepared by oxidation of the corresponding phosphine with oxygen. The phosphine was prepared from phenyldichlorophosphine (Victor Chemical Co.) and methyllithium and purified by distillation. The oxide is very hygroscopic and when very dry melts at 115–119° (lit.[29] 107–110°). The infrared spectrum show absorption at 1430 and 1410 cm^{-1} (aromatic) and 1285 cm^{-1} (P=O). The nmr spectrum in CDCl$_3$ exhibits a doublet at τ 8.22 with J_{PCH} = 13 cps and multiplets at τ 2.47 and 2.2 integrating as expected.

Dimethyl Methylphosphonate. This ester was prepared by treating trimethyl phosphite with methyl iodide. The ester was distilled at 84–89° (34–35 mm) [lit.[30] 71° (13 mm)]. The infrared spectrum shows absorptions at 1245 cm^{-1} (P=O) and 1030 and 1055 cm^{-1} (POC) as well as 1182 cm^{-1}. The nmr shows a doublet at τ 8.55 (area = 1) with J_{PCH} = 17 cps and a doublet at τ 6.33 with J_{POCH} = 11 cps; integrations were in the expected ratio.

Diphenylmethylphosphine Sulfide. This sulfide was prepared by refluxing diphenylchlorophosphine and sulfur in CS$_2$ overnight.[31] The solvent was removed, ether added, and an equimolar amount of methyllithium added to the solution. The sulfide distilled at 183–185° (2 mm) [lit.[32] 181° (1.5 mm)]. The infrared spectrum shows bands at 1410, 1434, and 1478 cm^{-1} (aromatic) and at 619 and 608 cm^{-1} (P=S).[33] The nmr spectrum shows a doublet at τ 7.82 with J_{PCH} = 12 cps and multiplets centered at τ 2.25 and 2.7 with the expected integration.

Dimethylphenylphosphine Sulfide. The corresponding phosphine was treated with sulfur in ethereal solution, the solvent evaporated off, and the product, dimethylphenylphosphine sulfide, was recrystallized from hot water, mp 42–43° (lit.[32] mp 42°). The infrared spectrum includes bands at 1431, 1405, and 1413 cm^{-1} (aromatic) and at 585 cm^{-1} (P=S).[33] The nmr spectrum shows a

(26) J. D. Dunitz and J. S. Rollett, *Acta Cryst.*, 9, 327 (1956).
(27) L. M. Sweeting and K. Yates, *Can. J. Chem.*, 44, 2395 (1966).

(28) (a) C. Seveflos and A. F. Isbell, *J. Org. Chem.*, 27, 2573 (1962); (b) A. Michaelis and H. v. Soden, *Ann.*, 229, 295 (1885).
(29) G. Wittig and U. Schollkopf, *Chem. Ber.*, 87, 1318 (1954).
(30) G. Schrader, unpublished results; K. Sasse, "Methoden der Organischem Chemie (Houben–Weyl)," XII/1, Georg Thieme Verlag, Stuttgardt, 1963, p 270.
(31) Similar to procedure of A. Michaelis, *Ann.*, 181, 335 (1876).
(32) R. A. Zingaro and R. E. McGlothlin, *J. Chem. Eng. Data*, 8, 226 (1963).
(33) R. A. Zingaro, *Inorg. Chem.*, 2, 192 (1963).

doublet at τ 8.1 with J_{PCH} = 13 cps and multiplets at τ 2.15 and 2.52 with the expected integration.

Anal. Calcd for $C_8H_{11}PS$: C, 56.44; H, 6.52. Found: C, 56.28; H, 6.60.

Sodium Dimethyldithiophosphinate. Tetramethylbiphosphine disulfide was treated with an equimolar amount of SO_2Cl_2 to give dimethylthiophosphinyl chloride,[34] bp 50–55° (3 mm) [lit.[34] 82–83° (16 mm)]. The acid chloride was treated with sodium hydrogen sulfide[35] and the sodium salt of the dithio acid recrystallized from benzene–ethanol. The infrared spectrum shows bands at 3300–3400, 1619, 1400 and 1272, 937, 905, 731, and 717 cm⁻¹. The nmr spectrum in D_2O exhibits a doublet at τ 8.01 with J_{PCH} = 13 cps (standard = $(CH_3)_3Si(CH_2)_3SO_3Na$). The preparation of dimethylphosphinic acid has been described.[13]

(34) R. Cölln and G. Schrader, *Chem. Zentr.*, 12696 (1959).

(35) T. A. Mastryukova, A. E. Shipov, and M. E. Kabachnik, *Zh. Obshch. Khim.*, 31, 507 (1961); *Chem. Abstr.*, 55, 22101 (1961).

Measurement of pK's. The solutions were made up as previously described[13] at a concentration of $\sim$10⁻¹ M for both standard and substrate.

Chemical shifts (Δ) were plotted against H_0 (Figure 1) to give approximate pK and M values according to eq 2. The approximate pK can be obtained from the H_0 value at $^1/_2(\Delta_B - \Delta_{BH}{}^+)$. The approximate M value can be obtained graphically or by solution of eq 2 at some point other than H_0 = p$K_{BH}{}^+$. Values of Δ_B and $\Delta_{BH}{}^+$ were then obtained from the smoothed curve of Δ vs. H_0: Δ_B is the Δ at H_0 (0.5% protonation) = p$K_{BH}{}^+$ − 2.3/M, $\Delta_{BH}{}^+$ is the Δ at H_0 (99.5% protonation) = p$K_{BH}{}^+$ + 2.3/M. A least-squares analysis of the data was then done using eq 2 and points between 5 and 95% protonation, *i.e.*, between H_0 = pK ± (1.3/M).

Comparison of Liquid-Phase and Gas-Phase Reactions of Free Radicals[1]

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Abstract: The theoretical and practical effects of gas–liquid phase change on rates and products of free radical reactions are discussed, mostly in terms of ratios of rate constant for competing reactions. Effects of free volumes, concentration changes, solvent cages, and third bodies are now fairly well understood, but when enough competing reactions are involved, the effect of phase change may become complicated. Previous work provides several examples where phase change has, or has not, affected competing free radical reactions and several instances where solvent change has affected competitions. The present survey now suggests that solvation effects are widespread in free radical reactions but often obscured by the necessity of studying them in competing reactions. Solvation effects in the most inert solvents appear to be as far from gas-phase results as they are from solvation effects in the most polar solvents. Thus, comparisons of gas-phase and liquid-phase reactions of free radicals are important in any absolute measure of solvation effects.

During the development of free radical chemistry, the organic and polymer chemists have been concerned mostly with liquid-phase reactions, while physical chemists have been concerned mostly with gas-phase reactions. There has been little effort to correlate the work of the two groups. As considerable data have accumulated on each phase, with little overlap, several related questions arise. To what extent can we predict rates or products in one phase from data in the other? Is there any discernible change in rate constants with phase change? Why do some reactions proceed in both phases while others proceed only in one? Which phase should be chosen for preparative purposes? The object of this paper is to consider some reactions for which data on both phases are available, to deduce some generalizations, and to point out remaining problems. The next two portions of this section consider some theoretical aspects of phase changes, then some generalities about free radical reactions. The following section then reviews experimental data. Conclusions are summarized in the last section.

Theoretical Aspects of Phase Changes. One interesting aspect of phase change is the free-volume effect. When we assume that the activities of the reactants and the activated complex are measured by their vapor pressures and that attractive forces with other molecules are negligible, the partial pressure of each reactant is given by

$$p(v - b) = nRT$$

Here $v - b$ is the corrected volume in the van der Waals equation, corresponding roughly to the free volume of the container not occupied by molecules. When we go from (say) 0.01 M reactant in the gas phase to a 0.01 M solution in benzene at 50°, $v - b$ changes from about 999.7 ml/l. to about 250 ml/l. (assuming that there is no free volume in benzene at 0°K) and the vapor pressure of the reactant, in the absence of all interactions with the solvent, is increased fourfold. We neither find nor expect phase change to have much effect on rates of first-order reactions: although the vapor pressure of the reactant (in the liquid phase) is four times as great, the reactant is present in only one-fourth of the volume. However, for a second-order reaction, the product of the vapor pressures of the reactants is increased 16-fold while the volume is decreased only fourfold, and the