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THE APPLICATION OF THE HAMMETT EQUATION TO THE THEORY OF TAUTOMERIC EQUILIBRIUM

THIONE–THIOL EQUILIBRIUM, ACIDITY, AND STRUCTURE OF PHOSPHORUS THIO-ACIDS*†

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Abstract—The applicability of the Hammett equation to the effective ionization constants of tautomeric substances has been investigated. The tautomeric equilibrium being shifted toward one of the forms, a good linear dependence of pK_A on σ is observed. When at particular σ values the second tautomeric form makes its appearance in the equilibrium to a noticeable extent one observes the deviation from linearity. It is seen to run parallel to the increase of that form in the equilibrium. The tautomeric equilibrium constant is related to the deviations form linearity '*a*' by a simple correlation $K_T = K_1/K_2 = 10^a - 1$ Thus has been established the quantitative relationship between the ionization constants of particular forms, the effective ionization constants of tautomeric substances and the σ values.

The relationships determined were used to investigate the thione–thiol tautomerism of thio-organo-phosphorus compounds. To this end the Hammett equation has been previously shown to be applicable to organo-phosphorus acids of the type RR'P(O)OH and RR'P(*S*)*SH* and the σ constants, characteristic of phosphorus compounds, have been determined. 25 phosphorus monothio- and 16 dithio-acids were synthesized, their ionization constants determined in aqueous 7 per cent and 80 per cent alcohol and the tautomeric equilibrium constants evaluated. For most phosphorus thio-acids the equilibrium has been shown to be shifted toward the thione form RR'P(S)OH, the second, or thiol form RR'P(O)SH appearing in noticeable amounts only with such substituents whose σ value is near to 0. This effect is stronger in the 7 per cent than in the 80 per cent alcohol.

1. *General considerations*

AN important place is occupied in the theory of isomeric equilibrium or tautomerism by the dependence of the equilibrium on the structure of isomeric forms, the media, and other factors. In our previous work it had been shown[1-11] that it is possible to obtain efficient results by applying to prototropic tautomerism the modern theory of

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* Translated by A. L. Pumpiansky, Moscow.

† Read at the Jubilee Conference of the Hungarian Chemist Society 12, May 1958 in Budapest; *Acta Chim. Hung.* **18**, 407 (1959), and at the Mendeleev Congress, Moscow, 18 March 1959.

[1] M. I. Kabachnik, *Dokl. Akad. Nauk SSSR* **83**, 407 (1952).

[2] M. I. Kabachnik, *Dokl. Akad. Nauk SSSR* **83**, 859 (1952).

[3] M. I. Kabachnik and T. A. Mastrukova, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* 163 (1953).

[4] M. I. Kabachnik and S. T. Joffe, *Dokl. Akad. Nauk SSSR* **91**, 833 (1953).

[5] M. I. Kabachnik, *Proceedings of the Kiev Conference, June* 1952, p. 126. AN, U.S.S.R. (1954).

[6] M. I. Kabachnik, *Izv. Akad. Nauk SSSR* 98 (1955).

[7] M. I. Kabachnik, S. T. Joffe and T. A. Mastrukova, *Zh. Obshch. Khim.* **25**, 684 (1955).

[8] M. I. Kabachnik, N. I. Kurochkin, T. A. Mastrukova, S. T. Joffe, E. M. Popov and N. P. Rodionova, *Dokl. Akad. Nauk SSSR* **104**, 861 (1955).

[9] M. I. Kabachnik, *Usp. Khim. SSSR* **25**, 137 (1956).

[10] M. I. Kabachnik, S. T. Joffe and Yu. N. Sheinker, *Zh. Obshch. Khim.* **26**, 2025 (1956).

[11] M. I. Kabachnik, S. T. Joffe and K. V. Vatzuro, *Tetrahedron* **1**, 317 (1957).

acid–base equilibrium in solutions, as proposed by Brønsted[12] and later developed by other authors.[13]

The qualitative ionic theory of tautomerism due to Lapworth *et al.*[14–17] as well as to Arndt and Eistert,[18–20] starting from the concept of the formation of a "common ion" has been quantitatively interpreted.[1–11] By using the Brønsted equation[12] and the relationship*

$$K_{TS} = C_{2S}/C_{1S} = K_{1S}/K_{2S} = K_1/K_2 \cdot f_{1S}/f_{2S} \qquad \text{(I)}$$

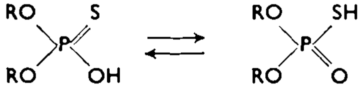
it proved possible to elucidate the regularities concerning the effect of solvents on the tautomeric equilibrium constants, at least within the limitations of the acid–base equilibrium theory, as to the effect of the solvents on the strength of acids and bases.

In particular, it was shown that the logarithms of the tautomeric equilibrium constants in two different solvents are in a linear relationship[1]

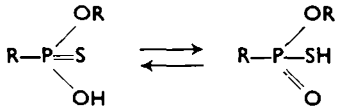
$$\mathrm{p}K_{TS_1} = \mathrm{p}K_{TS_2} + \mathrm{Const} \qquad \text{(II)}$$

This linear relationship proved valid not only for keto-enols that were the first to exemplify it, but for a number of other types of tautomeric systems as well, such as α-acylaminopyridines and α-acylaminothiazols,[21] derivatives of dithizone,[22] thiocarboxylic acids,[23] etc.

The application of the Brønsted equation to the solutions of tautomeric compounds enabled to work out a method to evaluate the tautomeric equilibrium constants in terms of the data obtained by measuring the effective ionization constants of tautomeric mixtures in two particular solvents.[4] This method has been, in particular, used by two of the authors and Joffe to evaluate the tautomeric equilibrium constants of dialkyl hydrogen thiophosphates in 7 per cent and 80 per cent alcohol.



It was thereby found that in the latter case the equilibrium is shifted toward the thione forms and in the former one toward the thiol forms. The equilibrium of alkyl hydrogen alkylthiophosphonates



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*K_{TS} is the tautomeric equilibrium constant; K_{1S} and K_{2S} are ionization constants; K_1 and K_2 are the thermodynamic constants of acidity, and f_{1S} and f_{2S} are the respective coefficients of activity in the medium *S*, taken in terms of a standard for all solvents; C_{1S} and C_{2S} are the concentrations of form (1) and (11) in the medium (*S*).

[12] Y. N. Brønsted, *Chem. Rev.* **5**, 291 (1928); *Z. Phys. Chem.* **A169**, 32 (1939).
[13] N. A. Izmailov, *Z. Phys. Khim.* **23**, 639, 643 (1949); **24**, 321 (1950)
[14] A. Lapworth and A. O. Hann, *J. Chem. Soc.* **81**, 1512 (1912).
[15] T. Lowry, *J. Chem. Soc.* 2557 (1927).
[16] C. Ingold, C. Shoppe and J. F. Thorpe, *J. Chem. Soc.* 1477 (1926).
[17] J. Baker, *Tautomerism.* Routledge, London (1934).
[18] F. Arndt and C. Martius, *Liebigs Ann.* **499**, 262 (1932).
[19] F. Arndt and B. Eistert, *Ber. Dtsch. Chem. Ges.* **74**, 423 (1941).
[20] F. Arndt, L. Loewe and R. Ginkök, *Rev. Fac. Sci. Univ. Istambul* **A11**, 1947 (1946).
[21] Yu. N. Sheinker, *Dokl. Akad. Nauk. SSSR* **113**, 5 (1957).
[22] P. S. Pelkis and R. G. Dubenko, *Ukrain Khim. Zh.* **23**, 748 (1957).
[23] S. T. Joffe, Yu. N. Sheinker and M. I. Kabachnik, *Izv. Akad. Nauk S.S.S.R.* In press.

was found to be shifted in both alcohol and water toward the thione forms.[8] Thus it has been proved that the thione-thiol equilibrium of phosphorus thioacids depends to a great extent both on the nature of the solvent and the structure of tautomeric acids, such a relationship being also characteristic of many other types of tautomerism. The effect of the solvent can be therby interpreted in terms of the Brønsted–Izmailov theory of acid–base equilibrium. As to the effect of the structure of tautomeric substances it has been up to now possible to consider it only qualitatively on the basis of the known laws of organic chemistry. At the same time it seemed of great interest to establish the quantitative relationship between the structure of the forms and the tautomeric equilibrium. The tautomeric equilibrium being determined by the ratio of the ionization constants of the forms, the question of the effect of the structure on the equilibrium is that of the effect of the structure on their acid–base properties. In its general case the latter point is rather involved, but in particular cases one can make use of the empirical Hammett equation,[24]

$$\text{(III)} \qquad \log K/K^\circ = \rho\sigma, \qquad \text{or} \qquad pK = pK^\circ - \rho\sigma \qquad \text{(IV)}$$

that is particularly well applicable to the *meta-* and *para-* substituted aromatic acids. This led us to conduct the investigation of thione–thiol tautomerism of organo thiophosphorus acids along two lines, namely to consider firstly the general case of applying the Hammett equation to the ionization constants of tautomeric mixtures and secondly the particular case of applying this equation to the ionization of phosphorus acids.

2. *The application of the Hammett equation to the ionization constants of tautomeric compounds*

The Hammett equation has been applied by different authors to the problems of tautomerism. Thus, for instance, Jaffe,[25] Willy and Meyer[26] evaluated the tautomeric equilibrium constants through ionization constants calculated following Hammett. It is to be noted that the Hammett formula, though usually valid as a statistical equation for many uniform compounds, may lead to noticeable errors when used to evaluate the constants of a particular substance. A more general application of the equation is suggested in a recently published paper by Jaffe and Gardner[27] who have concurrently with the present authors dealt with two intersecting Hammett straight lines characteristic of the tautomeric equilibrium. The former authors have considered this approach only as a particular case to be applied to the tautomeric equilibrium of substituted azobenzenes and limited it to the case when the ionization constants K° of unsubstituted forms are equal (the two nitrogen atoms being equivalent in azobenzene). Neither have they given the problem under investigation a quantitative treatment.

We believe that being applied to the problems of tautomerism the Hammett equation should receive a more general and exhaustive treatment, involving the quantitative aspect of this problem.

As the tautomeric forms (ketones and enols, thiones and thiols, etc.) refer to acids of different chemical types, the relationship between their pK's and σ's must be

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[24] L. P. Hammett, *Physical Organic Chemistry*. McGraw-Hill, New York (1940).

[25] H. H. Jaffe, *J. Amer. Chem. Soc.* **77**, 4445 (1955).

[26] A. V. Willi and W. Meyer, *Helv. Chem. Acta* **39**, 54, 318 (1956).

[27] H. H. Jaffe and R. W. Gardner, *J. Amer. Chem. Soc.* **80**, 319 (1958).

expressed by different values of pK° and ρ. Thus for the tautomeric forms 1 ⇆ 11 we must write

$$pK_1 = pK_1^\circ - \rho_1\sigma \tag{IVa}$$

and

$$pK_2 = pK_1^\circ - \rho_2\sigma \tag{IVb}$$

In the general case a plot of pK vs. σ should be expressed by two intersecting straight lines (1) and (2), see Fig. 1, each of which expresses the relationship between pK and σ for one type of forms. The tautomeric equilibrium constant being equal to the ionization constants ratio of the forms in a given medium and hence

$$pK_T = pK_1 - pK_2 \tag{V}$$

it must be calculated for each substance (for each σ value) by the intercept "C" of the ordinate between the two straight lines. The intersection point of the straight lines refers to that substituent which results in the tautomeric equilibrium constant being equal to unity. The region to the left from this point corresponds to the equilibrium shift toward form (1), that to the right toward form (11). In all cases the equilibrium is shifted to the forms corresponding to the above lying rays of straight lines. Thus if ρ_1 and ρ_2, and, respectively, pK_1° and pK_2° are known, it is possible to obtain a complete picture of the effect of the structure (the nature of the substituent, and the σ value) on the tautomeric equilibrium and acidity of tautomeric forms.

In most cases, however, the direct experimental determination of ionization constants of single forms proved to be impossible. The attempted determination by Schwarzenbach and Lutz[28] using an extremely precise flowing potentiometric procedure met with failure.

Actually when determining the ionization constants of tautomeric compounds one determines some effective ionization constant related to the ionization constants of single forms by the equation (VI).[2]

$$K_a = K_1K_2/K_1 + K_2 \tag{VI}$$

It is thereby to be noted that if $K_2 \gg K_1$ then $K_a \cong K_1$, and if $K_2 \ll K_1$ then $K_a \cong K_2$.

The effective constant is always close to the ionization constant of that form which under given conditions is less acidic. With pK and σ the relationship between effective constant K_a and σ is expressed by a curve with two asymptotes overlapping with two above lying rays of the straight lines. Analytically it can be expressed through equation (VII) derived from (VI) by substituting K_1 and K_2, taken from equations (IVa) and (IVb)

$$K_a = \frac{K_1^\circ \cdot 10^{\rho_1\sigma} \cdot K_2^\circ \cdot 10^{\rho_2\sigma}}{K_1^\circ \cdot 10^{\rho_1\sigma} + K_2^\circ \cdot 10^{\rho_2\sigma}} \tag{VII}$$

This curve passes above the intersection point of two straight lines at a distance equal to log 2*.

One can suggest therefrom two ways of determining the tautomeric equilibrium constants on the basis of experimental determination of effective ionization constants

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* The formula, suggested by Jaffé and Gardner is derived from VII at $K^\circ = K_1^\circ = K_2^\circ$ that is to say, it is applicable to the particular case when the ionization constants of two unsubstituted tautomeric forms are equivalent (at $\sigma = 0$).

[28] G. Schwarzenbach and K. Lutz, *Helv. Chem. Acta* **23**, 1147 (1940).

K_a of various uniform tautomeric mixtures differing as to the nature and position of substituents (that is, in the magnitude of σ's).

The first is used to evaluate the ionization constants of two sets of compounds, whose substituents cause the tautomeric equilibrium shift practically entirely either to the form 1 or to the form 2, respectively. The plot of pK vs. σ leads to two intercepts of above lying rays of intersecting straight lines at some distance from the point of intersection. Extrapolating to the middle one obtains two intersecting lines characteristic of the tautomeric equilibrium depending on σ. Investigations have shown the

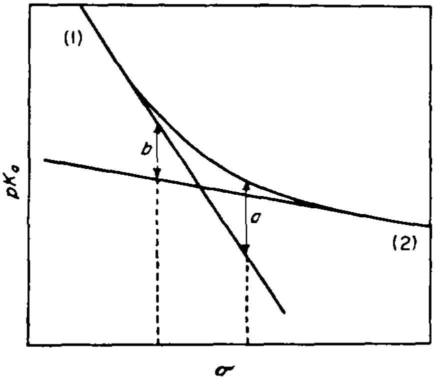


FIG. 1. A plot of pK_a vs. σ for tautomeric compounds.

application of this treatment to be limited to those rare cases when the nature of the substituent exerts such a strong influence on the equilibrium that it is possible to obtain experimental points corresponding to both rays.

As to the second way of determining the tautomeric equilibrium constants used in this paper, it is enough to have one ray and the region of deviation from it. Indeed from formula (VI) we obtain

$$pK_a - pK_1 = \log (K_1 + K_2) - \log K_2 \qquad \text{(VIII)}$$

or else, taking into account formula (1),

$$pK_a - pK_1 = \log (K_T + 1) \qquad \text{(IX)}$$

The $pK_a - pK_1$ being the ordinate deviation of the experimental curve from the linear relationship or the intercepts a (Fig. 1), one finally obtains:

$$K_T = 10^a - 1 \qquad \text{(X)}$$

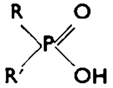
Thus, the intercept of the straight line and the deviations from its extension obtained experimentally enable one to reproduce the two intersecting straight lines, that is the whole picture of the relationship between the tautomeric equilibrium constants or the ionization constants of particular forms and σ.

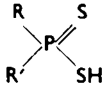
Practically, the investigation proceed as follows. The effective ionization constants of tautomeric mixtures of various uniform compounds differing in the nature of substituents (or the magnitudes of σ) are evaluated. According to the data obtained pK is plotted against σ. If the plot gives a linear relationship it is concluded that for all compounds under study the tautomeric equilibrium is almost entirely shifted to one of the forms. But if the experimental data give rise to a curve with only one branch showing the linear relationship and the other deviating from it, then the conclusion is drawn that firstly the equilibrium is shifted to one of the forms for the compounds corresponding to the linear part of the curve and secondly, in the region of deviation appears a second form in equilibrium. The intercepts a enclosed between the curve and the straight line produced by extrapolating the linear part of the curve are characteristic of the tautomeric equilibrium constant according to equation (X).

3. *The application of the Hammett equation to organophosphorus compounds*

Jaffe *et al.*[29] have shown the Hammett equation to be applicable to the constants of the first and second ionization steps of aromatic phosphonic acids whose benzene ring involves a system transmitting the substituent effect to the reaction centre $PO(OH)_2$.

As far as organophosphorus compounds are concerned it is however possible to apply the Hammett equation far more extensively. It is to be expected that the readily polarizable electronic sphera of P=O and P=S groups can well transmit the substituent effect to the reaction centre, say, to OH or SH groups of acids and thio acids of phosphorus, such as





no matter whether the aromatic rings are present or not. The large atomic radius of phosphorus provides for the lack of steric hindrance between atoms and atom groups bound to phosphorus or, in any case, minimizes them. Thus all conditions are met for the Hammett formula to be applied to such compounds, the P=O group playing hereby the part of the aromatic ring transferring the polar effects and the R and R′ groups bound to phosphorus producing the substituent effect. To prove this postulate we treated[30,31] the experimental data (partly obtained in our laboratory and partly taken from the literature) of the ionization constants of about 100 phosphorus acids in various solvents (water, 7 per cent, 50 per cent, and 80 per cent alcohol) that roughly gave rise to 200 ionization constants. Hypophosphorus acid ($R = R' = H$, $\sigma = 0$) was taken as reference acid. With other acids the R and R′ groups were H, OH, AlkO, ArO, Alk, and Ar with different substituents in the hydrocarbon radical and in various combinations. The constant ρ was taken for the first ionization step in aqueous solution as unity. The calculation was carried out in terms of the formula $pK = pK^\circ - \rho\Sigma\sigma$ with $\Sigma\sigma$ being the sum of the σ constants of R and R′ substituents. By successive approximation were calculated the σ constants characteristic of each substituent and the values of ρ and pK°. The linear relationship $pK = pK^\circ - \rho\Sigma\sigma$ proved to hold in all cases, as is seen from Figs. 2–6. In Table 1 are listed the σ constants obtained. It is natural that the σ constants for organophosphorus compounds are different from those evaluated by Hammett and subsequent workers[32] for the substituents in the benzene ring. Table 2 lists the corresponding values of constants ρ, pK° and correlation coefficients r.

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[29] H. H. Jaffe, L. D. Freedman and G. O. Doak, *J. Amer. Chem. Soc.* **75**, 2209 (1953).
[30] M. I. Kabachnik, *Dokl. Akad. Nauk SSSR* **110**, 393 (1956).
[31] T. A. Mastrukova, A. E. Shipov, T. A. Melentyeva and M. I. Kabachnik, *Zh. Obshch. Khim.* **29**, 2178 (1959).
[32] H. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958).

Considerable deviations from linear relationship are observed only with compounds containing the CCl_3 and CF_3 groups. Again, the σ constant for C_6H_5 and p-$CH_3C_6H_4$ groups depends on the number of these groups bound to the phosphorus atom. With

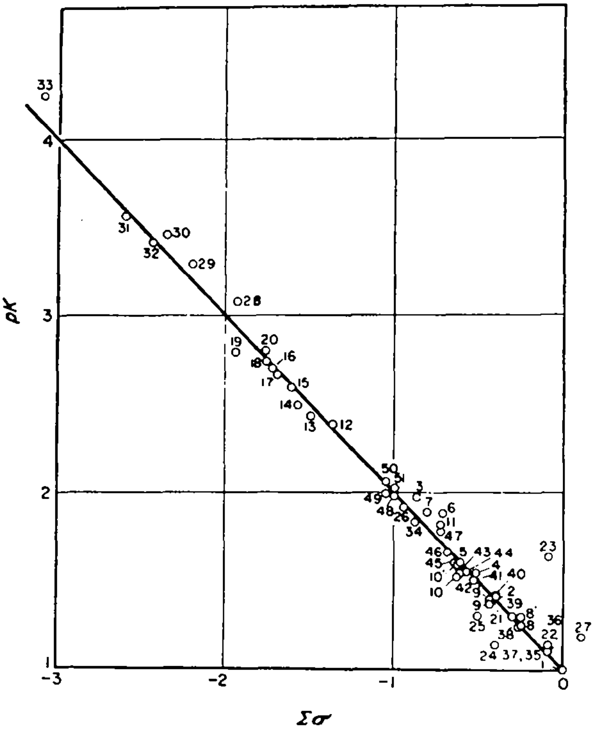
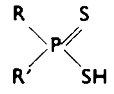


FIG. 2. Acids RR′P(O)OH in water, the first step $(pK_1)^{7,30,33-41}$ R and R′: (1) H, H; (2) H,HO; (3) HO,HO; (4) CH_3O,HO; (5) C_2H_5O,HO; (6) C_3H_7O,HO; (7) C_4H_9O,HO; (8) CH_3O,CH_3O; (9) C_2H_5O, C_2H_5O*; (10) C_3H_7O, C_3H_7O*; (11) C_4H_9O, C_4H_9O; (12) CH_3,HO; (13) C_2H_5,HO; (14) C_3H_7,HO; (15) C_4H_9,HO; (16) i-C_4H_9,HO; (17) i-C_3H_7,HO; (18) s-C_4H_9,HO; (19) t-C_4H_9,HO; (20) $C_{12}H_{25}$,HO; (21) $ClCH_2$,HO; (22) Cl_2CH,HO; (23) Cl_3C,HO; (24) $BrCH_2$, HO; (25) ICH_2,HO; (26) $HOCH_2$,HO; (27) F_3C,HO; (28) CH_3,CH_3; (29) C_2H_5,C_2H_5; (30) C_3H_7,C_3H_7; (31) i-C_3H_7,i-C_3H_7; (32) C_4H_9,C_4H_9; (33) t-C_4H_9,-C_4tH_9, (34) C_6H_5,HO; (35) m-$CH_3N^+H_2C_6H_4$,HO; (36) p-$(CH_3)_2N^+HC_6H_4$, HO; (37) m-$C_2H_5N^+H_2C_6H_4$,HO; (38) p-$NO_2C_6H_4$,HO; (39) m-$NO_2C_6H_4$,HO; (40) p-$NH_2SO_2C_6H_4$, HO; (41) p-$HOOCC_6H_4$,HO; (42) m-BrC_6H_4,HO; (43) m-ClC_6H_4,HO; (44) m-$HOOCC_6H_4$,HO; (45) p-BrC_6H_4,HO; (46) p-ClC_6H_4,HO; (47) m-HOC_6H_4,HO; (48) p-$CH_3C_6H_4$,HO; (49) p-HOC_6H_4,HO; (50) p-$C_2H_5OC_6H_4$,HO; (51) p-$CH_3OC_6H_4$,HO.

* Data obtained in 7 per cent alcohol.

one aromatic group the σ values amount to —0·481 ± 0·020 and —0·602 ± 0·010 and with two groups —0·592 ± 0·017 and —0·674 ± 0·016, respectively. This seems to be due to steric hindrance.

We have also investigated the relationship between pK and Σσ for dithio-acids of phosphorus such as



The data obtained are summarized in Fig. 7. The ionization constants of the acids of the dithio series proved to be little dependent on the nature of the radicals R and R′. In 7 per cent and 80 per cent alcohol, ρ amounts to 0·007 and −0·022 respectively[4] pK° being 1·74 and 2·64.

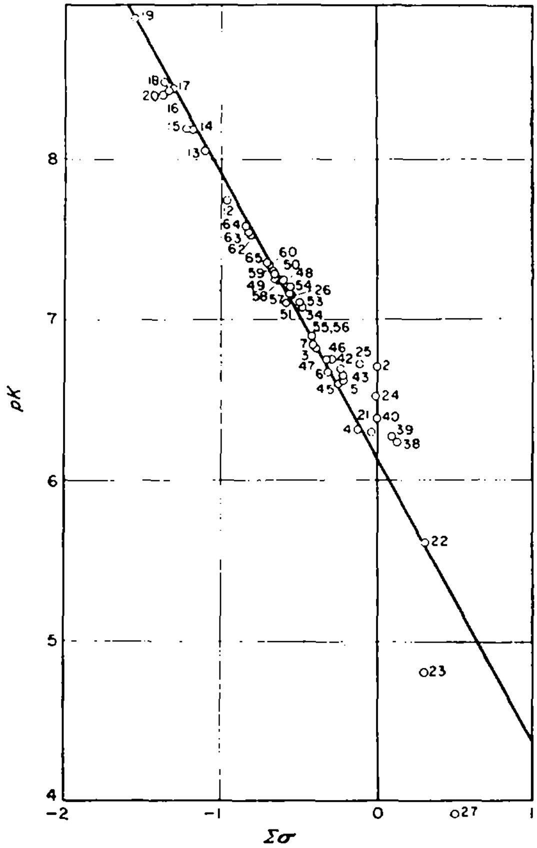


Fig. 3. Acids RR′P(O)OH in water; the second step (pK_2)[30,33–41] R and R′: denominations as in Fig. 2 and in addition: (53) p-$CH_3CONHC_6H_4$,HO; (54) 3,4-$CH_2O_2C_6H_3$,HO; (55) p-$^{-}OOCC_6H_4$,HO; (56) m-$^{-}OOCC_6H_4$,HO; (57) m-$NH_2C_6H_4$,HO; (58) m-$C_2H_5NHC_6H_4$,HO; (59) m-$CH_3NHC_6H_4$,HO; (60) m-$C_4H_9NHC_6H_4$,HO; (62) p-$NH_2C_6H_4$,HO; (63) p-$NH_2NHC_6H_4$,HO; (64) p-$CH_3NHC_6H_4$,HO; (65) p-$(CH_3)_2NC_6H_4$,HO.

4. *Phosphorus thio-acids. Synthetic methods and ionization constants*

To proceed to the investigation we synthesized 25 phosphorus monothio-acids involving derivatives of thiophosphoric, alkylthiophosphonic and dialkyl- (diaryl) thiophosphinic acids, mostly not described in the literature. To this end we have

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[33] H. H. Jaffe, *Chem. Rev.* **53**, 191 (1953).
[34] A. C. Mitchell, *J. Chem. Soc.* **117**, 957 (1920),
[35] F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.* 3598 (1954).
[36] W. D. Kumler and J. J. Eiler, *J. Amer. Chem. Soc.* **65**, 2355 (1943).
[37] P. C. Crofts and G. M. Kosolapoff, *J. Amer. Chem. Soc.* **75**, 3379 (1953).
[38] P. Rumpf and V. Chavane, *C.R. Acad. Sci., Paris* **224**, 919 (1947).
[39] P. C. Crofts and G. M. Kosolapoff, *J. Amer. Chem. Soc.* **75**, 5738 (1953).
[40] H. J. Emeléus, R. N. Haszeldine and R. C. Paul, *J. Chem. Soc.* 563 (1955).
[41] H. H. Jaffe, L. D. Freedman and G. O. Doak, *J. Amer. Chem. Soc.* **75**, 2209 (1953).
[42] P. Lesfauries and P. Rumpf, *C.R. Acad. Sci., Paris* **228**, 1018 (1949).

elaborated some general synthetic procedures that enabled us to obtain different acids in good and fair yields in a pure state.

Dialkyl thiophosphates $(RO)_2PSOH$ were obtained by treating triethylammonium dialkyl thiophosphates with mineral acids, the former being, in turn, synthesized by the sulphur addition to dialkyl hydrogen phosphites in the presence of triethylamine as follows:

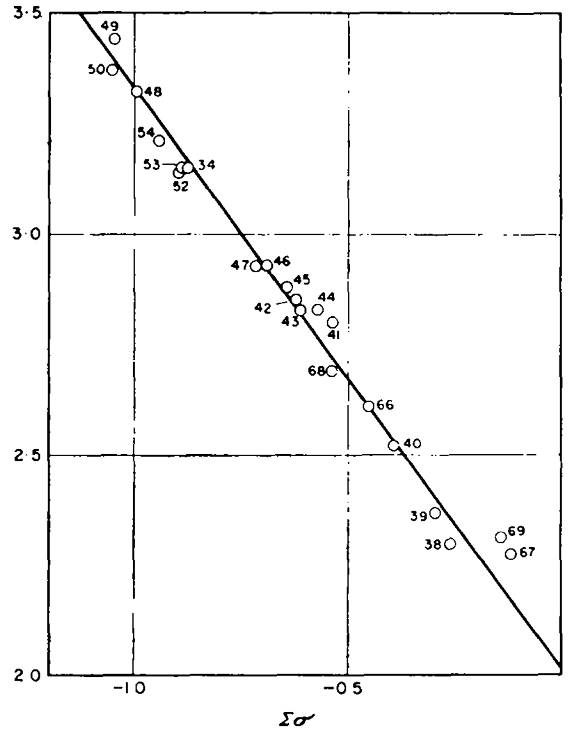

Fig. 4. Acids RR′P(O)OH in 50 per cent alcohol; the first step $(pK_1)^{30,38-41}$ R and R′: Denominations as in Figs. 2 and 3 and in addition: (66) C_6H_5O,HO; (67) C_6H_5O, C_6H_5O; (68) $p\text{-}CH_3C_6H_4O,HO$; (69) $p\text{-}CH_3C_6H_4O, p\text{-}CH_3C_6H_4O$.

$$(RO)_2PHO \xrightarrow[(C_2H_5)_3N+S]{} (RO)_2PSONH(C_2H_5)_3 \xrightarrow[HCl]{} (RO)_2PSOH \qquad \text{(Method A)}$$

We also used the route via sodium dialkyl thiophosphates following Arbuzov[43] and Foss[44]:

$$(RO)_2PHO \xrightarrow[Na]{} (RO)_2PONa \xrightarrow[S]{} (RO)_2PSONa \xrightarrow[HCl]{} (RO)_2PSOH \qquad \text{(Method B)}$$

Diphenyl thiophosphoric acid was produced as triethylammonium salt from diphenyl chlorophosphate, hydrogen sulphide, and triethylamine:

$$(ArO)_2POCl \xrightarrow[H_2S+(C_2H_5)_7N]{} (ArO)_2PSONH(C_2H_5)_3 \qquad \text{(Method C)}$$

Alkyl hydrogen alkylthiophosphonates RPS(OR)(OH), were prepared via two routes.

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[43] A. E. Arbuzov, *VIth Mendelew Congress Abstracts* Part 11, p. 124. Kharkov (1932).

[44] O. Foss, *Acta Chem. Scand.* 1, 8 (1947).

1. From dialkyl hydrogen thiophosphites according to the following scheme:

$$(RO)_2PHS \xrightarrow[Na]{} (RO)_2PSNa \xrightarrow[R'X]{} R'PS(OR)_2 \xrightarrow[NaOH]{} R'PS(OR)(ONa) \xrightarrow[HCl]{} R'PS(OR)(OH) \quad \text{(Method D)}$$

2. From alkyl hydrogen alkylphosphonous acids:

$$R'P(OR)HO \xrightarrow[Na]{} R'P(OR)(ONa) \xrightarrow[S]{} R'PS(OR)ONa \xrightarrow[HCl]{} R'PS(OR)(OH) \quad \text{(Method E)}$$

Diarylthiophosphinic acids, Ar_2PSOH, were produced following the known procedure due to Higgins *et al.*[45] (Method F). To obtain dialkylthiophosphinic acids, R_2PSOH, we made use of the Kosolapoff reaction[46] of dialkyl hydrogen phosphites with organo-magnesium compounds. The magnesium salts produced thereby are found readily to add sulphur to give magnesium dialkylthiophosphinates.[47] The general synthetic scheme is as follows:

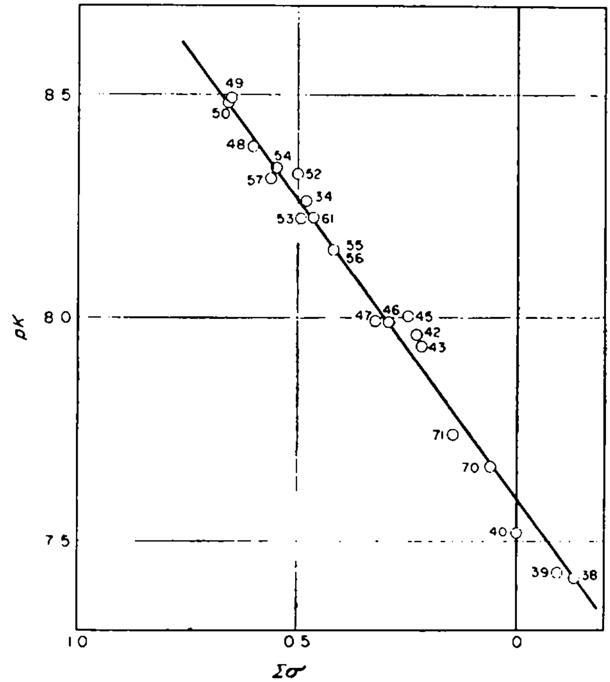

FIG. 5. Acids R-PO(OH)$_2$ in 50 per cent alcohol; the second step (pK_2)[30,33–41] R: Denominations as in Figs. 2, 3 and 4 and in addition: (70) C_6H_5O; (71) p-$CH_3C_6H_4O$.

$$(RO)_2PHO \xrightarrow{R'MgX} R_2'POMgX \xrightarrow{S} R_2'PS(OMgX) \xrightarrow[HCl]{} R_2'PSOH \quad \text{(Method G)}$$

An exception proved to be di-t-butylthiophosphinate, that we succeeded in obtaining by substituting t-butyllithium for t-butylmagnesium chloride.

The data concerning phosphorus thio-acids produced are given in Table 3.

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[45] W. A. Higgins, P. W. Vogel and W. G. Craig, *J. Amer. Chem. Soc.* **77**, 1864 (1955).
[46] G. M. Kosolapoff and R. M. Watson, *J. Amer. Chem. Soc.* **73**, 4101 (1951).
[47] T. A. Mastrukova, A. E. Shipov and M. I. Kabachnik, *Zh. Obsch. Khim.* **29**, 1450 (1959).

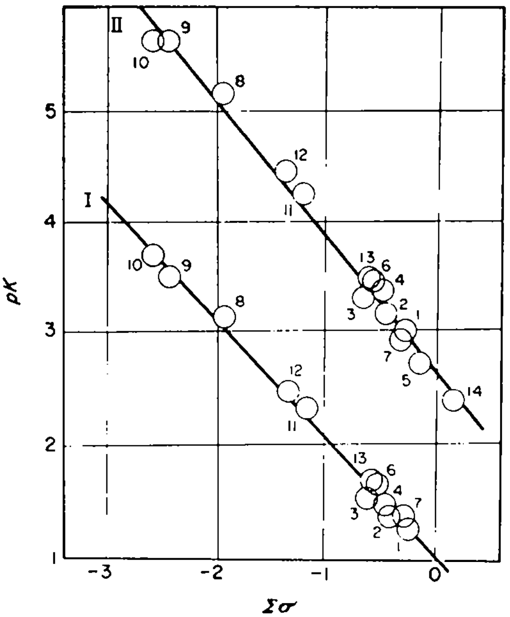

FIG. 6. Acids RR'P (O)OH in 7 per cent alcohol and 80 per cent alcohol at 20°. The first step (pK_1). R and R': (1) CH_3O, CH_3O; (2) C_2H_5O, C_2H_5O; (3) C_3H_7O, C_3H_7O; (4) C_6H_5O, HO; (5) C_6H_5O, C_6H_5O; (6) p-$CH_3C_6H_4O$,HO; (7) p-$CH_3C_6H_4O$, p-$CH_3C_6H_4O$; (8) CH_3, CH_3; (9) C_4H_9, C_4H_9; (10) i-C_4H_9, i-C_4H_9; (11) C_6H_5,C_6H_5; (12) p-$CH_3C_6H_4$, p-$CH_3C_6H_4$; (13) p-ClC_6H_4, p-ClC_6H_4; (14) m-$NO_2C_6H_4$, m-$NO_2C_6H_4$.

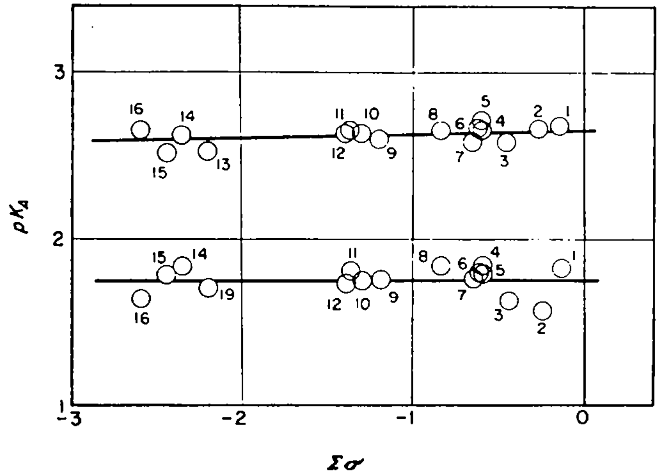

FIG. 7. Acids RR'P(S)SH in 7 per cent alcohol (1) and 80 per cent alcohol (2) at 20°. The first step (pK_1). R and R': (1) C_6H_5O, C_6H_5O; (2) CH_3O,CH_3O; (3) C_2H_5O,C_2H_5O; (4) i-C_3H_7O; i-C_3H_7O; (5) p-ClC_6H_4, p-ClC_6H_4; (6) i-C_4H_9O, i-C_4H_9O; (7) C_3H_7O,C_3H_7O; (8) C_4H_9O, C_4H_9O; (9) C_6H_5,C_6H_5; (10) CH_3,C_3H_7O; (11) p-$CH_3C_6H_4$, p-$CH_3C_6H_4$; (12) CH_3,C_4H_9O; (13) C_2H_5,C_2H_5; (14) C_3H_7, C_3H_7; (15) C_4H_9,C_4H_9, (16) i-C_3H_7, i-C_3H_7.

TABLE 1. THE CONSTANTS OF SUBSTITUENTS $\sigma^{30,31}$

R	σ	$\pm\Delta\sigma$	R	σ	$\pm\Delta\sigma$
H	0		m-$CH_3N^+H_2C_6H_4$	0·30	
HO	−0·393	0·007	p-$(CH_3)_2N^+HC_6H_4$	0·30	
CH_3O	−0·124	0·014	m-$C_2H_5N^+H_2C_6H_4$	0·30	
C_2H_5O	−0·214	0·014	p-$NO_2C_6H_4$	0·132	0·045
C_3H_7O	−0·315	0·048	m-$NO_2C_6H_4$	0·096	0·041
i-C_3H_7O	−0·291	0·004	p-$NH_2SO_2C_6H_4$	0·000	0·039
C_4H_9O	−0·411	0·043	p-$HOOCC_6H_4$	−0·140	0·040
i-C_4H_9O	−0·300	0·000	m-$HOOCC_6H_4$	−0·177	0·027
C_6H_5O	−0·061	0·012	m-ClC_6H_4	−0·219	0·024
p-$CH_3C_6H_4O$	−0·141	0·011	m-BrC_6H_4	−0·229	0·028
CH_3	−0·965	0·023	p-BrC_6H_4	−0·248	0·015
C_2H_5	−1·101	0·020	p-ClC_6H_4	−0·292	0·014
C_3H_7	−1·177	0·025	m-HOC_6H_4	−0·322	0·022
i-C_3H_7	−1·300	0·036	p-$^-OOCC_6H_4$	−0·418	0·008
C_4H_9	−1·219	0·015	m-$^-OOCC_6H_4$	−0·418	0·008
i-C_4H_9	−1·297	0·010	m-$HN_2NHC_6H_4$	−0·465	
s-C_4H_9	−1·363	0·023	C_6H_5	−0·481	0·020
t-C_4H_9	−1·546	0·098	C_6H_5*	−0·592	0·017
$C_{12}H_{25}$	−1·369	0·031	p-$CH_3CONHC_6H_4$	−0·493	0·028
$ClCH_2$	−0·034	0·034	p-$C_2H_5SC_6H_4$	−0·500	0·045
Cl_2CH	0·272	0·019	3,4-$CH_2O_2C_6H_3$	−0·549	0·018
Cl_3C	0·30	0·53	m-$NH_2C_6H_4$	−0·563	0·026
$BrCH_2$	−0·01	0·27	p-$CH_3OC_6H_4$	−0·586	0·034
$HOCH_2$	−0·546	0·036	p-$CH_3C_6H_4$	−0·602	0·010
F_3C	−0·50	0·27	p-$CH_3C_6H_4$*	−0·674	0·016
^-O	0		m-$C_2H_5NHC_6H_4$	−0·621	
			p-HOC_6H_4	−0·652	0·017
			m-$CH_3NHC_6H_4$	−0·654	
			p-$C_2H_5OC_6H_4$	−0·658	0·005
			m-$C_4H_9NHC_6H_4$	−0·671	
			p-$(CH_3)_2NC_6H_4$	−0·682	
			p-$NH_2C_6H_4$	−0·783	
			p-$NH_2NHC_6H_4$	−0·789	
			p-$CH_3NHC_6H_4$	−0·811	

* With two phenyl or p-tolyl groups at the phosphorus atom.

TABLE 2. THE REACTIONS CONSTANTS ρ AND THE VALUES OF p$K°$ AND r FOR THE IONIZATION OF ACIDS RR′PO(OH) AND $RPO(OH)_2$

Solvent	Ionization step	n	p$K°$	ρ	r
Water	K_1	58	1·00	0·990 (1·000)	0·976
Water	K_2	47	6·13	1·788	0·955
7% alcohol	K_1	12	1·01	1·050	0·996
50% alcohol	K_1	17	2·01	1·312	0·993
50% alcohol	K_2	19	7·59	1·358	0·992
80% alcohol	K_1	14	2·68	1·219	0·994

TABLE 3. PHOSPHORUS THIO-ACIDS RR′PSOH ⇄ RR′POSH

No.	R	R′	B.p.		M.p. °C	Synthetic method	Yield	n_D^{20}	d_4^{20}	Neutralization equivalent		Analyses					
												%C		%H		%P	
			°C	Pmm						Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1.	C_6H_5O	$C_6H_5O^a$	—	—	86–87	C	78	—	—	—	—	58·8 58·8	58·8	7·1 7·1	7·1	8·4 8·3	8·4
2.	CH_3O	CH_3O^b	—	—	156 dec.	B	67	—	—	—	—	—	—	—	—	18·7 18·8	18·9
3.	C_2H_5O	C_2H_5O	106–107	2·5	—	A,B	54·60	1·4719	1·1806	168·5 167·0	170·2	28·3 28·4	28·2	6·6 6·7	6·5	—	—
4.	i-C_3H_7O	i-C_3H_7O	89–90	1·5	—	A	72	1·4592	1·0906	198·5 197·6	198·2	36·3 36·7	36·4	7·6 7·5	7·6	15·4 15·8	15·6
5.	p-ClC_6H_4	p-ClC_6H_4	—	—	103–104	F	77	—	—	303·5 303·9	303·2	—	—	—	—	10·4 10·4	10·2
6.	iso-C_4H_9O	i-C_4H_9O	82·5–84	0·05	—	A	68	1·4570	1·0386	227·5 228·3	226·3	42·6 42·7	42·5	8·3 8·3	8·4	13·6 13·7	13·7
7.	C_3H_7O	C_3H_7O	108·5–109·5	0·09	—	A	62	1·4678	1·1023	199·6 198·7	198·2	36·2 36·6	36·4	7·8 7·9	7·6	15·8 15·6	15·6
8.	C_4H_9O	C_4H_9O	88–89	0·08	—	A,B	77·70	1·4654	1·0672	228·5 229·1	226·3	42·4 42·3	42·5	8·4 8·2	8·4	13·6 13·6	13·7
9.	CH_3	C_2H_5O	72·5	1	—	D	53	1·4927	1·0800	136·4 140·3	140·2	25·6 25·6	25·7	6·5 6·5	6·5	21·8 21·8	22·1
10.	C_6H_5	C_6H_5	—	—	141–142	F	79	—	—	234·3 234·1	234·3	61·4 61·6	61·5	4·5 4·7	4·7	13·0 13·1	13·2
11.	CH_3	i-C_4H_9O	112–112·5	0·5	—	D	60	1·4819	1·0824	168·1 168·3	168·2	36·0 36·0	35·7	7·9 7·9	7·8	18·1 18·3	18·4
12.	CH_3	C_3H_7O	106–107	2·5	—	D	62	1·4883	1·1293	154·0 154·3	154·2	31·3 31·4	31·2	7·2 7·2	7·1	—	—
13.	C_2H_5	C_2H_5O	84·5–85·5	2	—	D,E	65	1·4916	1·1337	154·2 154·0	154·2	31·0 31·0	31·2	7·2 7·2	7·1	20·0 19·7	20·1
14.	CH_3	C_4H_9O	90	0·5	—	D	60	1·4891	1·0998	169·7 168·2	168·2	35·6 35·4	35·7	7·8 7·9	7·8	18·1 18·2	18·4

TABLE 3 (*contd.*)

No.	R	R′	B.p.		M.p. °C	Synthetic method	Yield	n_D^{20}	d_4^{20}	Neutralization equivalent		Analyses					
												%C		%H		%P	
			°C	Pmm						Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
15.	C_3H_7	C_2H_5O	101–102	2	—	D	33	1·4875	1·0974	165·0 166·8	168·2	36·1 36·0	35·7	8·0 7·8	7·8	18·5 18·6	18·4
16.	C_4H_9	C_2H_5O	64·5–65	0·015	—	D	45	1·4831	1·0721	181·9 182·9	182·2	39·3 39·2	39·5	8·3 8·4	8·3	16·5 16·8	17·0
17.	C_2H_5	C_4H_9O	110	1	—	E	74	1·4873	1·0810	182·9 181·5	182·3	39·8 39·6	39·6	8·3 8·5	8·3	16·7 17·0	17·0
18.	i-C_4H_9	C_4H_9O	82	0·1	—	E	70	1·4821	1·0321	209·7 209·8	210·3	45·8 46·0	45·7	9·1 9·0	9·0	14·6 14·4	14·7
19.	C_2H_5	C_2H_5	88·5–89	1·5	11·5	G	69	1·5262	1·1090	138·1 138·0	138·2	34·6 34·5	34·8	7·6 7·9	8·0	22·4 22·1	22·4
20.	C_3H_7	C_3H_7	98·5–99	2	31	G	81	—	—	166·3 166·0	166·2	43·4 43·5	43·4	9·4 9·4	9·1	18·7 18·9	18·6
21.	C_4H_9	C_4H_9	81–81·5	0·25	c	G	74	—	—	193·9 193·9	193·3	49·4 49·2	49·4	9·8 10·0	9·9	16·0 16·2	15·9
22.	i-C_4H_9	i-C_4H_9	—	—	69·5–70·5	G	69	—	—	194·2 194·4	194·3	49·4 49·5	49·4	9·8 9·8	9·9	16·3 16·2	15·9
23.	i-C_3H_7	i-C_3H_7	—	—	76–77·5	G	64	—	—	166·2 166·3	166·2	43·6 43·6	43·4	9·1 9·2	9·1	—	—
24.	s-C_4H_9	s-C_4H_9	102–102·5	0·8	55·5–57	G	45	—	—	194·7 193·3	194·3	49·6 49·6	49·4	9·9 9·6	9·9	15.8 15·9	15·9
25.	t-C_4H_9	t-C_4H_9	—	—	144–5	G	23	—	—	191·7 194·4	194·3	49·8 49·5	49·4	9·8 9·8	9·9	15·6 15·8	15·9

[a] Sodium salt. [b] Triethylammonium salt. [c] M.P. Not determined, the acid being extremely hygroscopic.

Dialkyl dithiophosphoric acids, $(RO)_2PSSH$, were obtained following Carius and Pishchimuka[48–51].

Alkyl hydrogen alkyldithiophosphonates, RPS(OR′)SH, were produced by treating alkyl alkylchlorothiophosphonates with sodium hydrosulphide[52] as follows

$$R'PS(OR)Cl + NaSH \longrightarrow R'PS(OR)SNa \longrightarrow R'PS(OR)SH$$

Diaryldithiophosphinic acids, Ar_2PSSH, were obtained following Higgins *et al.*[45]

Dialkyldithiophosphinic acids were produced from dialkylthiophosphinic acids according to the scheme[53]:

$$R_2PSOH \xrightarrow[PCl_5]{} R_2PSCl \xrightarrow[NaSH]{} R_2PSSNa \xrightarrow[HCl]{} R_2PSSH.$$

In Table 4 are summarized the dithio-acids synthesized, their constants, analyses and ionization constants.

All pK_a's were evaluated by measuring the pH's of the partly neutralized solutions using a glass electrode (potentiometer Moskip LP-5, biphthalate buffer with pH=4·00, temperature 20°, acid concentration $5 \cdot 10^{-3}$). K_a was calculated by the equation:

$$^{*}K_a = (H^+) \cdot \frac{(Na^+) + (H^+) - K_w/(H^+)}{M - [/(Na^+) + (H^+) - K_w/(H^+)]}$$

within the experimental error of up to ±0·05 pK.

In Table 5 are listed the results of the determination of ionization constants of phosphorus thio-acids in 7 per cent† and 80 per cent alcohol by weight.

Results and discussion

As seen from Table 5 the ionization constants of phosphorus monothio-acids contrary to those of dithio-acids are steadily increasing with increasing $\Sigma\sigma$. In Fig. 8 the pK_a of phosphorus monothio-acids is plotted against $\Sigma\sigma$. Thus, for acids with $\Sigma\sigma < -1$ in 80 per cent alcohol one can see a good linear relationship. This region corresponds to acids whose tautomeric equilibrium has been shown to be shifted toward the thione form.[7,8]

The least squares treatment resulted in $pK_1^\circ = 2{\cdot}00$, $\rho_1 = 1{\cdot}329$ with the correlation coefficient, r_1 being 0·998. Where $\Sigma\sigma > -1$, one observes deviations from linearity, the greater the larger is the $\Sigma\sigma$. In 7 per cent alcohol the deviations start at lower values of $\Sigma\sigma$ so that only the points with $\Sigma\sigma < -2$ make the extrapolation reliable. Thereby $pK_1^\circ = 0{\cdot}69$, $\rho_1 = 0{\cdot}924$, and $r_1 = 0{\cdot}962$.

---

* K_w for 80% alcohol may be estimated to be 10^{-18} to 10^{-16} and in any case $K_w < 10^{-16}$.

$K_w/H \ll Na + H$ when measuring K_a of acids of medium acidity (pK_a 2–6). Therefore K_w/H may be disregarded. The K_a constants obtained in this work are apparent ionization constants. This is due to the use of glass electrodes for measurements in low aqueous media and the liquid connexion of chains, as well as concentrations instead of activities is known to lead to systematic errors. The deviations are nearly constant when concentrations are sufficiently low (ionin force $i = 0{\cdot}01$) and conditions are strictly constant as is the case in this work.

† 7 per cent alcohol was used because some of the acids under investigation are not soluble in pure water.

[48] L. Carius, *Liebigs Ann.* **112**, 190 (1859); **119**, 291 (1861).

[49] P. S. Pishchimuka, *J. Russ. Phys. Chem. Soc.* **44**, 1206 (1912).

[50] M. I. Kabachnik and T. A. Mastrukova, *Izv. Akad. Nauk SSSR* 121 (1953).

[51] W. E. Bacon and W. M. Le Suer, *J. Amer. Chem. Soc.* **76**, 670 (1954).

[52] N. N. Godovikov, *Chemistry and Application of Organophosphorus Compounds* p. 212. AN, Moscow (1957).

[53] M. I. Kabachnik, T. A. Mastrukova, A. E. Shipov and T. A. Melentyeva, *Dokl. Akad. Nauk SSSR* **124**, 1061 (1959).

TABLE 4. PHOSPHORUS DITHIO-ACID RR'PSSH

No.	R	R'	B.p.		n_D^{20}	d_4^{20}	Neutralization equivalent		$\Sigma\sigma$	pK		Analyses					
			°C	mm			Found	Calc.		7% Alc.	80% Alc.	%C		%H		%P	
												Found	Calc.	Found	Calc.	Found	Calc.
1.	C_6H_5O	C_6H_5O	m.p. 60–61		—	—	281·9 282·2	282·2	−0·122	1·81	2·66	51·0 50·9	51·1	3·9 3·8	3·9	11·0 10·8	11·0
2.	CH_3O	CH_3O	56–57	4	1·5340	1·2869	157·6 158·4	158·1	−0·248	1·55	2·64	15·0 14·9	15·2	4·4 4·4	4·5	—	—
3.	C_2H_5O	C_2H_5O	77–78	4	1·5073	1·1651	185·3 186·1	186·2	−0·428	1·62	2·56	25·8 25·9	25·8	6·1 6·1	5·9	16·5 16·7	16·7
4.	i-C_3H_7O	i-C_3H_7O	71–72	3	1·4918	1·0911	214·3 213·8	214·3	−0·582	1·82	2·65	—	—	—	—	14·4 14·5	14·5
5.	p-ClC_6H_4	p-ClC_6H_4	m.p. 82–83		—	—	318·7 318·2	319·2	−0·584	1·79	2·69	d					
6.	i-C_4H_9O	i-C_4H_9O	77·5–78	1·5	1·4921	1·0620	242·0 242·3	242·3	−0·600	1·79	2·65	20·0 19·9	19·8	3·6 3·7	3·7	12·6 12·7	12·8
7.	C_3H_7O	C_3H_7O	85–86	3	1·4987	1·1040	213·5 213·3	214·3	−0·630	1·75	2·57	—	—	—	--	14·4 14·4	14·5
8.	C_4H_9O	C_4H_9O	99–99·5	2	1·4971	1·0722	242·3 242·0	242·3	−0·822	1·83	2·64	19·7 19·6	19·8	3·6 3·6	3·7	12·6 12·8	12·8
9.	C_6H_5	C_6H_5	m.p. 56		—	—	250·2 250·4	250·3	−1·184	1·75	2·60	57·7 57·5	57·6	4·5 4·4	4·4	12·2 12·0	12·4
10.	CH_3	$C_3H_7O^{a,f}$	m.p. 62–63		—	—	190·9[b] 191·2	192·2	−1·280	1·74	2·63	24·8 24·9	25·0	5·3 5·1	5·2	—	—
11.	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	m.p. 80–81		—	--	278·5 278·6	278·4	−1·348	1·81	2·65					11·0 11·0	11·1
12.	CH_3	C_4H_9O	60·5–62	0·5	1·5298	1·1131	184·3 184·6	184·2	−1·376	1·73	2·63	32·6 32·5	32·6	7·1 7·2	7·1	--	—
13.	C_2H_5	$C_2H_5^a$	m.p. 122·5–124		—	—	179·1[b] 178·2	176·2	−2·202	1·71	2·53	22·6[c] 22·8	22·6	6·7[c] 6·6	6·8	--	—
14.	C_3H_7	C_3H_7	91–91·5	2	1·5632	1·0691	181·4 181·9	182·3	−2·354	1·84	2·63	39·2 39·1	39·5	8·1 8·0	8·3	16·6 16·8	17·0
15.	C_4H_9	C_4H_9	99–99·5	2	1·5481	1·0314	210·7 209·1	210·4	−2·438	1·79	2·52	45·8 45·7	45·7	9·2 9·0	9·1	14·3 14·5	14·7
16.	i-$C_3H_7^a$	i-$C_3H_7^a$	m.p. 153–154·5		—	—	206·6[b] 204·2	204·3	−2·600	1·64	2·66	32·0[e] 31·8	32·4	7·4[e] 7·3	7·3	—	—

[a] Sodium salt. [b] Iodomtric equivalent of the salt determined. [c] Analysis of $(C_2H_5)PSSNa{\cdot}2H_2O$. [d] Analysis for Cl: Found %: 22·4, 22·3. Calc. %: 22·2. [e] Analysis of $(i\text{-}C_3H_7)_2PSSNa{\cdot}H_2O$. [f] $CH_3(C_3H_7O)PSSH$ b.p. 56·5° (0·55 mm), n_D^{20} 1·5400, d_4^{20} 1·1430.

TABLE 5. pK_a AND K_T OF PHOSPHORUS THIO-ACIDS RR′PSOH ⇄ RR′POSH

No.	R	R′	Σσ	p*Ka*		a = p*Ka* − pK_1		$K = 10^a - 1$		Thiol form in per cent			
				7% Alc.	80% Alc.	7% Alc.	80% Alc.	7% Alc.	80% Alc.	7%		80%	
										Present work	7, 8	Present work	7, 8
1	2	3	4	5		6		7		8			
1	C_6H_5O	C_6H_5O[a]	−0·122	1·50	[b]	0·70	—	4·01	—	80		79	
2	CH_3O	CH_3O[c]	−0·248	[d]	2·80	—	0·47	—	1·95	74	72	68	22
3	C_2H_5O	C_2H_5O	−0·428	1·49	2·84	0·41	0·27	1·57	0·86	64	70	46	21
4	i-C_3H_7O	i-C_3H_7O	−0·582	1·59	2·90	0·37	0·13	1·34	0·35	54	74	29	25
5	*p*-ClC_6H_4	*p*-ClC_6H_4	−0·584	1·60	3·00	0·32	0·22	1·34	0·66	54		28	
6	i-C_4H_9O	i-C_4H_9O	−0·600	1·55	2·94	0·31	0·14	1·04	0·38	52	76	27	26
7	C_3H_7O	C_3H_7O	−0·630	1·55	2·93	0·28	0·09	0·91	0·23	50	76	24	26
8	C_4H_9O	C_4H_9O	−0·822	1·65	3·14	0·20	0·05	0·58	0·12	38		11	
9	CH_3	C_2H_5O	−1·179	1·82	3·51					19	0	2	0
10	C_6H_5	C_6H_5	−1·184	1·88	3·58					18		2	
11	CH_3	i-C_4H_9O	−1·265	1·81	3·69					16		1	
12	CH_3	C_3H_7O	−1·280	1·87	3·78					15		1	
13	C_2H_5	C_2H_5O	−1·315	1·88	3·72					14	0	1	0
14	CH_3	C_4H_9O	−1·376	1·95	3·77					12		0·8	
15	C_3H_7	C_2H_5O	−1·391	2·00	3·81					12	0	0·7	0
16	C_4H_9	C_2H_5O	−1·433	2·11	3·95					10	0	0·6	0
17	C_2H_5	C_4H_9O	−1·512	2·21	4·01					9		0·4	
18	i-C_4H_9	C_4H_9O	−1·708	2·20	4·29					5		0·2	
19	C_2H_5	C_2H_5	−2·202	2·80	4·88					1		0·1	
20	C_3H_7	C_3H_7	−2·354	2·83	5·10					1		0	
21	C_4H_9	C_4H_9	−2·438	2·91	5·14					0·8		0	
22	i-C_4H_9	i-C_4H_9	−2·594	3·17	5·46					0·5		0	
23	i-C_3H_7	i-C_3H_7	−2·600	3·03	5·46					0·5		0	
24	s-C_4H_9	s-C_4H_9	−2·726	3·10	5·71					0·4		0	
25	t-C_4H_9	t-C_4H_9	−3·092	3·91	6·09					0		0	

[a] The pH of triethylammonium salt solution was measured, p*K* was calculated from the salt hydrolysis constant within ±0·1 p*K*.

[b] The p*K* evaluation from the salt hydrolysis constant was hindered because of the unreliability of the constant K_w for 80% al% alcohol.

[c] Sodium salt. [d] Data not precise due to the ready hydrolysis of the CH_3O group.

Table 5 lists the deviations from linearity of acids 1 to 8 (Column 6) as well as the tautomeric equilibrium constants calculated therefrom in terms of equation X (Column 7). It will be seen that at high $\Sigma\sigma(\Sigma\sigma > -0{\cdot}8)$ the equilibrium is characterized by an increased amount of the thiol form, particularly in the 7 per cent aqueous alcoholic solution. In this solvent the two forms of diisobutyl thiophosphoric acid ($\Sigma\sigma = -0{\cdot}600$) are equivalent. At still higher $\Sigma\sigma$ values the thiol form predominates, amounting to 80 per cent with diphenyl thiophosphoric acid ($\Sigma\sigma = -0{\cdot}122$). In the 80 per cent alcohol the forms are balanced at $\Sigma\sigma \cong -0{\cdot}300$ and then the thiol form percentage is rapidly growing with increasing $\Sigma\sigma$.

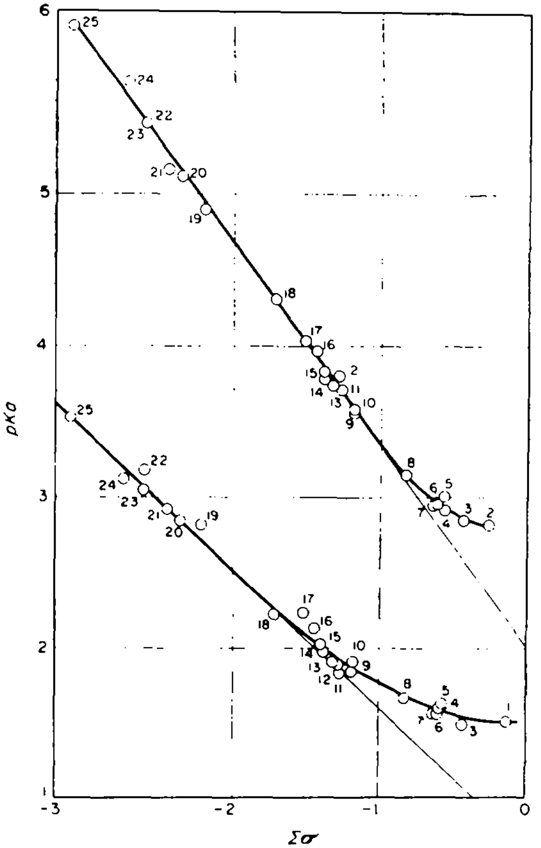

Fig. 8. A plot of pK_a vs. $\Sigma\sigma$ for phosphorus monothio-acids

The deviations from linear relationship provide thus a means to follow quantitatively the effect of the structure of phosphorus thioacids and the nature of the solvent on the equilibrium of tautomeric forms.

In turn, the tautomeric equilibrium constants must correspond to the Hammett equation

$$\mathrm{p}K_T = \mathrm{p}K_T{}^{\circ} - \rho_T\Sigma\sigma \qquad \text{(XI)}$$

The plot of pK_T versus $\Sigma\sigma$ in 7 per cent and 80 per cent alcohol is given in Fig. 9. It will be seen that the linearity is fairly good. The conventional treatment resulted for 7 per cent alcohol in $\log K_T^\circ = 0{\cdot}74$, $\rho_T = 1{\cdot}172$, $r = 0{\cdot}970$ and for 80 per cent alcohol: $\log K_T^\circ = 0{\cdot}85$, $\rho_T = 2{\cdot}139$, $r = 0{\cdot}961$.

These data allow to calculate the percentage of thiol forms of all compounds under investigation in 7 per cent and 80 per cent alcohol, the data being listed in Table 5, Column 8.

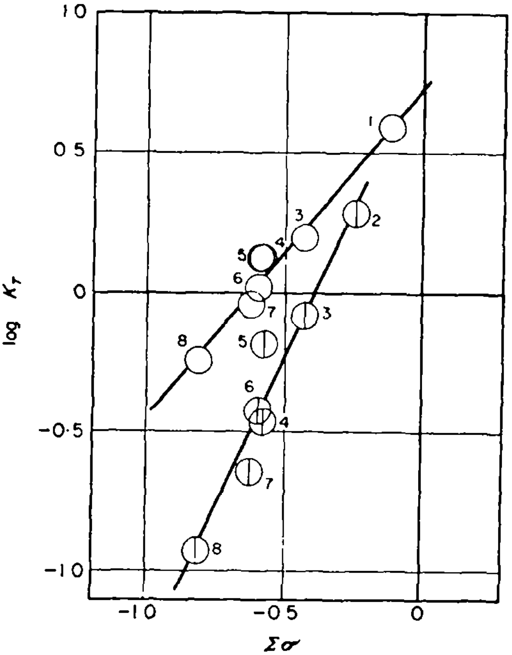

FIG. 9. A plot of pK_T vs. $\Sigma\sigma$ for phosphorus thio-acids

In the same column (8) are listed comparative data previously obtained with some acids using another method.[7,8]* The agreement is seen to be rather satisfactory particularly if one bears in mind that the two methods are based on different principles.

* These data were previously obtained starting from the concept that the Brønsted equation is strictly valid for organo-phosphorus acids.[7,8] Our investigation of a great number of compounds has however shown that the slope of the straight line $pK_{a_1} = \alpha pK_{a_2} +$ const. for acids RR′POOH is not equal to 45°, but somewhat differs from it. As to acids RB′PSSH, the overlapping of the ionization constants of different acids of this type in the 7 per cent and 80 per cent alcohol makes it extremely difficult to plot the Brønsted straight line. Therefore these data cannot be claimed to be exact.