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Quantitative Analysis of Influence of Structure on Reactivity of Four-coordinated Phosphorus Compounds

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A survey of the systematic application of correlation analysis to structural effects in organic compounds of four-coordinated quinquevalent phosphorus showed that the axiomatics of modern analysis (including possible types of intramolecular interaction between fragments of organic molecules and mathematical models of such interaction) will provide an adequate description of the effects of substituents attached to the phosphorus atom. Quantitative resolution into individual components of the structural effects governing the strengths of organophosphorus acids indicates that the widely used σ^{ph} constants are complicated in nature, comprising contributions by inductive, steric, and resonance interactions of substituents with the phosphorus atom. A list of 104 references is included.

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I. INTRODUCTION

The intensive development of the chemistry of organophosphorus compounds is due to their widespread use in industry, medicine, agriculture, and other fields. Identification of the properties of practical importance and especially problems involved in the planned synthesis of such compounds make necessary further broadening and deepening of theoretical research in organophosphorus chemistry. One fundamental problem common to the whole of organic chemistry—the search for quantitative relations describing the effects of various factors on the reactivity and the physical and physicochemical properties of compounds—has now been satisfactorily solved in terms of correlation analysis[1-3]. Correlation equations are widely employed also in the chemistry of organophosphorus compounds. As early as 1953 Jaffe et al. showed that the Hammett equation will give a good description of the pK_a of aromatic phosphonic acids[4]. Later Kabanchik[5] found that this equation is applicable to the most diverse organic acids of phosphorus, provided that special constants σ^{ph} are used for *P*-substituents. These constants and their resolution into inductive and resonance components[6] have provided satisfactory descriptions of many types of reactions occurring both at the phosphorus atom and in a side-chain, and also of various physical and physicochemical properties of organophosphorus compounds[7,8]. Since, like the Hammett σ-constants, these are empirical constants, simple equations containing a single parameter can be employed, which has proved convenient for solving many problems of organophosphorus chemistry. However, their use automatically excludes the possibility of comparing, on the basis of correlation analysis and the corresponding equations, reaction series of organophosphorus compounds with those involving other organic or hetero-organic compounds.

Qualitative ideas on possible universal types of interaction (and their mechanisms) between fragments of organic molecules were formulated in theoretical organic chemistry long ago[9]. Correlation analysis, having established a list of possible interactions, conferred a quantitative form on these ideas[1,10] (mathematical models of individual types of interaction), by regarding any interaction as a departure from additivity[11-13] and introducing measures of the ability of substituents (molecular fragments) to undergo various types of interaction. Inspection of a large quantity of factual information on the effect of substituent structure on reactivity of organic compounds led to the formulation of axioms of correlation analysis, which reduced essentially to the following postulates.

1. Three types of intramolecular interactions—inductive, steric, and resonance—are possible between uncharged fragments (substituents) in organic molecules.
2. The change in free energy accompanying reaction or activation can be represented quite accurately as the sum of contributions by these interactions (Taft's first postulate[10]).
3. The principle of linearity of free energies applies to each of these contributions (Taft's second postulate[10]).
4. The contribution by any interaction between two structural fragments is proportional to the product of the corresponding constants characterising the ability of the fragments to undergo the given type of interaction (the Hine–Pal'm postulate[11-15]).
5. In addition to the above types of interaction, charged fragments can also have electrostatic interaction, described by an appropriate mathematical model[1,16] and inversely proportional to the macroscopic dielectric constant of the medium (Palm's postulate).

The scales of the ability of various substituents to undergo the above types of interaction (measured by the constants σ^*, E_S, σ^0, σ^+, etc.) have been calculated from experimental data for different series with variation in substituents mainly at a carbon atom. However, it has now been firmly established that these axioms and also the corresponding measures of the capacity of substituents for various types of interaction can be satisfactorily applied to the quantitative description of diverse kinetic and equilibrium series in which substituents are varied at atoms other than carbon—sulphur, nitrogen, oxygen, silicon, etc.—as is indicated by ample

practice of correlation analysis[1-3,17,18]. Special investigations[1,19-26] have been made on problems associated with the limits of applicability of these axioms (completeness of the list of interactions, universality of the corresponding measures (constants), etc.).

Systematic application, to the enthalpies of formation of diverse organic compounds in the gas phase, of the principle of polylinearity[11,27] together with the above postulates not only has enabled a fundamentally new and accurate scheme of calculation to be constructed for these most important standard thermodynamic characteristics of compounds but also has shown that the mathematical models of correlation analysis for individual types of interaction agree well with the corresponding contributions to heats of formation[19-23].

Nor have accurate measurements of the acidity and basicity of various classes of organic compounds in the gas phase necessitated a fundamental revision of the main concepts of correlation analysis (if the problem of the nature of the influence of alkyl groups is disregarded), since a good correlation usually exists between structural effects on dissociation in the gas phase and in solution[28-34], indicating that structural effects on the strengths of acids and bases in the gas phase and on the capacity of their neutral and ionic forms for solvation are of the same type. It would have been difficult to expect a different result in these terms, since correlation equations provide an adequate description of the influence of structural factors on the strengths of organic acids and bases in the most diverse pure media and their mixtures which vary markedly in dielectric properties, polarisability, and capacity for various types of specific solvation[18,25,26,35]. The nature of the influence of alkyl groups, however, has long been a matter of controversy in the correlation analysis of structural effects in the liquid phase[1,2,15,19,20,36-39], as also the physical nature of the inductive (polar) effect. But there is no doubt about the actual existence of such effects.

The satisfactory correlation of the properties of organophosphorus compounds with the σ^{pH} constants indicates that the principle of the linearity of free energies can be widely applied to describe the influence of *P*-substituents on the reactivity of these compounds. Isolated studies have shown also that certain of their properties can be described in terms of correlation relations based on the "carbon" constants of the substituents[4,40-44]. However, the fundamental applicability of the entire axiomatics of correlation analysis to the structural effects of *P*-substituents has remained an open question until recently, as also the limits of applicability of the axiomatics in organophosphorus chemistry. Other non-trivial questions that have not been settled are whether (i) the list of possible types of interaction and (ii) the mathematical models for individual types are adequate to describe the effects of such substituents.

Attempts by Pal'm[45] and by Charton[46] to solve these problems did not give unambiguous results[8]. The aim of the present Review consists in setting out the main results of investigations[47-55] which the Reviewers regard as providing answers to the above questions and leading to some unexpected but logically self-evident conclusions. In view of the great diversity of the valency and coordination states of the phosphorus atom in various organophosphorus compounds, only the effects of substituents attached to a four-coordinated quinquevalent phosphorus atom of the type $\rangle$PO have been considered, since such compounds have been most widely investigated in terms of their reactivity and various physicochemical properties, and the correlation of these properties with structure has also been studied. Furthermore, analogies for processes occurring at such a group can be found in classical organic chemistry, in particular among those taking place at a carbonyl group[56-62].

Because of the wide applicability of σ^{ph} constants in organophosphorus chemistry an analysis has been made of them[47-55] and also of the dissociation of various acids of general formula XYPOOH, the standard reaction series for their determination. Furthermore, a systematic comparison has been made of the influence of substituents on reaction centres containing carbonyl and phosphoryl to reveal specific structural effects characteristic of the phosphorus atom alone; the combined influence of substituents attached to a four-coordinated phosphorus atom has been examined.

II. EQUATION FOR pK_a OF ACIDS XYPOOH

On the above postulates the difference $\Delta\Delta G^0$ between the changes in free energy $\Delta G^0(XY)$ and $\Delta G^0(X_0Y_0)$ accompanying dissociation of the acids XYPOOH and X_0Y_0POOH can be written as the sum

$$\Delta\Delta G^0 = \Delta G^0(XY) - \Delta G^0(X_0Y_0) = \Delta\Delta G^0_{ind} + \Delta\Delta G^0_{ster} + \Delta\Delta G^0_{res}. \quad (1)$$

of contributions $\Delta\Delta G^0_{ind}$, $\Delta\Delta G^0_{ster}$, and $\Delta\Delta G^0_{res}$ by inductive, steric, and resonance interactions of the substituents X (X_0) and Y (Y_0) with the reaction centre and between themselves X and Y or X_0 and Y_0. The quantity $\Delta\Delta G^0$ corresponds to the change in free energy in the equilibrium proton transfer

$$XYP(O)OH + X_0Y_0P(O)O^- \rightleftharpoons XYP(O)O^- + X_0Y_0P(O)OH.$$

The quantities

$$\Delta\Delta G^0_{ind} = \Delta G^0_{ind}(XY) - \Delta G^0_{ind}(X_0Y_0),\ \Delta\Delta G^0_{ster} = \Delta G^0_{ster}(XY) - \Delta G^0_{ster}(X_0Y_0),\ \Delta\Delta G^0_{res} = \Delta G^0_{res}(XY) - \Delta G^0_{res}(X_0Y_0)$$

are the differences between the contributions by the corresponding interactions to the changes in free energy accompanying detachment of a proton from the acids XYPOOH and X_0Y_0POOH. In conformity with the practice of correlation analysis we adopt as standard substituent the methyl group: i.e. $X_0 = Y_0 = CH_3$.

In terms of the principle of polylinearity[1,27] and the homogeneity of inductive interaction[1]

$$\Delta\Delta G^0_{ind} = \Delta G^0_{ind}(XY) - \Delta G^0_{ind}(X_0Y_0) = -\alpha^*\Delta\sigma^*_{rc}\sum\sigma^* - \alpha^*\Delta Z^*\sigma^*_X\sigma^*_Y \quad (2)$$

where α^* is the universal constant[25] of inductive interaction,

$$\Delta\sigma^*_{rc} = \sigma^*(CH_3POOH) - \sigma^*(CH_3POO^-)$$

is the difference between the inductive constants of the reaction centre in initial and final states, and

$$\Delta Z^* = Z^*(\rangle POOH) - Z^*(\rangle POO^-)$$

is the difference between the conductivities of inductive interaction between X and Y through the reaction centre in its initial and final states. The first term in Eqn.(2) is the contribution to $\Delta\Delta G^0$ by inductive interaction of X and Y with the reaction centre†, and the second term by inductive interaction between X and Y through the reaction centre.

If the acid and its anion have a tetrahedral structure[63,64], it is obvious from symmetry considerations that the contribution

$$\Delta\Delta G^0_{ster} = \Delta G^0_{ster}(XY) - \Delta G^0_{ster}(X_0Y_0) = -\Delta a\sum E_s \quad (3)$$

† Here and subsequently. $\sum\sigma^*\left(\sum E_s\right) = \sigma^*_X + \sigma^*_Y\left(E_{sX} + E_{sY}\right)$.

where

$$\Delta\alpha = \alpha(CH_3POOH) - \alpha(CH_3POO^-)$$

is the difference in sensitivity of the reaction centre, in initial and final states, to steric interaction with substituents#. Equation (3) contains no cross terms: i.e. contributions by steric interactions between substituents X and Y in the acid and in its anion are assumed to be similar (or equal) in magnitude, a hypothesis which has been confirmed[47].

Substitution of Eqns.(2) and (3) in (1) followed by conversion to pK_a values yields

$$pK_a(XYP(O)OH) = pK_a(Me_2P(O)OH) - \rho^* \sum \sigma^* - \gamma\sigma_X^*\sigma_Y^* - \delta \sum E_s + \Delta\Delta G^0_{res}/2.303RT \quad (4)$$

where

$$\rho^* = \alpha^*\Delta\sigma^-_{ph}/2.303RT;\ \gamma = \alpha^*\Delta Z^*/-2.303RT;\ \delta = \Delta\alpha/2.303RT.$$

Hence, provided that all the above postulates are valid, the pK_a values of XYPOOH acids, in which X and Y are uncharged substituents, should be given by Eqn.(4).[47] With regard to experimental verification of this equation, the question of resonance interaction merits the special comment that, since hyperconjugation plays no great part[1,19] in the ground state of organic compounds, it was accepted[47-55] that aryl groups, αβ-unsaturated substituents, and substituents whose first atom is a heteroatom having a lone pair of electrons are capable of conjugating with an electron-deficient reaction centre of $-C$ type: all other substituents—alkyl groups, $X^1X^2X^3M[CH_2]_m$, $X^1X^2CH[CH_2]_m$, and $XCH_2[CH_2]_m$ (the X are various electronegative groups, and $m = 0, 1, 2, \ldots$)—were regarded as incapable of conjugation[19,47].

III. ANALYSIS OF σ^{ph} CONSTANTS

The dissociation of XYPOOH acids was chosen[5] as standard series for deducing σ^{ph} constants, and the hydrogen atom was adopted as standard substituent:

$$pK_a(XYP(O)OH) = pK_a(H_2P(O)OH) - \sum \sigma^{ph} \quad (5)$$

It follows from Eqns.(4) and (5) that the σ^{ph} constants of substituents incapable of conjugation with the reaction centre should be given by[47]

$$\sigma^{ph} = \sigma^{ph}(Me) + \rho^*\sigma^* + 0.5\gamma(\sigma^*)^2 + \delta E_s \quad (6)$$

The regression dependence

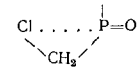
$$\sigma^* = -(0.938 \pm 0.036) + (1.151 \pm 0.076)\sigma^* - (0.199 \pm 0.031)(\sigma^*)^2 + (0.149 \pm 0.030)E_s$$

$$n = 25;\ R = 0.987;\ S_0 = 0.11 \quad (7)$$

has been found[47] for 25 such substituents. Here and subsequently n is the number of experimental points described by a given equation, $r(R)$ the (multiple) correlation coefficient, and $s_0(S_0)$ the (multiple) regression standard. All coefficients in the relation (7) are statistically significant, and from (6) the independent term is identical with $\sigma^*(CH_3)$.[7]

The reproducibility of pK_a values determined by potentiometric titration has been estimated[66,67] as 0.04–0.05 logarithmic unit. The pK_a values used[7] in calculating σ^{pH} have been measured at 20–25 °C, in which temperature range the divergence in estimates of pK_a for organic acids of phosphorus may reach estimates of pK_a for organic acids of phosphorus may reach ±0.03 lg unit[68]. In virtue of the law of the accumulation of errors the uncertainty in the calculation of σ^{ph} is thus at least ±0.09 lg unit. Furthermore, the σ^{ph} constants recommended[7] for use had been averaged over many reaction series, and such averaging replaces[17] the apparent reliability by considerable uncertainty in the constants. Consequently the regression (7) is close to adequacy.

In the resolution of σ^{ph} constants into inductive and resonance components σ^{ph}_{ind} and σ^{ph}_{res} non-zero resonance constants were ascribed[6,7] to many substituents and were not αβ-unsaturated and had no n-electrons on the α-atom. The especially high σ^{ph}_{res} values for mono-, di-, and tri-halogenomethyl groups were attributed[7,69] to a contribution by a transannular dative bond of type



However, such a bond was not detected[70] in the chlorine-35, bromine-79, and iodine-127 nuclear quadrupole resonance spectra of the compounds $(ClCH_2)_3PO$, $(ClCH_2)_2CH_3PO$, $(ICH_2)_3PO$, $(ICH_2)_2CH_3PO$, and $(BrCH_2)_2CH_3PO$. In terms of the regression (7) the resonance constants σ^{ph}_{res} for such substituents should be a combination of inductive and steric components (owing to incorrect resolution[6,7] of the σ^{ph} constants). In fact, for substituents described by regression (7) the relation

$$\sigma^{ph}_R = (0.059 \pm 0.046) - (1.202 \pm 0.042)\sigma^* + (0.237 \pm 0.050)E_s$$

$$n = 24;\ R = 0.9902;\ S_0 = 0.138$$

was found[47], from which only the point for cyanoethyl departs significantly.

Table 1. Values of $\overline{\Delta\sigma^{ph}}$ averaged over individual structural types of substituents*[48].

Type of substituent	m	$\overline{\Delta\sigma^{ph}}$
R_2N(R — Alk)	2	—0.79±0.06
PhO	1	—0.65
RO(R—H, Alk)	10	—0.62±0.02
RS(R — Alk)	4	—0.18±0.03
XC_6H_4(X—H, Alk, electroneg. subst.)	24	—0.07±0.01

*Here m is the number of substituents of the given structural type for which $\Delta\sigma^{ph}$ have been calculated.

Values of σ^{ph}_{calc} calculated by means of Eqn.(7) for substituents capable of conjugation are usually more positive than the experimental values σ^{ph}_{exp}: i.e. such substituents are characterised not only by inductive and steric effects but also by an additional effect that lowers the acidity of the compounds. This may be solely due to conjugation of the substituents with the reaction centre. On this basis the differences $\Delta\sigma^{ph} = \sigma^{ph}_{exp} - \sigma^{ph}_{calc}$ for these substituents were adopted as measures of their resonance capacity. For substituents of the same structural type calculated differences

Steric interaction is inhomogeneous[1,13,65], and therefore cannot be described by a mathematical model similar to that used for inductive interaction.

$\Delta\sigma^{ph}$ do not exceed the experimental uncertainty in the constants σ^{ph}_{exp}:[48] i.e. the ability of, for example, substituents RO, RS, and R_2N to conjugate is to a first approximation independent of R. Therefore average values $\overline{\Delta\sigma^{ph}}$ (Table 1) were taken[48] as the estimated capacities of such substituents for conjugation. An obvious correlation exists (Fig.1) between the $\Delta\sigma^{ph}$ values and the σ^{+}_{res} constants[24] representing the ability of the substituents to conjugate with a $-C$ type of reaction centre.

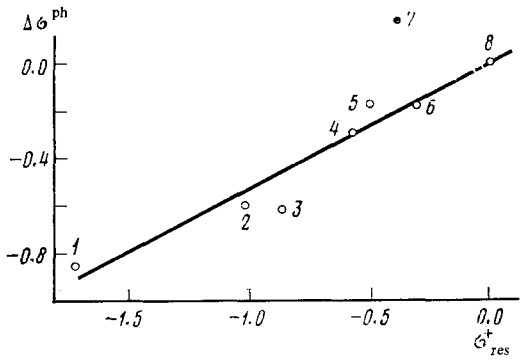


Figure 1. Correlation[48] between deviations $\Delta\sigma^{ph} = \sigma^{ph}_{exp} - \sigma^{ph}_{calc}$ and resonance constants σ^{+}_{res} for the substituents: 1) $(CH_3)_2N$; 2) CH_3O; 3) C_6H_5O; 4) F; 5) CH_3S; 6) C_6H_5; 7) Cl; 8) H.

The whole set of σ^{ph} constants (see compilation in Ref.48) is adequately described by the equation[48]

$$\sigma^{ph} = -(0.956 \pm 0.015) + (1.129 \pm 0.030)\,\sigma^{*} - (0.187 \pm 0.011)(\sigma^{*})^2 + (0.166 \pm 0.014)\,E_s - (0.952 \pm 0.44)\,\overline{\Delta\sigma^{ph}}$$
$$n=71;\ R=0.992;\ S_0=0.073\ . \qquad (8)$$

The estimated coefficients obtained in this regression, of the sensitivity of substituents to inductive and steric effects, coincide within the limits of their errors with the corresponding quantities in regression (7). The independent term, as Eqn.(6) requires, is identical with the $\sigma^{ph}(CH_3)$ constant. The coefficient accompanying the resonance contribution should be unity if $\overline{\Delta\sigma^{ph}}$ values have been introduced: the estimate of this coefficient in regression (8) is indeed close to unity.

Thus the above results[47,48] indicate that the σ^{ph} constants for *P*-substituents comprise inductive, steric, and resonance contributions that are adequately described in terms of the usual "carbon" constants σ^{*} and E_S and by means of $\Delta\sigma^{ph}$ values linearly related to the σ^{+}_{res} constants.

IV. INFLUENCE OF STRUCTURAL FACTORS ON STRENGTHS OF ACIDS XYPOOH

It has been shown above that the pK_a values of XYPOOH acids should be described by Eqn.(4), which itself should be defined by the pK_a of phosphinic acids, the pK_{a_1} and pK_{a_2} of phosphonic acids, and also all three pK_a of phosphoric acid if the fragment O^- is regarded as a substituent. In order to take into account the electrostatic interaction between two O^- substituents the electrostatic correction $\Delta pK_{el} = 1.2$ was calculated[49] from the equation suggested in Ref.16 and the geometry of the anion of phosphoric acid[63]. This correction was assumed to be constant for all phosphonic acids. The fundamental possibility of describing pK_{a_1}, pK_{a_2}, and pK_{a_3} by means of a single equation can be illustrated by the simple relation

$$pK_{a_3}(H_3PO_4) = 2pK_{a_2}(MeP(O)(OH)_2) - pK_a(Me_2P(O)OH) + \lg 3 - \lg 2$$

which follows from (4) and takes into account statistical corrections. This gives for $pK_{a_3}(H_3PO_4)$ an estimated 12.3, while the experimental value is 12.0–12.3.[71]

Table 2. Analysis of pK_a values (in water at 20–25 °C) by means of Eqn.(9).[49]

Coeff. or statistical criterion	Regression		
	№ 1*	№ 2**	№ 3***
a_0	3.075±0.055	3.075±0.54	3.122±0.046
a_1	−1.374±0.046	−1.275±0.046	−1.358±0.040
a_2	0.161±0.042	0.163±0.042	0.166±0.037
a_3	−0.230±0.027	−0.230±0.076	−0.230±0.024
a_4	1.259±0.077	1.250±0.076	1.221±0.084
a_5	0.271±0.076	0.263±0.091	0.256±0.041
a_6	3.242±0.054	4.486±0.041	3.160±0.041
a_7	1.815±0.079	1.813±0.079	1.790±0.078
n	72	72	109
R	0.9963	0.9976	0.9967
S_0	0.182	0.181	0.166

*Calculated disregarding compounds in which X and (or) Y = Ar.

**Calculated disregarding both compounds in which X and (or) Y = Ar and also the electrostatic correction.

***Calculated for the complete set of pK_a values (see compilation in Ref.49).

Table 2 lists results of an analysis[49] of pK_a values of XYPOOH acids given with statistical and electrostatic corrections by the equation

$$pK_a(XYP(O)OH) = a_0 + a_1\sum\sigma^{*} + a_2\sigma^{\bullet}_X\sigma^{\bullet}_Y + a_3\sum E_s + a_4 n_{RO} + a_5 n_{Ar} + a_6 n_{O^-} + a_7 n_{ArO} \qquad (9)$$

in which a_0–a_7 are the unknown coefficients (a_0–a_3 should include analogous coefficients in Eqn.(4) and a_4–a_7 are resonance contributions by the corresponding substituents) and n_{RO}, n_{Ar}, n_{O^-}, and n_{ArO} are the numbers of substituents RO (R = H, Alk), *p*- or *m*-XC_6H_4, O^-, and *p*-XC_6H_4O respectively. Such allowance for the resonance component is based on the hypothesis, made in analysing the σ^{ph} constants[48], that substituents capable of conjugation and of the same structural type make a constant resonance contribution§.

It was assumed[49] for all *p*- or *m*-XC_6H_4 groups that $E_S = 0$. Since this postulate is arbitrary[72], the inclusion of arylphosphinic and arylphosphonic acids in the general set with other

§ This procedure for isolating the resonance contribution was adopted also because experimental data[71] for phosphinic acids containing substituents incapable of conjugation were insufficient for the construction of a reliable regression.

acids may lead to errors in the estimated regression of coefficients. Consequently regression No.1 must be regarded as basic in Table 2. The agreement between the estimated coefficients in regressions 1 and 3 and the quite high statistical indices of the latter indicate that the postulated equality of the steric constants of methyl and aryl groups produces no appreciable errors. Disregard of the electrostatic correction increases the resonance contribution of the O^- substituent by this amount, while the remaining regression coefficients remain unchanged (cf. regressions 1 and 2).

Thus use of the constants σ^* and E_S respectively to characterise inductive and steric effects of substituents enables Eqn.(9) to provide a good description of pK_a values for phosphinic acids, pK_{a1} and pK_{a2} for phosphonic acids, and the three values for phosphoric acid. The range of variation in acid strength covered by this equation is 12 lg units: i.e. the relative precision of the description $S = 1.4\%$. The results in Table 2 indicate that substituents destabilise by an inductive mechanism ($a_1 < 0$), and stabilise by a conjugation mechanism ($a_4 - a_7 > 0$), the initial state in the dissociation of organic acids of phosphorus. The difference $\Delta\sigma^*_{rc}$ (Section II) calculated from $a_1 = -\alpha^*\Delta\sigma^*_{rc}/2.303RT$ (see Eqn.4) is 0.66. The corresponding value for the dissociation of aliphatic carboxylic acids (in water at 25 °C) is 0.77.[25] Since $\sigma^*(CH_3POOH) = 1.47$, we obtain $\sigma^*(CH_3POO^-) = 0.81$, whereas $\sigma^*(COOH) = 1.7$ and $\sigma^*(COO^-) = 0.93$.[25] Hence for the dissociation of organic acids of phosphorus and of aliphatic carboxylic acids not only are the $\Delta\sigma^*_{rc}$ values closely similar but also the inductive constants of initial and final states respectively of their reaction centres.

The statistical significance of the coefficient a_3 in Eqn.(9) indicates different intensities of steric interaction of the substituents X, Y with the fragment $\rangle$POOH and with the corresponding anion. The sign of a_3 shows that the acid becomes weaker as the steric effects of the substituents become greater. This can be explained by steric hindrance to solvation stabilisation of the anion by X and Y, as occurs in the dissociation of carboxylic acids containing bulky substituents[73-75]. Significant steric influence of substituents on the strengths of XYPOOH acids is demonstrated by the regression[54]

$$pK_{a_2}(XP(O)(OH)_2) = (7.987 \pm 0.048) - (1.345 \pm 0.037)\sigma^* - (0.210 \pm 0.046)E_s$$
$$n=6;\ R=0.9987;\ S_0=0.073 \qquad (10)$$

obtained for very accurate measurements[76] of pK_{a2} for six phosphonic acids containing substituents incapable of conjugation. The independent term coincides with the experimental value[76] of $pK_{a2}(CH_3PO(OH)_2)$, and estimates of the coefficients for inductive and steric contributions agree well with the corresponding estimates in the regression in Table 2. Exclusion of the steric contribution from regression (10) produces a sharp impairment of its statistical indices[54] (for example, the standard deviation is doubled).

V. NON-ADDITIVITY OF EFFECTS OF SUBSTITUENTS ATTACHED TO A FOUR-COORDINATED PHOSPHORUS ATOM

Equation (4) contains a cross term, a contribution proportional to the product of the inductive constants of the substituents. The presence of cross terms is implied by the general form of polylinear equations[1,27], and is interpreted as a change in the intensity of the effect of one factor under the influence of another factor. These non-additive effects are closely connected with the phenomenon of isoparametricity[1,77,78], and have now been shown for various pairs of factors (medium and structure, pressure and structure, reactant and substrate structures, etc.) in many organic reactions[1,77-89]. A well known example of such non-additivity is the dependence of activation energy on reactant structure[1,12,77,89]. The character of the combined influence of different factors is obviously determined by the detailed mechanism of the chemical process[1,27,77].

The statistical significance of a_2 in the regressions in Table 2 presupposes non-additivity of the inductive effects of substituents X and Y on the dissociation of XYPOOH acids. However, exclusion of the cross term from these regressions neither impairs appreciably the quality of the description nor changes the estimated coefficients a_0, a_1, and a_3–a_7.[49] The variables $\Sigma\sigma^*$, $\sigma^*_X\sigma^*_Y$, and ΣE_S in the regressions are strongly interdependent (non-orthogonal). Because of the many-sided interrelationship the estimate of one coefficient (e.g. a_2) may be shifted relative to its true value without appreciably displacing the estimates of other coefficients.

The non-orthogonality of the scales of constants representing the abilities of substituents (or solvents) to undergo various types of interaction is a common weak point in multidimensional correlation analysis, to which many investigators do not pay due attention. A frequent consequence of such non-orthogonality is that the absolute estimates of regression coefficients obtained by least squares lose their physical content and in general cannot be compared either within a single regression or with corresponding parameters in analogous equations for other processes.

There are in principle two possible escapes from such a situation—(i) rejection of the convenient method of least squares and (ii) preliminary factorisation of the variables—both unattractive for correlation analysis[90]. The latter procedure, which is widely used in experiment design, leads to variables losing their concrete meaning (physical or quasi-physical), and furthermore does not permit the construction of invariant scales of constants for substituents (or solvents). In the Reviewers' opinion, therefore, the most acceptable way at present is first to deduce various equations based on some *a priori* considerations (theoretical or formal), followed by logical analysis of the parameters in regression corresponding to these equations, in terms of the meaning that had been implied *a priori* in these parameters. In some cases a model calculation may prove very useful: coefficients therein are specified that are close to those in the regression obtained, values of the function to be correlated are then calculated from these coefficients and the corresponding set of variables, and these values are "coarsened" (errors close to those in the experimental data are introduced). After this the coefficients in the regression are found from the resulting values of the function and the original set of variables. Comparison of the results with the specified coefficients will indicate whether the correctibility of the variables will lead in a given case to displacement of the estimated coefficients.

A model calculation[49] made to test the displaceability of the estimated coefficient a_2 in the regressions in Table 2 indicates that with a given set of variables, even when the cross term is *a priori* significant, its exclusion leads to no significant deterioration in the quality of the description and to no displacement of the estimates of other coefficients in the regression. Thus there is no direct confirmation of the presence of a cross term in Eqn.(4).

Little information is available on non-additive effects of substituents attached to four-coordinated phosphorus. Thus non-additivity was shown[91] in the influence of two alkoxy-groups X and Y on the alkaline hydrolysis of the esters $XYPOOC_6H_4NO_2$-*p*, but a recent analysis[92] of a larger number of results has indicated complete additivity. This example illustrates how changing the set of substituents and using

experimental results from different sources can influence the apparent character of the combined effects of substituents in a reaction series. In the Reviewers' opinion a solution to this problem should be based in each particular case on detailed analysis of the parameters of the correlation model for the given process, and it is desirable that self-consistent data should be used to deduce this model.

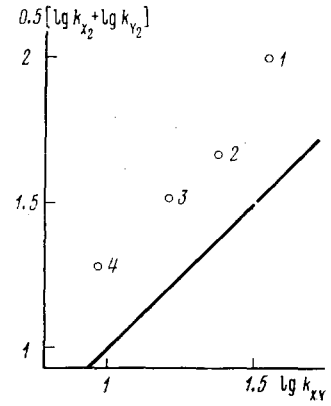


Figure 2. *Non-observance*[55] of additivity test for effects of substituents in alkaline hydrolysis of $X(C_2H_5)POF$, with X: 1) CH_3O; 2) C_2H_5O; 3) n-C_3H_7O; 4) iso-C_3H_7O.

Table 3. Coefficients and statistical criteria of Eqn.(11)*[53].

Coeff. or statistical criterion	№ 1	№ 2	№ 3
a_0	3.317±0.072	3.037±0.098	3.372±0.082
a_1	2.131±0.218	2.350±0.442	2.549±0.172
a_2	0.196±0.032	—	0.211±0.037
a_3	0.175±0.069	0.160±0.143	—
a_4	−5.085±0.394	−5.100±0.761	−5.868±0.295
n	18	18	18
R	0.9971	0.9866	0.9957
S_0	0.069	0.155	0.083

*The compounds used are given in Ref.53.

A clear example of non-additivity of the effects of *P*-substituents is alkaline hydrolysis of the acid fluorides XYPOF, for which the criterion of additivity[55] is not observed: i.e. experimental points for the plot of $\lg k$(XYPOF) against $0.5[\lg k(X_2POF) + \lg k(Y_2POF)]$ do not lie on a straight line of unit slope passing through the origin (Fig.2). The rate of this reaction (in water at 25 °C) [93] is well described (Table 3) by the non-additive equation[53]

$$\lg k\,(XYP(O)F) = a_0 + a_1 \sum \sigma^* + a_2\sigma^*_X\sigma^*_Y + \\ + a_3 \sum E_s + a_4 n_{RO} \qquad (11)$$

in which a_4 is the resonance contribution by the RO substituents and n_{RO} the number of such substituents in the molecule. Omission of the cross term $a_2\sigma^*_X\sigma^*_Y$ impairs the quality of the description (regression 2 in Table 3).

The contribution by non-additive interaction of the substituents is small when X and Y are alkyl, and amounts to 0.3 to 0.4 lg unit when they are alkoxyl groups. Alkaline hydrolysis of the acid fluorides XYPOF is obviously greatly hindered by the resonance effect of the alkoxy-groups, which stabilises the initial state. It is curious that this resonance effect in this reaction series is largely balanced by the inductive effect of these groups. Omission of the contribution $a_3\Sigma E_S$ also somewhat impairs the quality of the description: i.e. reactivity in the series is influenced by spatial factors, for steric effects of substituents X and Y hinder the reaction, by destabilising the transition state. Despite the smallness of the coefficient a_3 (Table 3), the steric contribution to $\lg k$ may be considerable: thus for the compound $(iso\text{-}C_3H_7O)_2POF$ it is 0.33 lg unit, but the corresponding value when X = Y = t-C_4H_9O should be 0.61.

Confirmation of the non-additive character of the influence of substituents on the rate of substitution of fluorine in the compounds XYPOF can be obtained also by direct application of the principle of polylinearity[1], according to which the rate should be given by

$$\lg k(XYP(O)F) = a_0 + X' + a_1Y' + a_2X'Y', \qquad (12)$$

if the effects are defined as

$$X' = \lg k(X_iY_0P(O)F) - \lg k(X_0Y_0P(O)F);$$
$$Y' = \lg k(X_0Y_iP(O)F) - \lg k(X_0Y_0P(O)F),$$

where $\lg k(X_0Y_0POF)$ relates to the compound containing substituents X_0 and Y_0 chosen as standard. The principle imposes on the coefficients in (12) the limitations[1,27] $a_0 = \lg k(X_0Y_0POF)$ and $a_1 = 1$. The use of such scales to analyse the real significance of the coefficient a_2 in Eqn.(12) is extremely convenient, since mathematical expectancies are available for all the other coefficients. This prevents the appearance of a significant cross term because of shifts in the estimates of a_0 and a_1, e.g. owing to non-orthogonality of the variables X', Y', and $X'Y'$, in cases in which the effects of the factors are actually additive. Furthermore, use of the X' and Y' scales enables the presence to be revealed of small cross terms, whose omission does not affect significantly the statistical indices but leads to displaced estimates of a_0 and a_1. Choice of $X_0 = Y_0 = C_2H_5$ and calculation of X' and Y' for various groups X and Y gave[53] values of $\lg k$ for alkaline hydrolysis of compounds XYPOF well described by Eqn.(12) with a statistically significant cross term $a_2X'Y'$, exhibiting good convergence of estimates of a_0 and a_1 with the theoretical coefficients.

The structural effects of the departing aryloxy-group and the nucleophile on the rate of reaction of 2-aryloxy-2-oxo-1,3,2-dioxaphosphorinans with various nucleophilic reagents are also significantly non-additive[83]. A bimolecular mechanism of direct substitution $S_N2(P)$ is involved[83], so that departing group and attacking nucleophile should interact strongly in the transition state. Thus the effects of two substituents attached to a phosphorus atom may indeed be non-additive. Such non-additivity has been confirmed in a study of alkaline hydrolysis of the esters $XYPSOC_6H_4X$-$p(m)$.[94]

VI. COMPARISON OF INFLUENCE OF STRUCTURAL FACTORS ON DISSOCIATION OF XYPOOH AND XCOOH ACIDS

It is generally accepted in organophosphorus chemistry[95,96] that the electronic effects of substituents on reaction centres involving phosphorus and carbon atoms—including phosphinico and carboxyl—are different in nature. It has been shown above that substituents X and Y influence the strengths of

XYPOOH acids mainly by inductive and resonance mechanisms. The constant of sensitivity to the inductive effect for this series $\rho_P^* = 1.358 \pm 0.040$ (Table 2) is close to the corresponding value $\rho_C^* = 1.809 \pm 0.028$ for the dissociation of XCOOH acids[25].

Table 4. Resonance contributions ΔpK_P and ΔpK_C by substituents to pK_a (in water at 25 °C) of XYPOOH and XCOOH.[51]

X	ΔpK_P^* (F) **	ΔpK_C
OH	1.221±0.084 (51)	1.74
O⁻	3.160±0.041 (40)	3.98
O⁻	4.486±0.041 (40)	5.25***
Ph	0.256±0.041 (20)	0.57
R****	0.00	0.00

*Values taken from regressions in Table 2.
**F = number of degrees of freedom.
***Without electrostatic correction.
****Here R = CH_3 and other substituents incapable of conjugation.

Table 4 lists the resonance contributions ΔpK_P made by phenyl, hydroxyl, and oxide substituents (with and without the electrostatic correction) to the pK_a values of XYPOOH acids and the corresponding contributions ΔpK_C made by them¶ to the pK_a values of XCOOH acids, the latter calculated by means of the equation[1]

$$\Delta pK_C = pK_a(XCOOH) - 4.748 + 1.809\sigma^*.$$

Comparison was impossible withother substituents capable of conjugation, for either experimental data for such carboxylic acids were lacking or the pK_a values available for the corresponding organic acids of phosphorus were unreliable. Fig.3 shows a linear relation between ΔpK_C and ΔpK_P. The corresponding regression[51]

$$\Delta pK_C = (1.29 \pm 0.05)\Delta pK_P;\ r = 0.9976;\ s_0 = 0.18$$

passes through the origin, i.e. through the point X = Y = CH_3. Such a relation indicates that the effects of these substituents on the pK_a values of phosphororganic and carboxylic acids are identical in nature. The ratio of ΔpK_C to ΔpK_P is given by the slope of the straight line in Fig.3, which coincides with the ratio $\rho_C^*/\rho_P^* = 1.37 \pm 0.04$: i.e. the ratio of the resonance contributions in the dissociation of XCOOH and XYPOOH acids is equal to that of the corresponding inductive contributions. Hence it follows by proportion that the ratio of inductive and resonance contributions to the overall effect of a substituent is the same in the series under comparison.

The reaction centres COOH and POOH are of the $-C$ type, so that a correlation should be observed between the conjugation contributions ΔpK_C (ΔpK_P) and the constants $\sigma_{res}^+ = \sigma^+ - \sigma^0$ for the $+C$-type substituents C_6H_5, OH, and O⁻. A very good linear relation does indeed exist[51] between ΔpK_C and σ_{res}^+, passing through the origin, i.e. through the point for the methyl substituent (Fig.4):

$$\Delta pK_C = (-2.209 \pm 0.003)\sigma_{res}^+;\ r = 0.9999;\ s_0 = 0.005.$$

The point for the resonance contribution of the substituent O⁻ without the electrostatic correction does not lie on the line. This demonstrates unambiguously the necessity for such correction in the case of charged substituents capable of conjugating with the reaction centre†.

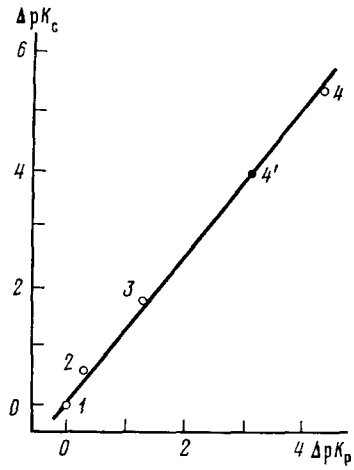


Figure 3. Relation[51] between resonance contributions to pK_a of carboxylic and organophosphorus acids (ΔpK_C and ΔpK_P) by the substituents: 1) CH_3; 2) C_6H_5; 3) HO; 4) O⁻; 4') as (4) with electrostatic correction.

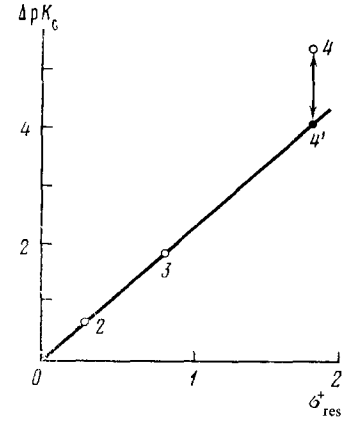


Figure 4. Correlation[51] between resonance contributions ΔpK_C and σ_{res}^+ constants: numbering as in Fig.3.

¶ The electrostatic correction ΔpK_{al} for pK_{a2} of carbonic acid was calculated[51] from the geometry of the carbonate anion CO_3^{2-}, by a procedure similar to that adopted for phosphonic acids and phosphoric acid.

† The need to allow for electrostatic interaction has been shown[1,25] for charged substituents incapable of conjugation with the reaction centre.

Thus the electrostatically and statistically corrected pK_a values of XYPOOH acids are described by the equation[51]

$$pK_a(XYP(O)OH) = pK_a(Me_2P(O)OH) + \rho_P^* \sum \sigma^* + a_1\sigma_X^*\sigma_Y^* + \rho_{res\,P}^+ \sum \sigma_{res}^+ \quad (13)$$

and the pK_a values of XCOOH acids by[51]

$$pK_a(XCOOH) = pK_a(MeCOOH) + \rho_C^*\sigma^* + \rho_{res\,C}^+\sigma_{res}^+ \quad (14)$$

where $\sigma_{res,P}^+ = -1.709$ and $\sigma_{res,C}^+ = -2.209$ are the sensitivities of the series to the resonance influence of substituents. In these equations the ratio of the inductive contributions by substituents is equal to that of their resonance contributions:

$$\rho_P^*/\rho_C^* = \rho_{res\,P}^+/\rho_{res\,C}^+ = \alpha = 0.760 \pm 0.028. \quad (15)$$

From this formula together with Eqns.(13) and (14) it necessarily follows for the pK_a of XYPOOH acids in which Y remains unchanged that

$$pK_a(XYP(O)OH) = A_Y + \alpha pK_a(XCOOH) + a\sigma_X^*\sigma_Y^* + \delta_P E_{s,X} \quad (16)$$

where

$$A_Y = pK_a(MeYP(O)OH) - \alpha pK_a(MeCOOH).$$

Hence with any substituent X and any given substituent Y the experimental pK_a values should obey (16) with statistically significant contributions $\delta_P E_{s,X}$ and $a\sigma_X^*\sigma_Y^*$.

Conformity to Eqn.(16) has been verified[52] for the pK_{a_1} and pK_{a_2} values (Y respectively OH and O^-) of substituted phosphonic acids, for which this equation becomes

$$pK_{a_1}(XP(O)(OH)_2) = A_{OH} + \alpha pK_a(XCOOH) + a\sigma_{OH}^*\sigma_X^* + \delta_P E_s \quad (16a)$$

$$pK_{a_2}(XP(O)(OH)_2) = A_{O^-} + \alpha pK_a(XCOOH) + \delta_P E_{s,X}. \quad (16b)$$

The contribution $a\sigma_X^*\sigma_{O^-}^*$ is absent from the latter formula, since $\sigma_{O^-}^* = 0$.[26,49] Mathematical expectancies are known for all the coefficients in (16a) and (16b): δ_P and a should not differ significantly from -0.230 ± 0.027 and 0.161 ± 0.042 respectively (Table 2); from experimental values of pK_{a_1}. $.(CH_3PO(OH)_2)$, $pK_{a_2}(CH_3PO(OH)_2)$, and $pK_a(CH_3COOH)$ it has been found[52] that $A_{OH} = -0.93 \pm 0.147$ and $A_{O^-} = 2.71 \pm 0.147$, while $\alpha = 0.760 \pm 0.028$.

Checking the validity of Eqns.(16a) and (16b) reveals poor statistical indices (Table 5) only for the dependence of pK_{a_1} and pK_{a_2} (regressions 1 and 3 respectively) of phosphonic acids on the pK_a of the corresponding carboxylic acids.

Inclusion of the terms $a\sigma_{OH}^*\sigma_X^*$ and $\delta_P E_S$ in pK_{a_1} and of $\delta_P E_S$ in pK_{a_2} (regressions 2 and 4) sharply improves the quality of the description. The estimates of A_{OH}, A_{O^-}, and α agree well with the values expected mathematically; the estimates of δ_P and a have the required signs and also agree satisfactorily with their theoretical values (above). Consequently the pK_a of corresponding phosphonic and carboxylic acids are indeed represented by the above relations.

It is evident also from formulae (16a) and (16b) and the corresponding regressions that the pK_{a_1} and pK_{a_2} values of phosphonic acids should be given by the single equation[52]

$$pK_{a_{1(2)}}(XP(O)(OH)_2) = A_{OH} + \beta T + \alpha pK_a(XCOOH) + a\sigma_{OH}^*\sigma_X^* + \delta_P E_s \quad (17)$$

in which T is respectively 0 and 1. Here $\beta = -3.64 \pm 0.071$ is the difference between the independent terms in regressions 2 and 4 (Table 5).

The graphical illustration of Eqn.(17) in Fig.5 shows that the large majority of points lie close to a straight line of slope α. It is interesting that the pK_{a_2} values for trifluoro- and trichloro-methylphosphonic acids are located closest to the regression line if negative pK_a values are used for the corresponding carboxylic acids[72], whereas points corresponding to the pK_{a_1} of the above acids depart considerably from the straight line whatever the pK_a values of trifluoro- and trichloro-acetic acids. The pK_{a_1} values of the two phosphonic acids deviate also from the regressions in Table 2, apparently because they had been determined incorrectly.

Equation (17) corresponds to regression 5 in Table 5, covering 41 pK_a values for 22 phosphonic acids. All its coefficients agree well with the corresponding coefficients of regressions 2 and 4 and with their theoretical values. The statistical indices of the regression are good.

Thus the good adherence to relations (16a), (16b), and (17) for acids containing diverse substituents X, including charged groups (O^-) and those capable of conjugation with reaction centres, finally confirms the correctness of Eqns. (13)–(15). This indicates that the structural effects of substituents on the strengths of XYPOOH and XCOOH acids are entirely of the same type.

VII. CONCLUSION

Among the results covered in the Review the most unexpected to the Reviewers is the good linear relationship between the contributions by the conjugation of substituents with POOH and COOH reaction centres, as well as the closely similar relations between inductive and resonance contributions to the overall effect of substituents for dissociation of the two series of acids XYPOOH and XCOOH. However, an analogous conclusion follows logically from the good correlation observed in 1953 [4] between the pK_a values of arylphosphonic acids and the Hammett σ-constants. The linear

Table 5. *Coefficients and statistical criteria of relations (16a), (16b), and (17) between pK_{a_1} and pK_{a_2} values of phosphonic and carboxylic acids $XPO(OH)_2$ and XCOOH*[52].*

Eqn.	Regression	A_Y	α	δ_P	a	β	n	R	S_0
(16a)	1	−0.310±0.251	0.670±0.055	—	—	—	21	0.9419	0.337
(16a)	2	−1.189±0.176	0.809±0.034	−0.327±0.045	0.319±0.057	—	21	0.9915	0.139
(16b)	3	2.768±0.271	0.799±0.059	—	—	—	21	0.9517	0.364
(16b)	4	2.528±0.154	0.804±0.033	−0.419±0.063	—	—	21	0.9871	0.199
(17)	5	−1.196±0.0116	0.805±0.021	−0.363±0.036	0.320±0.052	−3.805±0.055	41	0.9976	0.159

*Regressions were calculated from statistically and electrostatically corrected pK_a values for the acids $XPO(OH)_2$ (see reviews[49,52]) and XCOOH (compilation[52]).

dependence of ΔpK_P on ΔpK_C, which moreover passes through the origin, indicates either absence of any specific interactions of the substituents with the POOH fragment (e.g. involving *d*-orbitals of the phosphorus atom) or complete proportionality of the contribution by such interactions to the resonance contribution (which is described by the "carbon" constants σ_{res}^{+}) and (or) to the inductive contribution.

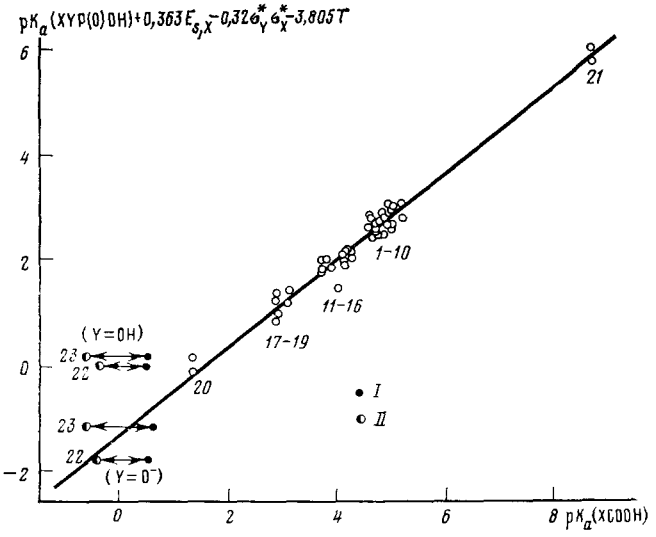


Figure 5. Graphical illustration of relation (17) [52] between the statistically and electrostatically corrected pK_{a_1} and pK_{a_2} values (Y = OH and O^-) of phosphonic acids XYPOOH and the pK_a values of carboxylic acids XCOOH, with X: 1) $n\text{-}C_3H_7$; 2) CH_3; 3) C_2H_5; 4) $iso\text{-}C_3H_7$; 5) $s\text{-}C_4H_9$; 6) $t\text{-}C_4H_9$; 7) $iso\text{-}C_4H_9$; 8) $n\text{-}C_4H_9$; 9) $t\text{-}C_5H_{11}$; 10) $(CH_3)_3.SiCH_2$; 11) $C_6H_5CH_2$; 12) $HOCH_2$; 13) C_6H_5; 14) HO; 15) $BrCH_2CH_2$; 16) H; 17) $ClCH_2$; 18) $BrCH_2$; 19) ICH_2; 20) Cl_2CH; 21) O^-; 22) F_3C; 23) Cl_3C; I) with $pK_a > 0$ for the acids CF_3COOH and CCl_3COOH; II) $pK_a < 0$ for these acids.

The steric effect exerted[47-54] by substituents X and Y on the strengths of XYPOOH acids cannot be regarded as an artefact, since the magnitude of the sensitivity coefficient δ is very stable: it depends neither on the size of the sample nor on the specific form of the equation. Exclusion of the steric contribution always impairs the accuracy of the description of experimental data, which is shown especially clearly by recent self-consistent values[76] for the pK_{a_2} of several phosphonic acids.

It is noteworthy that the steric contribution to the pK_a of XYPOOH acids may be considerable despite the small sensitivity coefficient δ to this type of interaction. The reason is the large absolute magnitudes of the constants E_s for bulky substituents[97]. The appearance of a steric contribution is obviously due not to steric hindrance by substituents to detachment of a proton but to their destabilisation of the anion by causing steric hindrance to formation of its solvation sheath. The view that substituents cause significant steric hindrance to solvation of carboxylate anions was expressed many years ago[98,75] and is supported by recent data[99,100].

Thus the results presented in this Review are evidence firstly of the adequacy of the list of types of intramolecular interaction used and of the satisfactory applicability of the mathematical models of the individual types of interaction using the "carbon" constants σ^*, E_s, and σ_{res}^{+} to represent the influence of substituents on the properties of four-coordinated quinquevalent phosphorus compounds, and secondly that the mathematical models of interactions (inductive, steric, resonance) and the corresponding substituent constants do indeed contain chemical and physical meaning axiomatically "incorporated" in them. Furthermore, the results of a recent series of studies[47-54] yet again confirm the objective character and a definite universality of the axiomatics of correlation analysis. Its limits of applicability in describing the influence of *P*-substituents on various properties of organophosphorus compounds are apparently determined by the general limits of applicability of the polylinearity principle[1,27] to these properties.

Analysis shows that the σ^{ph} constants widely used in organophosphorus chemistry are composite, comprising contributions by inductive, steric, and resonance effects of substituents#. The good description of diverse properties of organophosphorus compounds provided by these constants indicates that in many of their reaction series the relative contributions by individual interaction mechanisms to the overall effect of a *P*-substituent are about the same as in the dissociation of XYPOOH acids. Hence it is obvious that these constants are inapplicable only in reaction series in which the relative contributions differ markedly from those "incorporated" in these constants.

The σ^{ph} constants secure on important virtue—simplicity of the correlation equations—despite their complicated nature. In the Reviewers' opinion, therefore, they should be used as before to describe those reaction series to which they are readily applicable, provided comparison of organophosphorus reaction series with other series is not involved.

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