[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

# Arylphosphinic Acids: Dissociation Constants and Reaction with Diazomethane[1]

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The acid dissociation constants of several arylphosphinic acids were determined by potentiometric titrations in water. Hammett's equation was found applicable to this class of compounds ($\rho = 0.830$). No evidence for secondary ionization was found. The acids were readily converted to methyl arylphosphinates with diazomethane. This reaction represents a useful synthesis of these esters, and also indicates no involvement of the phosphorus function in a shift to tricovalent form.

We report in this paper the results of two studies on the properties of arylphosphinic acids: their acidity and their reaction with diazomethane. The studies are related through a bearing on the structural organization about the phosphorus atom in the phosphinic acid group.

Phosphinic acids are known to have the structure I, although as in related classes of phosphorus compounds, consideration has been given to the possible existence of a tautomeric equilibrium

$$\underset{\text{I}}{\text{ArPH(O)OH}} \rightleftharpoons \underset{\text{II}}{\text{ArP(OH)}_2}$$

with the tricovalent form II.[2] Until very recently, the known properties of the phosphinic acids were explicable on the basis of I as the exclusive structure. Frank,[3] however, reported an example of the formation of a tricovalent derivative from arylphosphinic acids; on reaction with phosphorus trichloride, the acids were converted to arylphosphonous dichlorides.

$$3\text{ArPO}_2\text{H}_2 + 2\text{PCl}_3 \longrightarrow 3\text{ArPCl}_2 + 2\text{H}_3\text{PO}_3$$

This reaction was offered as evidence for the existence of the tautomeric shift, structure II being considered the reactive form in this case.

*Acidity of arylphosphinic acids.* Lesfauries and Rumpf[4] obtained the $pK_a$ values of phenylphosphinic acid and two para-substituted derivatives. These acids were slightly stronger than the corresponding phosphonic acids. They were monobasic; no evidence for secondary ionization was obtained.

We have determined the $pK_a$ values in water for a larger and more diversified group of acids (Table I) and in general have confirmed the earlier findings.[4] Sufficient data were collected to test the applicability of the Hammett equation[5] to this group of acids. A plot of log K/K° for six meta- and para-substituted acids against Hammett's substituent constants[6] was linear; the correlation coefficient (r) of 0.988 and the standard deviation (s) of 0.0391 indicated a good fit[7] of the data to the equation. The reaction constant, $\rho$, was 0.830. The magnitude of this value indicates that the electrical effects of the substituents are transmitted to the phosphinic acid group to about the same extent as they are to the carboxy group of benzoic acid. The value is slightly larger than that (0.755) reported for the primary ionization of phosphonic acids.[8]

TABLE I

DISSOCIATION CONSTANTS OF ARYLPHOSPHINIC ACIDS IN WATER AT 25°

| $XC_6H_4PO_2H_2$<br>X = | $pK_a$[a] | $\sigma$[b] |
|---|---|---|
| $p$-$CH_3$ | 1.83 | −0.170 |
| H | 1.75[c] | 0.000 |
| $p$-Cl | 1.57 | 0.227 |
| $m$-Br | 1.39 | 0.391 |
| $m$-Cl | 1.35 | 0.373 |
| $p$-COOH[d] | 1.32 | 0.430 |
| $p$-CN | 1.19 | 0.628 |

[a] The average of several values which agreed to within ±0.05 unit. [b] See ref. 6. [c] Lesfauries and Rumpf[4] reported $pK_a$ 1.35 at 17°. [d] $pK_a$ for the —COOH group was 4.06.

An approximate value for the substituent constant of the $—PO_2H^-$ group was obtained from the ionization of the carboxy group in $p$-carboxyphenylphosphinic acid. This value, 0.14, indicates that the $—PO_2H^-$ group is weakly electron-attracting. A similar observation has been made for the $—PO_3H^-$ group.[8]

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[1] A portion of this paper is taken from the thesis submitted in 1960 by Martha R. Dysart in partial fulfillment of requirements for the A.M. degree, Duke University. Presented at the Combined Regional A.C.S. Meeting, New Orleans, La., December 1961.

[2] J. R. Van Wazer, *Phosphorus and Its Compounds*, Vol. I, Interscience Publishers, Inc., New York, 1958, Chap. 7.

[3] A. W. Frank, *J. Org. Chem.*, **26**, 850 (1961).

[4] P. Lesfauries and P. Rumpf, *Compt. rend.*, **228**, 1018 (1949).

[5] L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, 1940, Chap. VII.

[6] The constants given in ref. 5 were used, with the exceptions of those for $p$-CN and $p$-COOH. The value for the former was taken from the list in ref. 7. The value for $p$-COOH was taken from ref. 8.

[7] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[8] H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Am. Chem. Soc.*, **75**, 2209 (1953).

TABLE II

PROPERTIES OF METHYL ARYLPHOSPHINATES

| $XC_6H_4PH(O)OCH_3$ X | B.P./Mm. | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Phosphorus, % Calcd. | Phosphorus, % Found |
|---|---|---|---|---|---|---|---|---|
| H | 91–93/1.0 | $C_7H_9O_2P$ | 53.85 | 53.77 | 5.81 | 5.67 | 19.84 | 19.60 |
| *m*-Cl | 88/0.25 | $C_7H_8ClO_2P$ | 44.12 | 44.05 | 4.23 | 4.25 | 16.26 | 16.25 |
| *m*-Br | 123–124/0.15 | $C_7H_8BrO_2P$ | 35.77 | 35.59 | 3.43 | 3.69 | 13.18 | 13.05 |

None of the titration curves showed detectable secondary ionization of the phosphinic acid group. Apparently variation of the aryl substituent on phosphorus has no observable influence on the position of the equilibrium between tetracovalent and tricovalent phosphorus, if such an equilibrium exists. That secondary ionization might occur at a slow rate, controlled by the shift of the equilibrium, appears excluded by the observation that precisely one equivalent of base was consumed after overnight standing of a typical acid (*m*-bromophenylphosphinic acid) in excess base. The fact that Hammett's equation is followed also suggests no change in structure about phosphorus on variation of substituents. One of the major causes for deviations from Hammett's equation has been a change in mechanism of the reaction under consideration.[7]

These observations do not necessarily bear, however, on the reality of a tautomeric equilibrium between I and II. The proper conclusion appears to be that the tautomerism

$$\underset{\text{III}}{ArPH(O)O^-} \rightleftharpoons \underset{\text{IV}}{ArP(OH)O^-}$$

does not occur to a detectable extent. Species III would exist in solution after one equivalent of base was consumed, and the failure of III, not I, to rearrange is responsible for the lack of secondary ionization.

*Reaction of arylphosphinic acids with diazomethane.* It is known that the P—OH group in phosphates reacts readily with diazoalkanes to form esters.[9] The P—H bond, however, appears to be unreactive to diazoalkanes under the same conditions; thus, phosphorous acid forms only diethyl phosphonate with diazoethane,[10] and dibenzyl phosphonate with phenyldiazomethane.[9] Similarly, hypophosphorous acid forms monoesters with diazoalkanes.[11] No record exists of the reaction of phosphinic acids with diazoalkanes.

It was found that diazomethane reacts rapidly with arylphosphinic acids according to the equation

$$ArPO_2H_2 + CH_2N_2 \longrightarrow ArPH(O)OCH_3 + N_2$$

The esters of three acids (Table II) were obtained analytically pure by distillation at low pressures. Their infrared spectra were in accord with the phosphinate structure. The esters appeared to be the only product of the reactions; none of the lower boiling dimethyl arylphosphonites seemed to be formed.

Kosolapoff[12] reported the first authentic synthesis of this class of compounds, employing the reaction

$$ArPCl_2 + 2ROH \longrightarrow ArPH(O)OR + RCl + HCl$$

The butyl ester of phenylphosphinic acid was readily obtained in a pure state. The same reaction was employed by later workers[13] to prepare the methyl as well as higher alkyl esters of the same acid. Yields in this reaction are in the 60–80% range. The diazomethane method appears to be equally attractive; yields are in the same range, and the reaction is very easily carried out. Extension to the preparation of higher alkyl esters has not been attempted, but should prove to be feasible.

The methyl phosphinates are thermally unstable. They must be distilled at low temperatures and even then develop a pronounced phosphine-like odor which is absent in the crude reaction product. Conditions for performing gas chromatography were sought for a typical ester but without success; no elution peaks were observed with a variety of columns operated at temperatures in the range where distillation was successful.

The esters are also readily hydrolyzed. Exposure to the atmosphere for 1–2 days resulted in complete hydrolysis to the phosphinic acid. No oxidation of the esters was detected during this period.

Exposure of the esters to excess diazomethane for overnight periods did not result in any further methylation, in agreement with earlier observations on the lack of reactivity of the P—H bond.[9–11] This observation is also significant through its implication that the equilibrium

$$\underset{\text{V}}{ArPH(O)OCH_3} \rightleftharpoons \underset{\text{VI}}{ArP(OH)OCH_3}$$

is not of importance. Compound VI should be reactive to diazomethane if it were formed in tautomeric equilibrium with V.

In contrast to the present observations on the failure of III and V to become involved in tauto-

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[9] F. R. Atherton, H. T. Howard, and A. R. Todd, *J. Chem. Soc.*, 1106 (1948).

[10] F. C. Pallazo and F. Maggiacomo, *Gazz. chem. ital.*, 38 [2], 115 (1908).

[11] M. I. Kabachnik, A. E. Shipov, and R. A. Mastryukova, *Izvest. Akad. Nauk S.S.S.R.*, 146 (1960).

[12] G. M. Kosolapoff, *J. Am. Chem. Soc.*, 72, 4292 (1950).

[13] A. N. Pudovik and D. K. Yarmukhametova, *Izvest. Akad. Nauk S.S.S.R.*, 902 (1952).

meric rearrangement is Frank's discovery[3] of the formation of arylphosphonous dichlorides from phosphinic acids with phosphorus trichloride. This reaction, however, does not necessarily depend on a rearrangement of the tetracovalent phosphinic acid I to the tricovalent phosphonous acid II. It seems likely that the placement of chlorine on phosphorus would occur in two steps. If I were the reactive form, as seems probable from the general behavior of these acids, the following sequence might be involved:

$$\mathrm{ArPH(O)OH} \xrightarrow{\mathrm{PCl_3}} \mathrm{ArPH(O)Cl}$$

$$\mathrm{ArPH(O)Cl} \rightleftharpoons \mathrm{ArP(OH)Cl}$$

$$\mathrm{ArP(OH)Cl} \xrightarrow{\mathrm{PCl_3}} \mathrm{ArPCl_2}$$

The conversion to a tricovalent form would thus occur with a chloro derivative and not with the phosphinic acid itself. An explanation would then be needed of why a structure such as ArPH(O)Cl undergoes rearrangement while ArPH(O)O— and $\mathrm{ArPH(O)OCH_3}$, as seen in the present work, do not. It is known[14] that there is little or no $\pi$ character to the P—Cl bond. On the other hand, P—O bonds have appreciable $\pi$ character.[14] These facts may be important in understanding the different reactivities. The chlorine atom, acting only through its inductive effect, would increase positive character in phosphorus, perhaps rendering the proton somewhat mobile. In structures III and V, with oxygen replacing chlorine, the phosphorus atom would acquire greater $\pi$ character, and hence become somewhat less positive. Relative to the chloro compound, then, the P—H bond would be less readily broken, and the tautomeric shift would in effect be retarded.

If II were indeed found to be the reactive form in the phosphorus trichloride reaction, an explanation of why the monochloro intermediate, ArP(OH)Cl, failed to rearrange before displacement of the second hydroxy group occurred might be found in the above argument.

## EXPERIMENTAL[15]

*Materials.* All phosphinic acids, except the carboxy derivative, were prepared by hydrolysis of the phosphonous dichlorides. This compound was prepared by hydrolysis of *p*-cyanophenylphosphinic acid. The details of this synthesis, carried out by Ronald E. Montgomery, will be reported later. Phenylphosphonous dichloride was obtained commercially. *p*-Tolylphosphonous dichloride was prepared as described in *Organic Syntheses.*[16] All other dichlorides were prepared by a new method recently discovered in this laboratory.[17] Diazomethane was prepared from *N,N'*-dinitroso-*N,N'*-dimethylterephthalamide (EXR-101, du Pont) according to the manufacturer's procedure.

*Determination of $pK_a$ values and reaction constant.* Approximately 1 mmole, weighed accurately, of the phosphinic acid was dissolved in 20.0 ml. or 30.0 ml. of distilled water, as necessary, at 25 ±1°. The solution was titrated with 0.2*N* sodium hydroxide. Determination of the *p*H during the titration was made with a Beckman Model G *p*H Meter using calomel and glass electrodes. The $pK_a$ values were then calculated according to standard methods.[18] Several values were obtained for each acid; agreement was within ±0.05 $pK_a$ unit. The average values appear in Table I. The ionic strength was not constant during a determination and liquid junction potentials were neglected; therefore, the values are nonthermodynamic.

A plot of log K/K° against Hammett's $\sigma$ constants[6] was linear. The slope ($\rho$) was calculated according to Jaffé[7]; a value of 0.830 was obtained, with a standard deviation (s) of 0.0391. The correlation coefficient (r) was 0.988, and the intercept of the best straight line at $\sigma = 0$, $-\log K°$, was 1.713.

*Preparation of methyl arylphosphinates.* The phosphinic acid (2–3 g.) was placed in 100 ml. of dry ether; sufficient absolute methanol was added to effect dissolution. The solution was then treated with excess diazomethane in ether; nitrogen was evolved briskly and the diazomethane color was discharged rapidly. After standing 1 hr., the solution was stripped of excess diazomethane and solvent, and the residual liquid, essentially colorless and odorless, was subjected to distillation *in vacuo*. The properties of three esters obtained in a pure state are recorded in Table II. The phenyl derivative has been reported previously[13]; b.p. 91–93° at 1.0 mm. The yield of recovered ester was 40–50%, but the mechanical loss associated with the small quantities used was high, and this value is not representative of the reaction.

The esters had infrared absorption bands[19] due to PH at about 2400 cm.$^{-1}$ (weak), to PO at about 1250 cm.$^{-1}$ (strong), and to $\mathrm{POCH_3}$ at 1190 and 1045 cm.$^{-1}$. No POH absorption was noted.

*p*-Chlorophenyl- and 3-chloro-4-methylphenylphosphinic acids were also methylated with diazomethane. The products boiled over a small range, 101–102° at 0.5 mm. and 120–121° at 0.4 mm., respectively, and no low or high boiling material was present. However, the analytical data were not entirely satisfactory. Insufficient material was available for further study at this time.

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(14) Ref. 2, Chap. 2.

(15) Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting and boiling points are uncorrected.

(16) B. Buchner and L. B. Lockhart, Jr., *Org. Syntheses*, **Coll. Vol. III**, 88 (1951).

(17) L. D. Quin and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **83**, 4124 (1961).

(18) *Cf.* S. Glasstone, *Textbook of Physical Chemistry*, 2nd Ed., D. Van Nostrand Co., Inc., New York, 1946, p. 1003.

(19) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley and Sons, Inc., New York, 1958, Chap. 18.