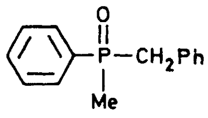
The Acid–Base Behaviour of Phosphoryl and Sulphinyl Groups in Some Organic Bases

By **Ruggero Curci, Arrigo Levi, Vittorio Lucchini,** and **Gianfranco Scorrano,**** Centro C.N.R. di Studio di Meccanismi di Reazioni Organiche, Istituto di Chimica Organica dell'Università, 35100 Padova, Italy

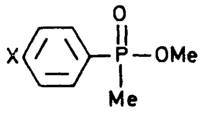
The pK_{BH^+} values of benzylmethylphosphine oxide, methyl methylphenylphosphinate (and its *para*-methyl and *para*-chloro-derivatives), methyl methanesulphinate, and methyl benzyl sulphoxide have been estimated in H_2SO_4 solutions by an n.m.r. technique. It is suggested that the acid–base behaviour of all the compounds studied is described better by the H_A than by the H_0 acidity function. Structural and substituent effects on basicity are discussed. In the case of methyl methylarylphosphinates different pK_{BH^+} values are obtained by following the change with medium acidity of the CH_3 or of OCH_3 proton resonance chemical shifts. A possible source of this discrepancy is suggested.

It is well known [1] that the acid–base behaviour of many organic compounds is now described by adopting separate acidity functions characteristic of a specific group of compounds as for example the acidity functions, H_0 (for primary nitroanilines),[2,3] H_0''' (which holds for tertiary anilines),[4] H_R (for carbonium ions),[5] H_I (for substituted indoles),[6] and H_A (for amides).[7]

On the other hand, Bunnett and Olsen [8] have shown that a general method for estimating the pK_{BH^+} of any base, with reference to a single acidity function H_0, is to plot $\log([BH^+]/[B]) + H_0$ *versus* $H_0 + \log[H^+]$. The slope (ϕ) of such plots is a parameter which measures the response of the equilibrium quotient to changing acid concentration. Since similar values of ϕ are found for amides,[7] pyridine 1-oxides,[9] carbamic esters,[10] αβ-unsaturated carbonyl compounds,[11] and sulphoxides,[12] it was proposed that the H_A acidity scale could be conveniently adopted to describe the acid–base behaviour of all the compounds above. This is not surprising since these substrates, having a basic oxygen atom which is part of a polarized bond, show obvious similarities with amides where at high acidity levels protonation at oxygen has been shown to occur.[3,13]

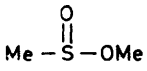


(1)



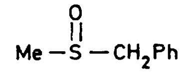
(2)

a, X = H; *b*, X = Me; *c*, X = Cl



$\mathrm{Me-\overset{O}{\overset{\|}{S}}-OMe}$

(3)



$\mathrm{Me-\overset{O}{\overset{\|}{S}}-CH_2Ph}$

(4)

It seemed interesting to us therefore to check whether the same H_A scale could be used to determine the pK_{BH^+} values of some other substrates in which protonation at oxygen is likely to take place. The compounds of choice were methyl benzylphenylphosphine oxide (1), methyl methylphenylphosphinate, and two other phenyl substituted derivatives (2*a*—*c*), and methyl methanesulphinate (3). The pK_{BH^+} of methyl benzyl sulphoxide (4) was also determined.

The pK_{BH^+} values of phosphinates (2*a*—*c*) were also needed in order to interpret kinetic data concerning the hydrolysis of these phosphorus substrates in acidic media.[14]

RESULTS AND DISCUSSION

To measure the pK_{BH^+} values of the compounds shown above, an n.m.r. technique, based upon the change in chemical shifts on varying the medium acidity, was followed. The same technique had been employed to estimate the pK_{BH^+} values of compounds similar to those investigated in this work.[12,15] Chemical shifts of CH_3, OCH_3, or CH_2–Ph protons were measured for compounds (1)—(4) in sulphuric acid solutions ranging from 0·5 to 18M at 25° ± 1°. In all cases Me_3NH^+ was used as internal standard to minimize solvent effects on chemical shifts.[12,15] Details of ^1H n.m.r. spectra of compounds (1)—(4) are given in the Experimental section.

Plots of $\Delta\nu$ *vs.* $-H_0$ gave typical sigmoid curves which were spread over 4—5 H_0 units; this made it possible to obtain $\Delta\nu_B$ and $\Delta\nu_{BH^+}$ values which represent the

---

[1] (*a*) C. H. Rochester, ' Acidity Functions,' Academic Press, New York, N.Y., 1970; (*b*) M. Liler, ' Reaction Mechanisms in Sulphuric Acid,' Academic Press, London, 1971.

[2] L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721, 4239.

[3] M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.

[4] E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, 1964, **86**, 2671.

[5] N. C. Deno, J. J. Jaruzeliki, and A. Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

[6] R. L. Hinman and J. Lang, *J. Amer. Chem. Soc.*, 1964, **86**, 3796.

[7] K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957.

[8] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1899.

[9] C. D. Johnson, A. R. Katritzky, and N. Shakir, *J. Chem. Soc.* (*B*), 1967, 1235.

[10] V. C. Armstrong and R. B. Moodie, *J. Chem. Soc.* (*B*), 1968, 275.

[11] R. I. Zalewski and G. E. Durrn, *Canad. J. Chem.*, 1968, **46**, 2469.

[12] D. Landini, G. Modena, G. Scorrano, and F. Taddei, *J. Amer. Chem. Soc.*, 1969, **91**, 6703.

[13] G. Fraenkel and C. Franconi, *J. Amer. Chem. Soc.*, 1960, **82**, 4478.

[14] D. V. Wells, H. J. Brass, R. Curci, J. F. Bunnett, and J. O. Edwards, unpublished results.

[15] P. Haake and G. Hurst, *J. Amer. Chem. Soc.*, 1966, **88**, 2544; P. Haake, R. D. Cook, and G. H. Hurst, *ibid.*, 1967, **89**, 2650.

chemical shifts for the free and completely protonated base respectively (see Table 1).

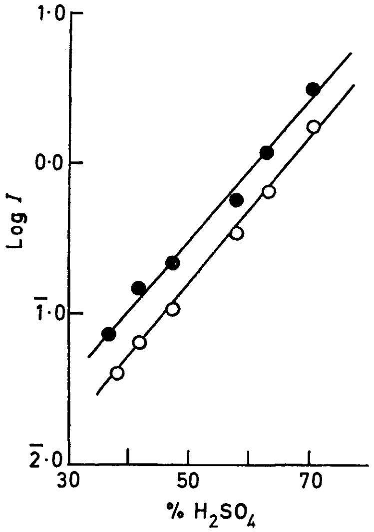
Table 1

Chemical shifts of unprotonated ($\Delta\nu_B$) and protonated ($\Delta\nu_{BH^+}$) compounds (1)—(4) in aqueous sulphuric acid [a]

	Proton resonances observed					
	CH_3		OCH_3		CH_2–Ph	
Compound	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$	$\Delta\nu_B$	$\Delta\nu_{BH^+}$
(1)	94·5	72·0			−57·3	−76·5
(2*a*)	98·2	67·3	−67·5	−90·5		
(2*b*)	101·2	70·3	−65·5	−88·2		
(2*c*)	98·7	66·7	−67·7	−92·5		
(3)	14·0	−31·7 [b]	−82·0 [b]	−112·0 [b]		
(4)	24·1	−8·0			−115·0	−149·5

[a] Values of chemical shifts are in Hz relative to Me_3NH^+ as taken at 90 MHz. [b] Blank values due to rapid hydrolysis of compound (3).

In the case of methyl methanesulphinate (3) $\Delta\nu_B$, $\Delta\nu_{BH^+}$, and $\Delta\nu$ values were only roughly estimated, due to the rapid hydrolysis of this compound.



Log plots of ionization ratios of methyl methyl-(*p*-chlorophenyl)-phosphinate as measured on the basis of CH_3 resonances (full circles) and of OCH_3 resonances chemical shifts (open circles), as a function of percent sulphuric acid

In each case the ionization ratio $I = ([BH^+]/[B])$ could be calculated by measuring chemical shifts ($\Delta\nu$) at intermediate acid concentrations by applying equation (1).

$$I = [BH^+]/[B] = (\Delta\nu_B - \Delta\nu)/(\Delta\nu - \Delta\nu_{BH^+}) \quad (1)$$

For all the compounds investigated plots of log *I vs.* % H_2SO_4 gave satisfactory straight lines. For compounds (1) and (4), at various medium acidities, values of *I* which are identical within the limit of experimental error (±2%) were obtained on measuring chemical shifts of either CH_3 or CH_2–Ph protons. For substituted methyl methylphenylphosphinates, on the other hand, different *I* values, *for the same medium acidity*, were observed on the basis of CH_3 or OCH_3 proton resonances. Inspection of the Figure, clearly reveals that these unexpected differences are quite outside the experimental errors.

For all the compounds investigated, ionization data were treated according to the Bunnett–Olsen equation: [8]

$$\log I + H_0 = \phi(H_0 + \log\,[H^+]) + pK_{BH^+} \quad (2)$$

Straight lines were observed, with ϕ values ranging from 0·47 to 0·67 (see Table 2). The ϕ values found in the case of amides lie between +0·42 and +0·55.[8] Therefore, it is apparent that the acidity scale for amides (H_A) can be adopted to describe the protonation equilibrium of the compounds investigated. In fact, plots of log *I vs.* $-H_A$ also give straight lines with slopes from 0·8 to 1·0 (Table 3); these plots allow one to evaluate the H_A values at half-protonation $(H_A)_{\frac{1}{2}}$ which appear in Table 3. These differ from pK_{BH^+} values summarized in Table 2 by some 0·3—0·8 H_A units. The reasons for these discrepancies are well understood, namely pK_{BH^+} values are estimated as the intercepts of equation (2) and this assumes linearity all the way to infinite dilution in water.[8] Furthermore, it is recognized that the H_A function is itself too negative by *ca.* 0·3 units.[8]

Table 2

pK_{BH^+} and ϕ Values [equation (2)] for equilibrium protonation in sulphuric acid solutions

	Proton resonances observed [a]					
	CH_3		OCH_3		CH_2–Ph	
Compound	ϕ	pK_{BH^+}	ϕ	pK_{BH^+}	ϕ	pK_{BH^+}
(1)	0·58	−1·57			0·49	−1·67
(2*a*)	0·58	−2·51	0·57	−2·80		
(2*b*)	0·63	−2·17	0·67	−2·30		
(2*c*)	0·65	−2·32	0·60	−2·73		
(4)	0·48	−1·98			0·47	−2·00

[a] Correlation coefficients better than 0·99 are obtained in each case.

Table 3

Slopes and H_A at half-protonation $(H_A)_{\frac{1}{2}}$ values from plots of log *I vs.* $-H_A$

	Proton resonances observed [a]					
	CH_3		OCH_3		CH_2–Ph	
Compd.	Slope	$-(H_A)_{\frac{1}{2}}$	Slope	$-(H_A)_{\frac{1}{2}}$	Slope	$-(H_A)_{\frac{1}{2}}$
(1)	0·88	2·07			1·01	2·00
(2*a*)	0·92	3·11	0·94	3·40		
(2*b*)	0·83	2·94	0·76	3·28		
(2*c*)	0·80	3·17	0·88	3·66		
(3)		4·05 [b]		3·90 [b]		
(4)	1·03	2·28			1·05	2·28

[a] See Table 2. [b] Roughly estimated from $\Delta\nu$ *vs.* $-H_A$ sigmoid plots.

In any case, it is significant that the larger discrepancies among pK_{BH^+} values and $(H_A)_{\frac{1}{2}}$ were encountered for compounds (2*a*—*c*), which show less-than-unit slopes in plots of log *I vs.* $-H_A$ (Table 3). On the other hand, H_A was found to be the acidity function best suited to analyse kinetic data concerning the hydrolysis of the same organophosphorus substrates in acidic media.[14]

On comparing compound (2*a*) with (1*a*) a significant decrease in the $(H_A)_{\frac{1}{2}}$ or pK_{BH^+} value is observed; this is expected due to the greater electron-withdrawing effect of OMe when compared to CH_2Ph. A similar decrease in basicity is found in the series of organosulphur compounds on passing from (3) to (4); it should be noted, however, that precise estimation of this decrease is precluded here in view of the experimental difficulties encountered in the determination of $(H_A)_{\frac{1}{2}}$ or pK_{BH^+} of compound (3).

In the series of methyl methylphenylphosphinates (2*a*—*c*), the pK_{BH^+} values found (Table 2) suggest that—similar to that observed for aryl-substituted methyl phenyl sulphoxides [12]—a rather small substituent effect is operative.

It is also interesting to compare the basicities of compound (1) with (4), and (2*a*) with (3). Indeed, the organosulphur compounds appear to be half-protonated in media significantly more acidic (by *ca.* 0·2—0·6 H_A units), and this in spite of the presence of an extra electron-withdrawing group such as Ph, which is linked to the heteroatom in the organophosphorus compounds.

Another point which deserves further comment is that values of pK_{BH^+} which are different by about 0·3 units on the H_A scale are obtained on measuring the CH_3 or OCH_3 proton chemical shifts in compounds (2*a*—*c*) (see Tables 2 and 3). At the present time we can offer no straightforward explanation of this unexpected phenomenon.

A reasonable guess, however, would be that such a difference is due to the choice of the internal standard. In fact, Me_3NH^+ is likely to be a reliable internal standard to balance solvent effects on chemical shifts of CH_3 groups directly bonded to the P=O or S=O groups undergoing protonation. This, however, might not be true for OCH_3 chemical shifts where the methyl group is separated from the central heteroatom by a basic oxygen.

This finding calls for renewed attention in evaluating protonation ratios and pK_{BH^+} by the n.m.r. method.

EXPERIMENTAL

Materials.—The ^1H n.m.r. spectra were taken in $CDCl_3$, with Me_4Si as internal standard, on a Bruker HFX-10 spectrometer at 90 MHz.

Benzylmethylphenylphosphine Oxide.—Compound (1) was prepared by treating methylphenylphosphinyl chloride [16] with benzylmagnesium chloride in dry Et_2O. Crude compound (1) was recrystallized from ligroin and purified by column chromatography (silica gel with acetone as eluant); m.p. 148—148·5° [lit.,[17] m.p. 148—149°]; δ 1·74 (CH_3, d, J_{PCH} 12·1 Hz), 3·30 (CH_2Ph, doublet of poorly resolved quadruplets, apparent A_2 spin system, J_{PCH} 14·5 Hz), and 7·24—7·85 p.p.m. (Ar*H*, m).

Methyl Methylarylphosphinates.—Compounds (2*a*—*c*) were obtained by following the general procedure described by Mislow *et al.*[18] starting with the appropriate aryldichlorophosphines.[19,20] Crude methyl methylarylphosphinates were purified by several vacuum fractional distillations; *methyl methylphenylphosphinate* (2*a*): b.p. 94—95° (0·05 mm) [lit.,[21] 119° (3·5 mm)]; δ 1·67 (CH_3, d, J_{PCH} 14·6 Hz), 3·61 (OCH_3, d, J_{POCH} 11·1 Hz), and 7·45—7·92 p.p.m. (Ar*H*, m); *methyl methyl-*(p*-chlorophenyl*)*phosphinate* (2*c*): b.p. 103—104° (0·15 mm); δ 1·67 (CH_3, d, J_{PCH} 14·5 Hz), 3·62 (OCH_3, d, J_{POCH} 11·5 Hz), and 7·24—7·85 p.p.m. (Ar*H*, m); *methyl methyl-*(p*-tolyl*)*phosphinate* (2*b*): b.p. 89—90° (0·1 mm); δ 1·65 (CH_3, d, J_{POH} 14·6 Hz), 2·41 ($ArCH_3$, s), 3·59 (OCH_3, d, J_{POCH} 11·2 Hz), and 7·24—7·80 p.p.m. (Ar*H*, m).

Methyl Methanesulphinate.—Compound (3) was prepared by reaction of methanesulphinyl chloride [22] with MeOH in dry Et_2O in the presence of quinoline, as reported by Modena *et al.*; [23] it was purified by distillation: b.p. 61° (40 mm); [23] δ 2·63 (CH_3, s) and 3·77 p.p.m. (OCH_3, s).

Benzyl Methyl Sulphoxide.—Compound (4) was obtained upon oxidation of the corresponding sulphide [24] with H_2O in MeOH (in the presence of catalytic amounts of $HClO_4$).[25] Crude compound (4) was distilled [lit.,[26] 116—118° (0·8 mm)] and further purified by column chromatography [silica gel; eluant, light petroleum (b.p. 30—50°)–Et_2O]; δ 2·44 (CH_3, s), 4·03 and 3·92 (CH_2, AB quartet, J_{AB} 12·8 Hz), and 7·22—7·42 p.p.m. (Ar*H*, m).

Trimethylamine and sulphuric acid were AnalaR grade commercial products.

Measurements of $(H_A)_{\frac{1}{2}}$ *and* pK_{BH^+} *Values.*—Sulphuric acid solutions were prepared by dilution and titrated with standard aqueous NaOH solutions. The H_0 and H_A values were evaluated by interpolation of data available in the literature.[7,27] The ^1H n.m.r. spectra of compounds (1)—(4) in sulphuric acid solutions were recorded on a Bruker HFX-10 instrument at 90 MHz with Me_3N as internal standard and internal lock on the acid–water band. Chemical shifts were read to ±0·1 Hz with a counter of frequency difference; temperature was checked by the methanol method. Values of chemical shifts for multiplet systems, where present, were taken at their 'centre of gravity'.

For all the compounds examined, solutions in sulphuric acid were made immediately before running the spectra; in the case of compound (3) these had to be recorded very quickly owing to its fast hydrolysis in acidic media. The ionization ratios $[BH^+]/[B]$ were calculated by the usual relations.[12]

We thank the Italian National Research Council (C.N.R., Rome) for generous support of this work and Professor G. Modena (this Research Centre) for many helpful discussions.

[2/1722 *Received*, 21*st July*, 1972]

---

[16] G. S. Gibson and J. D. A. Johnson, *J. Chem. Soc.*, 1928, 92.

[17] J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt, and W. Samuel, *Annalen*, 1926, **449**, 213.

[18] O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4842.

[19] B. Buchner and L. B. Lockhart, *J. Amer. Chem. Soc.*, 1951, **73**, 755.

[20] P. D. Bartlett and G. Meguerian, *J. Amer. Chem. Soc.*, 1956, **78**, 3710.

[21] H. J. Harwood and D. W. Grisley, *J. Amer. Chem. Soc.*, 1960, **82**, 423.

[22] I. B. Douglass and B. S. Farah, *Org. Synth.*, 1960, **40**, 62.

[23] B. Bonini, S. Ghersetti, and G. Modena, *Gazzetta*, 1963, **93**, 1222.

[24] B. Holmberg, *Arkiv. Kemi*, B. 21 (No. 7), 1945, 7.

[25] A. Cerniani and G. Modena, *Gazzetta*, 1959, **89**, 843.

[26] F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, 1955, **77**, 572.

[27] R. S. Ryabova, I. M. Medvetskaya, and M. I. Vinnik, *Russ. J. Phys. Chem.*, 1966, **40**, 182.