system for which the dielectric increment of sulfamic acid is largest. In comparison with results for an aqueous system, the electrostriction effect for glycine in water is 3·2 ml^3 $mole^{-1}$ [15], basing the value of Φ_{cryst} for glycine upon a crystal density of 1·607 g ml^{-3} [14]. In another study involving non-aqueous solvents [15], values of apparent molal volumes and electrostriction effects associated with betaines (N-substituted derivatives of glycine) have been found to similarly show considerable solvent dependency.

In view of the low conductances, large dielectric increments and electrostriction effects for sulfamic acid in 3Me2Ox, HMPA and TMU, it is reasonable to conclude that sulfamic acid predominantly retains its dipolar ionic structure after dissolution in these media.

Department of Chemistry
University of Kentucky
Lexington, Kentucky 40506

E. M. TURNER*
P. G. SEARS†

*Present address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.

†To whom inquiries should be addressed.

15. J. T. Edsall and J. Wyman, Jr., *J. Am. chem. Soc.* **57**, 1964 (1935).

J. inorg. nucl. Chem., 1973, Vol. 35, pp. 2090–2093. Pergamon Press. Printed in Great Britain

Basicities of $(X)(Y)PO(CH_3)$ with variation of *X* and *Y* substituents*

(*Received* 17 *August* 1972)

THE SUCCESSFUL correlation of substituent effects on the acidity of phosphoric, phosphonic and phosphinic acids in various solvent systems has been reported [1–4]. The next logical step would be to make a similar correlation of substituent effects on the basicity of organophosphorus compounds containing the PO (phosphoryl) moiety. Some reports of the basicity and substituent correlation of this type of compound have been made using spectroscopic method [5], distribution method [6], potentiometric titration method [7–9] and NMR method [10, 11]. However, these studies have been made on a very limited number of compounds where internal correlations were not possible.

In the work described below the basicities of several compounds with the general formula $(X)(Y)PO(CH_3)$ are reported. The *X* and *Y* substituents consist of the following groups (identical with

*Based on work performed under the auspices of the U.S. Atomic Energy Commission.

1. D. F. Peppard, G. W. Mason and C. M. Andrejasich, *J. inorg. nucl. Chem.* **27**, 697 (1965).
2. A. G. Cook and G. W. Mason, *J. inorg. nucl. Chem.* **28**, 2579 (1966).
3. T. A. Mastryukova and M. I. Kabachnik, *Usp. Khim.* **38**, 1751 (1969).
4. T. A. Mastryukova and M. I. Kabachnik, *J. org. Chem.* **36**, 1201 (1971).
5. C. A. Bunton and S. J. Farber, *J. org. Chem.* **34**, 3396 (1969).
6. F. Krasovec and C. Klofutar, *J. inorg. nucl. Chem.* **30**, 1640 (1968).
7. B. I. Stepanov, B. A. Korolev and A. I. Bokanov, *Zh. obshch. Khim.* **39**, 316 (1969).
8. A. I. Bokanov, B. A. Korolev and B. I. Stepanov, *Zh. obshch. Khim.* **39**, 301 (1969).
9. T. Y. Medved, B. A. Korolev, K. S. Yudina, B. I. Stepanov and M. I. Kabachnik, *Teor. Eksp. Khim.* **4**, 116 (1968).
10. P. Haake and G. Hurst, *J. Am. chem. Soc.* **88**, 2544 (1966).
11. P. Haake, R. D. Cook and G. Hurst, *J. Am. chem. Soc.* **89**, 2650 (1967).

those reported in previous acidity studies [1, 2]): phenoxyl (ϕO), hydrogen (H), cyclohexoxyl (CHO), hydroxyl (OH), phenyl (ϕ), and cyclohexyl (CH). The basicities were determined by NMR chemical shift measurements of methyl protons in sulfuric acid solutions of the organophosphorus compound [10–12]. Trimethylammonium chloride was used as the internal reference. The H_0 scale was used to determine the effective sulfuric acid concentration [13, 14]. The following equation was used in the evaluation of the pK_{BH^+}'s:

$$\log\frac{\delta_B-\delta_{\text{obsd.}}}{\delta_{\text{obsd.}}-\delta_{H^+}}=\log\frac{[BH^+]}{[B]}=m(pK_{BH^+}-H_0).$$

The slope (m), intercept (mpK_{BH+}) and standard deviation were determined by least squares analysis. B represents the organophosphorus base and BH^+ the protonated base. The protonation of such phosphoryl compounds has been shown to take place on the phosphoryl oxygen atom [15].

EXPERIMENTAL

Preparation or source of compounds

Methylphosphonic acid, $CH_3PO(OH)_2$, was obtained from Hooker Chemical Company. Methylphosphinic acid, $(CH_3)HPO(OH)$, was prepared by methanolysis of methylphosphonous dichloride* after the method of Fiat *et al.*[16]. Dicyclohexylmethylphosphine oxide [17], $(C_6H_{11})_2(CH_3)PO$, was synthesized using the method of Downie and Morris [18]. Cyclohexylphenylmethylphosphine oxide [19], $(C_6H_{11})(C_6H_5)(CH_3)PO$, was obtained by treating butyl phenylphosphinate with cyclohexylmagnesium chloride to give the Grignard reagent, $(C_5H_{11})(C_6H_5)P(O)MgCl$. This is further treated with methyl iodide [18] to give the desired product. Phenylmethylphosphine oxide [20], $(C_6H_5)(CH_3)HPO$, was synthesized by adding one mole of methyl magnesium iodide to one mole of phenylphosphonous dichloride (similar to a previously described reaction [21]) followed by hydrolysis. Phenylmethylphosphinic acid, $(C_6H_5)(CH_3)P(O)OH$, was produced by the method of Christol and Marty [22], and diphenyl methylphosphonate, $CH_3PO(OC_6H_5)_2$, was made by a standard procedure [23]. Dicyclohexyl methylphosphonate, $CH_3PO(OC_6H_{11})_2$, was synthesized in a manner similar to that described by Gryszkiewicz-Trochimowski *et al.*[24]. Cyclohexyl methylphosphonate [25], $CH_3PO(OC_6H_{11})(OH)$, and phenyl methylphosphonate [25], $CH_3PO(OC_6H_5)(OH)$, were produced by the base hydrolysis of dicyclohexyl methylphosphonate and diphenyl methylphosphonate, respectively.

Instruments

The NMR spectra were obtained on a JEOL C-60HL high resolution nuclear magnetic resonance spectrometer.

*The methylphosphonous dichloride used in this procedure was kindly provided by the Ethyl Corporation.

12. G. C. Levy, J. D. Cargioli and W. Racela, *J. Am. chem. Soc.* **92**, 6238 (1970).
13. F. A. Long and M. A. Paul, *Chem. Rev.* **57**, 1 (1957).
14. M. J. Jorgenson and D. R. Hartter, *J. Am. chem. Soc.* **85**, 878 (1963).
15. G. A. Olah and C. W. McFarland, *J. org. Chem.* **36**, 1374 (1971).
16. D. Fiat, M. Halmann, L. Kugel and J. Reuben, *J. chem. Soc.* 3837 (1962).
17. H. Hellmann, J. Bader, H. Birkner and O. Schumacher, *Justus Liebigs Annln Chem.* **659**, 49 (1962).
18. I. M. Downie and G. Morris, *J. chem. Soc.* 5771 (1965).
19. O. Korpiun, R. A. Lewis, J. Chickos and K. Mislow, *J. Am. chem. Soc.* **90**, 4842 (1968).
20. J. P. Albrand, D. Gagnaire and J. B. Robert, *Bull. Soc. chim. Fr.* 479 (1968).
21. J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt and W. Samuel, *Justus Liebigs Annln Chem.* **449**, 213 (1926).
22. H. Christol and C. Marty, *Cr. hebd. Séanc. Acad. Sci., Paris* **C262**, 1722 (1966).
23. P. W. Morgan and B. C. Herr, *J. Am. chem. Soc.* **74**, 4526 (1952).
24. E. Gryszhiewicz-Trochimowski, M. Bousquet and J. Quinchon, *Bull. Soc. Chim. Fr.* 1222 (1961).
25. V. P. Evdakov and L. I. Mizrakh, *Zh. obshch. Khim.* **34**, 1848 (1964).

RESULTS AND CONCLUSIONS

The experimentally determined pK_{BH^+}'s of these phosphoryl compounds are summarized in Table 1. Correlation of the substituent effects with basicity of the compound is fairly good, as can be seen by comparing the experimental pK_{BH^+} with the calculated pK_{BH^+} in Table 1, with the exception of compound 9 where $X = Y =$ cyclohexyl. Compound 9 is a stronger base than would be expected. The substituent constant for the basicity of these methylphosphoryl compounds is symbolized as *b* in the present work (analogous to *a* in the parallel acidity studies[1]). These *b* values are the average of the pertinent ΔpK values of Table 2 using the hydrogen group as a standard with a *b* value of zero. The calculated pK_{BH^+} values of Table 1 were evaluated by the use of *b* substituent correlation values of Table 2 along with the theoretical value of reference compound 10 where $X = Y =$ H.

It can be seen from Table 2 that the relative order of substituent *base-increasing* power* as shown by *b* values, namely,

$$\mathrm{CH} > \phi > \mathrm{H} > \mathrm{CHO} > \mathrm{OH} > \phi\mathrm{O}$$

is almost exactly the reverse of the *acid-increasing* powers of these substituents in organophosphorus

Table 1. Experimental and calculated basicities of $(X)(Y)\mathrm{PO(CH_3)}$

Compound No.	X	Y	pK_{BH^+} (Exp.)	Intercept	m	No. of Points	pK_{BH^+} (Calc.)*
1	OH	OH	−4·3±0·4	−1·19±0·11	0·28±0·01	27	−4·3
2	OH	ϕ	−3·6±0·5	−0·83±0·11	0·23±0·01	13	−3·7
3	OH	H	−4·2±0·3	−0·96±0·05	0·23±0·01	13	−4·1
4	OH	CHO	−4·3±0·4	−0·90±0·07	0·21±0·01	13	−4·2
5	OH	ϕO	−5·9±0·6	−0·66±0·07	0·11±0·01	16	−5·8
6†	ϕ	ϕ	−3·2	−2·23±0·25	0·45±0·02	10	−3·1
7	ϕ	H	−3·3±0·5	−1·08±0·14	0·32±0·03	11	−3·5
8	ϕ	CH	−2·5±0·3	−0·84±0·10	0·34±0·02	10	−2·7
9	CH	CH	−0·9±0·3	−0·50±0·16	0·55±0·03	13	−2·3
10	H	H					−3·9‡
11	CHO	CHO	−4·2±0·4	−1·09±0·08	0·26±0·01	13	−4·1
12	ϕO	ϕO	−7·3±1·8	−2·69±0·52	0·37±0·06	14	−7·4

*Calculated from the equation $pK_{BH^+}(\mathrm{Calc.}) = pK_{BH^+}^{(H)(H)PO(CH_3)} - \Sigma b$ where *b* is obtained from Table 2.

†Experimental values obtained from [11].

‡From intercept of $\Sigma b = 0$ axis for the least squares analysis of a plot of pK_{BH^+} + vs. Σb for all compounds except 9, slope $= -1{\cdot}1$.

Table 2. Values of *b* and ΔpK_{BH^+} for $(X)(Y)$-$\mathrm{PO(CH_3)}$ with respect to $(H)(Y)\mathrm{PO(CH_3)}$

X	$Y = \phi$	$Y =$ OH	b
OH	+0·3	+0·1	+0·2
ϕ	−0·1	−0·6	−0·4
CH	−0·8		−0·8
H	0·0	0·0	0·0
CHO		+0·1	+0·1
ϕO		+1·7	+1·7

---

*All of the substituents except cyclohexyl and phenyl are actually base-decreasing relative to the *H* substituent as standard. In the present work all of the substituents will be spoken of as base-increasing relative to the weakest base in the series, namely that with $X = Y =$ cyclohexyl. A parallel nomenclature will be used when speaking of acid-increasing power.

as determined by Peppard *et al.*[1], namely,

$$\phi O > H > CHO > OH > \phi > CH.$$

This follows along well with the broad generalization of Krasovec and Klofutar [6] concerning the base strength of neutral organophosphorus compounds. They concluded that the basicity of these compounds change as follows (decreasing basicity from left to right):

phosphine oxides > phosphinates > phosphonates > phosphates.

Chemistry Division
Argonne National Laboratory
Argonne, Illinois 60439

A. GILBERT COOK*
G. W. MASON

*Present address: Department of Chemistry, Valparaiso University, Valparaiso, Indiana 46383.

J. inorg. nucl. Chem., 1973, Vol. 35, pp. 2093–2096. Pergamon Press. Printed in Great Britain

Cobalt(II) complexes of N-salicylideneamino acids

(*First received* 21 *July* 1972; *in revised form* 14 *August* 1972)

ALTHOUGH metal complexes of Schiff bases derived from substituted salicylaldehyde and various amines have been studied extensively[1], comparatively little attention has been given to systems in which the Schiff base is derived from salicylaldehyde and α-amino acids. The ligands, abbreviated as (Sal: AA), are bivalent anions with tridentate ONO donors. It is of considerable interest to study these metal chelate systems in order to gain an insight into the complex systems in which metals are involved. For example N-salicylideneamino acid complexes may serve as models for N-pyridoxylideneamino acid systems which are believed to be intermediates in biologically important amination processes[2–4]. The preparation and characterization of some iron(III) and cobalt(III) compounds of N-salicylideneamino acids have been reported[5]. Earlier, we reported our investigation of the oxovanadium[6, 7] and nickel[8] complexes, and here we report the preparation, magnetic, and spectral properties of the cobalt compounds.

EXPERIMENTAL

Preparation of complexes

The complexes of the series $Co(Sal:AA)(H_2O)_2$ were prepared by the following general method. Salicylaldehyde (6·11 g, 0·05 mole) was dissolved in 400 ml of 95% ethanol. The amino acid (0·05 mole) was dissolved in a minimum quantity of distilled water, filtered, and added slowly to the magnetically stirring salicylaldehyde solution. A yellow colour developed immediately. Cobalt(II) acetate tetrahydrate (12·46 g, 0·05 mole) was then dissolved in 200 ml of water, filtered, and added dropwise to the Schiff base solution. A dark brown colour developed immediately and after a few minutes a heavy precipitate was observed. The mixture was allowed to stir at 42°C for 2 hr. The brown product

1. R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr Inorg. Chem.* **7**, 83 (1966).
2. G. L. Eichhorn and N. D. Marchand, *J. Am. chem. Soc.* **78**, 2688 (1956).
3. H. N. Christensen and S. Collins, *J. Biol. Chem.* **220**, 279 (1956).
4. E. Willstadter, T. A. Hamor and J. L. Hoard, *J. Am. chem. Soc.* **85**, 1205 (1963).
5. R. C. Burrows and J. C. Bailar, Jr., *J. Am. chem. Soc.* **88**, 4150 (1966).
6. L. J. Theriot, G. O. Carlisle and H. J. Hu, *J. inorg. nucl. Chem.* **31**, 2841 (1969).
7. L. J. Theriot, G. O. Carlisle and H. J. Hu, *J. inorg. nucl. Chem.* **31**, 3303 (1969).
8. L. J. Theriot, G. O. Carlisle and H. J. Hu, *J. inorg. nucl. Chem.* **31**, 2891 (1969).