1-Chlorobicyclo[3.2.2]decane (III, X = Cl).—A procedure similar to that reported[11a] for the preparation of 1-chlorobicyclo[3.2.2]nonane was employed. Thus, 1-bicyclo[3.3.2]decanol (187 mg, 1.2 mmol) was added to freshly purified thionyl chloride[30] (2 ml) and stirred for 12 hr. Chips of ice were then added to the reaction mixture until all excess thionyl chloride had decomposed. The product was extracted with ether and the ether extracts were washed with 10% Na_2CO_3, water, and brine and dried ($MgSO_4$). Removal of solvent by distillation and sublimation of the residue gave a white waxy solid (140 mg, 67%): mp 85–87°; nmr (CCl_4) δ 1.67 (11 H, m) and 2.28 (6 H, m); ir (CCl_4) 2900, 1450 cm^{-1}.

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.56; H, 9.86; Cl, 20.58. Found: C, 69.54; H, 9.71; Cl, 20.25.

Reduction of 1-Chlorobicyclo[3.3.2]decane (III, X = Cl).—To a solution of 1-chlorobicyclo[3.3.2]decane (75 mg, 0.44 mmol), lithium aluminum hydride (5 mg, 0.13 mmol), and 2,2-azobisisobutyronitrile (catalytic amount) in 5 ml of anhydrous ether was added triphenyltin chloride (193 mg, 0.5 mmol) in ether (15 ml) at room temperature.[31] Care was taken to exclude moisture. A fine, light-colored precipitate developed during the course of the addition (30 min). The reaction mixture was then refluxed for 3 hr, filtered, washed with water (two times) and brine, and dried ($MgSO_4$). Removal of solvent and sublimation of the residue gave a product (67%) whose physical (mp 177–178°) and spectroscopic properties were identical in every respect with those of bicyclo[3.3.2]decane (III, X = H).

Bromination of Bicyclo[3.2.2]nonane (II, X = H).—To bromine (5 ml) cooled in an ice bath was added bicyclo[3.2.2]nonane[14] (1 g). The reaction mixture was then gradually raised to room temperature and stirred for 20 hr. After addition of CCl_4 (35 ml), the excess bromine was destroyed with an aqueous solution of $NaHSO_3$. The organic layer was then separated, washed twice with water, and dried ($CaCl_2$). The solvent was removed *in vacuo* and the product distilled (1 g, 61%), bp 53–54° (0.3 mm). A sharp singlet attributable to $-CH_2Br$ appears at δ 3.33 in the nmr spectra indicating that rearrangement had occurred. The integration of this signal indicated that rearrangement was complete within experimental error. No conditions could be found for the separation of the two most likely products,[18] 1-bicyclo[3.2.1]octylcarbinyl bromide and 1-bicyclo[2.2.2]octyl carbinyl bromide.

1-Bromobicyclo[3.2.2]nonane (II, X = Br).—To freshly distilled thionyl bromide (0.56 ml, 7 mmol) was added 1-bicyclo[3.2.2]nonanol (0.5 g, 3.5 mmol) at room temperature. The reaction mixture was stirred at that temperature for 12 hr and heated at 85° for an additional 4 hr. Chips of ice were then added to decompose the excess thionyl bromide. The product was extracted with ether (two times) and the combined extracts were washed with 10% Na_2CO_3, water, and brine. After drying ($MgSO_4$) the solvent was removed *in vacuo* and the oily product was distilled (0.4 g, 55%): bp 123–125° (20 mm); nmr (CCl_4) δ 1.70 (9 H, m) and 2.40 (6 H, m); ir (CCl_4) 2925, 2860, 1460, 640 cm^{-1}.

Anal. Calcd for $C_9H_{15}Br$: C, 53.20; H, 7.39; Br, 39.41. Found: C, 53.27; H, 7.29; Br, 39.24.

1-Bicyclo[3.3.1]nonylcarboxylic Acid (I, X = COOH). A.—To a solution of 96% H_2SO_4 (125 ml), CCl_4 (50 ml), and 1-bicyclo[3.3.1]nonanol (6.5 g, 0.046 mol) cooled in an ice–salt bath was added 28 g of HCOOH with vigorous stirring over a period of 1.5 hr. The reaction temperature was not allowed to rise above 15°. After stirring for an additional hour, the reaction mixture was poured over ice (350 g). The organic layer was separated and the acid layer was extracted with CCl_4 (three times). The combined CCl_4 extracts were washed with two 50-ml portions of 15 *N* NH_4OH. The alkaline washes were then acidified with 12 *N* HCl. The precipitated product was extracted with chloroform, the chloroform extracts were dried (Na_2SO_4), and the solvent was removed to give 5.8 g (75%) of crude product. Recrystallization from methanol–water (7:1) gave I (X = COOH): mp 96–97.5° (lit. mp 98–99°,[21a] 95.5–97°,[21b] 82–84°[21c]); nmr (CCl_4) δ 1.70 (15 H, m) and 11.95 (1 H, s); ir (CCl_4) 3100, 2925, 1695 cm^{-1}.

B.—Similar results in somewhat decreased yield were obtained when bicyclo[3.3.1]nonane was used instead of the 1-alcohol and *tert*-butyl alcohol (15 g) was added with the formic acid.[22] Separation of the 1-bicyclo[3.3.1]nonylcarboxylic and pivalic acids obtained in this manner was accomplished by distillation. A fraction boiling at 113–118° (0.1 mm) gave a 47% yield of 1-bicyclo[3.3.1]nonylcarboxylic acid (I, X = COOH).

Registry No.—I (X = OH), 15158-56-2; I (X = CO_2H), 17530-63-1; II (X = OH), 28054-86-6; II (X = Br), 28054-87-7; III (X = OH), 18216-08-5; III (X = Cl), 28054-89-9; III 1,5-diol, 28054-90-2; V, 28054-91-3; V tosylhydrazone, 28054-94-6; VI, 19388-80-8; VI OTs, 28054-92-4; VII, 6571-74-0; chromic acid, 7738-94-5.

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[30] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 345.

[31] For leading references concerning tin hydride reductions, see H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968).

Correlation Constants in the Chemistry of Organophosphorus Compounds

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Two correlation methods of ionization constants of the organophosphorus acids are discussed. The first involves application of σ^{Φ} constants characteristic of the substituents bonded to phosphorus. In the second approach the σ_I and σ_R constants found for the substituents bonded to carbon are used. The best correlations are obtained for σ^{Φ} constants. Correlation of σ^{Φ} constants with σ_I and σ_R values employing the Taft equation gives only a fairly good correlation coefficients. Electronic effects of the substituents at phosphorus are of the same nature as those at carbon atom, but some specific difference in the resonance effects is observed probably owing to the difference between p–π or π–π and p–d or π–d overlaps. Thus the use of σ^{Φ} constants for correlation of the organophosphorus reactions is preferable.

Jaffé, Freedman, and Doak were the first to employ the Hammett equation in the chemistry of organophosphorus compounds in 1953.[1] They found that the ionization constants of aromatic phosphonic acids show linear correlation with σ_m and σ_p values reported by Jaffé.[2] In 1956 one of us found[3,4] that, besides for aromatic acids, the Hammett equation

$$pK = pK^0 - \rho\Sigma\sigma^{\Phi} \qquad (1)$$

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

[2] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[3] M. I. Kabachnik, *Dokl. Akad. Nauk SSSR*, **110**, 393 (1956).

[4] M. I. Kabachnik, *Z. Chem.*, **1**, 2893 (1961).

can be applied to a variety of phosphorus acids when σ^{Φ} constants specific for the substituents directly bonded to phosphorus atom are used. Work was done on approximately 150 ionization constants of phosphorus acids in water and 50% aqueous alcohol in order to determine σ^{Φ} constants. Excellent correlations were obtained in the majority of cases. In a later study the σ^{Φ} constants were used many times to correlate the ionization constants of the organophosphorus acids and bases and rate constants of some reactions in various media.[5-10]

Recently[11] we discussed in detail the application of the correlational analysis in the chemistry of organophosphorus compounds. In all we treated 124 reaction sets involving nearly 1300 rate and equilibrium constants. It was found that in the case of ionization of organophosphorus acids and bases the use of σ^{Φ} constants gives the best results and provides a universal correlation system. Thus for 27 reaction sets in correlations of pK_a values of different phosphorus acids with σ^{Φ} values 77.6% were excellent or good (r varied from 0.970 to 1.000), 18.5% were rather satisfactory (r varied from 0.950 to 0.969), and 3.7% had correlation coefficients below 0.950. Analysis of the nucleophilic substitution reactions at a phosphorus atom and some other reactions showed that good correlations are obtained by using eq 2, where σ_I^{Φ} and σ_R^{Φ} are, respectively, the inductive and resonance components of σ^{Φ}.

$$\log k = \log k^0 + \rho\Sigma(\sigma_I^{\Phi} + \alpha\sigma_R^{\Phi}) \qquad (2)$$

A method was advanced for the estimation of these constants from the experimental data, and a unified system of correlations of the rate and equilibrium constants was developed for a variety of organophosphorus reactions. The correlations were good or excellent in 62% of the 124 reaction sets, 20% were rather satisfactory, and 18% had a correlation coefficient below 0.950.

It should be pointed out that a comparison of the σ^{Φ} and σ constants derived from reactions of the pure carbon compounds revealed that in general these two sets of constants are not in any simple correlation. The linear dependences of σ^{Φ} and σ were only found for certain types of substituents. Thus Palm[12] was the first to find the linear correlation between the σ^{Φ} constants of the unsubstituted alkyl groups and the σ^* Taft constants (eq 3).

$$\sigma^{\Phi} = -0.960 + 1.99\sigma^* \qquad (3)$$

(The parameters of this equation were corrected in our work.[11]) The σ^{Φ} constants of the substituted aromatic groups at phosphorus were shown to be linearly dependent on the σ_p and σ_m (or σ^0) values of the aromatic ring substituents (eq 4).[13]

$$\sigma_{XC_6H_4}{}^{\Phi} = -0.415 + 0.634\sigma_X \qquad (4)$$

Thus the σ^{Φ} constants of the alkyl and cycloalkyl groups at phosphorous are purely inductive whereas those of the substituted aromatic groups contain the inductive and resonance components in the same ratio as σ_p and σ_m. For other groups (RO, RS, or R_2N, etc.) a dependence between the σ^{Φ} and σ constants of the substituents at carbon was not established. Thus the contribution of the inductive and resonance components to σ^{Φ} varies depending on the nature of the group bonded to phosphorus. It was due to these reasons that the derivation of the specific σ^{Φ} constants became necessary.

Recently Charton has published a paper in which he deals with this problem.[14] He examines the possible application of the σ_I and σ_R constants, obtained for the substituents at carbon, to the correlation of the ionization constants of organophosphorus acids and bases. Charton used the Taft equation[15]

$$Q_X = \alpha\sigma_I + \beta\sigma_R + h \qquad (5)$$

σ_I values were those obtained earlier by Charton,[16] and the σ_R constants were obtained from the equation

$$\sigma_R = \sigma_p - \sigma_I \qquad (6)$$

using σ_p values of McDaniel and Brown.[17]

In the correlation of σ^{Φ} values[18] with σ_I and σ_R the following values were obtained (eq 5): $\alpha = 4.01 \pm 0.34$, $\beta = 0.760 \pm 0.243$, $h = -0.915 \pm 0.067$, the multiple correlation coefficient $R = 0.946$. In the correlation of ionization constants with the σ_I and σ_R constants, Charton obtained correlations of which 57.9% were good or very good, 10.5% were satisfactory, and 31.6% had correlation coefficients below 0.950. It should be noted that good correlations can be obtained from the data of various authors only for certain combinations of their reaction sets or by division of the data of one work into several reaction sets and by omitting some substances that fall out of the linear correlation from the pK_a sets. It should also be mentioned that Charton's α and β differ significantly for acids of the same type measured under very similar conditions.

For example, for pK_1 in water for set 2 the α and β values -3.62 and -0.797 were obtained (β/α, 0.22), and for set 4 the α and β values were -3.52 and -1.74 (β/α, 0.49). Thus, in this case, the resonance contribution to the total substituents electronic effect difference is more than double. It is impossible to ascribe this difference to the temperature change from 20 to 25°.

Thus Charton came to the conclusion that the effect of the substituents bonded to pentavalent phosphorus

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(5) T. A. Mastryukova, T. A. Melentyeva, A. E. Shipov, and M. I. Kabachnik, *Zh. Obshch. Khim.*, **29**, 2178 (1959).

(6) M. I. Kabachnik, T. A. Mastryukova, A. E. Shipov, and T. A. Melentyeva, *Dokl. Akad. Nauk SSSR*, **124**, 1061 (1959).

(7) M. I. Kabachnik, T. A. Mastryukova, T. A. Melentyeva, and A. E. Shipov, *Tetrahedron*, **9**, 10 (1960).

(8) M. I. Kabachnik and G. A. Balueva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 536 (1962).

(9) T. Ya. Medved, B. A. Korolev, K. S. Yudina, B. I. Stepanov, and M. I. Kabachnik, *Teor. Eksp. Khim.*, **6**, 116 (1968).

(10) G. K. Genkina, B. A. Korolev, V. A. Gilyarov, B. I. Stepanov, and M. I. Kabachnik, *Zh. Obshch. Khim.*, **39**, 326 (1969).

(11) T. A. Mastryukova and M. I. Kabachnik, *Usp. Khim.*, **38**, 1751 (1969).

(12) V. A. Palm, *ibid.*, **30**, 1069 (1961).

(13) T. A. Mastryukova and M. I. Kabachnik, *Zh. Obshch. Khim.*, **38**, 677 (1968).

(14) M. Charton, *J. Org. Chem.*, **34**, 1877 (1969).

(15) R. W. Taft, Jr., and I. C. Lewis, *J. Amer. Chem. Soc.*, **80**, 2436 (1958).

(16) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).

(17) D. H. McDaniel and H. C. Brown, *ibid.*, **23**, 420 (1958).

(18) The Charton list of σ^{Φ} values had some errors:[14] for the OH group the -0.393 value should be used instead of -0.343; for the C_2H_5O group -0.214 should be used instead of -0.314; for the $ClCH_2$ group -0.051[19] should be used instead of -0.034. Besides, recently we have corrected the σ^{Φ} value for CF_3 group: 0.7 should be used instead of 0.50.[11]

(19) M. I. Kabachnik, T. A. Mastryukova, and S. T. Ioffe, *Zh. Obshch. Khim.*, **30**, 2763 (1960).

TABLE I

σ_X^{Φ} CONSTANTS OF X SUBSTITUENTS[a]

No.	X	σ_X^{Φ}	No.	X	σ_X^{Φ}	No.	X	σ_X
1	H	0.00	15	$(C_6H_5)_2CH$	−0.73	29	C_4H_9O	−0.41
2	CH_3	−0.96	16	$HOCH_2$	−0.55	30	$C_5H_{11}O$	−0.39
3	C_2H_5	−1.10	17	$ClCH_2$	−0.05	31	i-$C_5H_{11}O$	−0.38
4	C_3H_7	−1.18	18	$BrCH_2$	0.0	32	c-$C_6H_{11}O$	−0.35
5	i-C_3H_7	−1.30	19	ICH_2	−0.1	33	C_6H_5O	−0.06
6	C_4H_9	−1.22	20	$(CH_3)_3SiCH_2$	−1.6	34	CH_3S	+0.15
7	i-C_4H_9	−1.30	21	$CHCl_2$	+0.27	35	C_2H_5S	+0.09
8	sec-C_4H_9	−1.36	22	CCl_3	+0.3	36	C_3H_7S	−0.06
9	$tert$-C_4H_9	−1.55	23	CF_3	+0.7	37	i-C_3H_7S	−0.06
10	i-C_5H_{11}	−1.27	24	OH	−0.39	38	$(CH_3)_2N$	−1.22
11	Neo-C_5H_{11}	−1.44	25	CH_3O	−0.12	39	F	+0.56
12	c-C_6H_{11}	−1.19	26	C_2H_5O	−0.21	40	Cl	+0.93
13	$C_6H_5CH_2$	−0.69	27	C_3H_7O	−0.32	41	C_6H_5	−0.48
14	$CH_2{=\!=}CH$	−0.68	28	i-C_3H_7O	−0.29			

[a] Reference 11.

may be described as a function of the σ_I and σ_R constants obtained for the substituents bonded to carbon and that it is unnecessary to define the new substituent constants, *i.e.*, σ^{Φ}.

It is evident from the above that one can outline two approaches in the correlation of the rate and equilibrium constants of the organophosphorous reactions. The first is associated with the use of the σ^{Φ} constants specific to the substituents bonded to phosphorus. The second approach is based on application of the σ_I and σ_R constants obtained for the substituents bonded to carbon. In this regard we have carried out a comparative study of both these correlation methods.

Results

For the comparative correlations one can use only the data for the substituents with the three known constants σ^{Φ}, σ_I, and σ_R. Table I shows the σ^{Φ} constants of such substituents.[11] The σ_I values were taken according to Charton.[16] The σ_R constants were estimated from eq 6 using the σ_p constants of McDaniel and Brown.[17] In some cases they were taken from Jaffé's review.[2] We also used σ_I constants for the RO and RS groups calculated from the σ^* constants of these groups[11] from the relation $\sigma_I = \sigma^*/6.23$. Other constants employed are listed in Table II.

TABLE II

SUBSTITUENT CONSTANTS OF SOME X GROUPS

X	σ_I	σ_p	Ref	X	σ_I	σ_p	Ref
OH	0.29		*a*	$CHCl_2$		0.185	*b*
$CH_2{=\!=}CH$		0.14	*c*	CCl_3		0.407	*b*
$C_6H_5CH_2$		−0.109	*d*	F	0.52		*a*
$(C_6H_5)_2CH$		−0.038	*d*	Cl	0.47		*e*

[a] V. A. Palm, "Osnovy kolichestvennoy teorii organicheskikh reaktsii," Khimiya, Leningrad, 1967, p 164. [b] J. Hine and W. C. Bailey, *J. Amer. Chem. Soc.*, **81**, 2075 (1959). [c] B. A. Zaitsev, *Reakts. Sposobnost Org. Soedin.*, **4**, No. 4 (14), 726 (1967). [d] W. F. Little, C. N. Reilley, J. D. Johnson, and A. P. Sanders, *J. Amer. Chem. Soc.*, **86**, 1381 (1964). [e] O. Eksner, *Proc. Conf. Use Correlational Equations Org. Chem., Tartu*, **1**, 67 (1962).

First of all we correlated σ^{Φ} with the σ_I and σ_R constants. Table III (set 1) shows the results of this correlation.[20] It can be seen that our α and β values of eq 5 differ only slightly from Charton's data (α = 3.97 and 4.01, and β = 0.87 and 0.760). Values of h are also close (−0.89 compared with Charton's value, −0.915), but the multiple correlation coefficient was less good (0.931 compared with Charton's 0.946).[22] Probably such disagreements are a result of some inaccuracy in the σ^{Φ} constants of Charton (see footnote 18.). Moreover Charton correlated only a part of the known σ^{Φ} constants (20), whereas the present paper employs a larger number (41) of constants. Figure 1 shows a dependence of the σ^{Φ} constants on $\sigma_{\text{eff}} = 3.97\sigma_I + 0.87\sigma_R$).[23] Because of the low correlation coefficient, the points corresponding to the particular substituents lie in a wide band. Several separate linear dependences can be differentiated within this band.

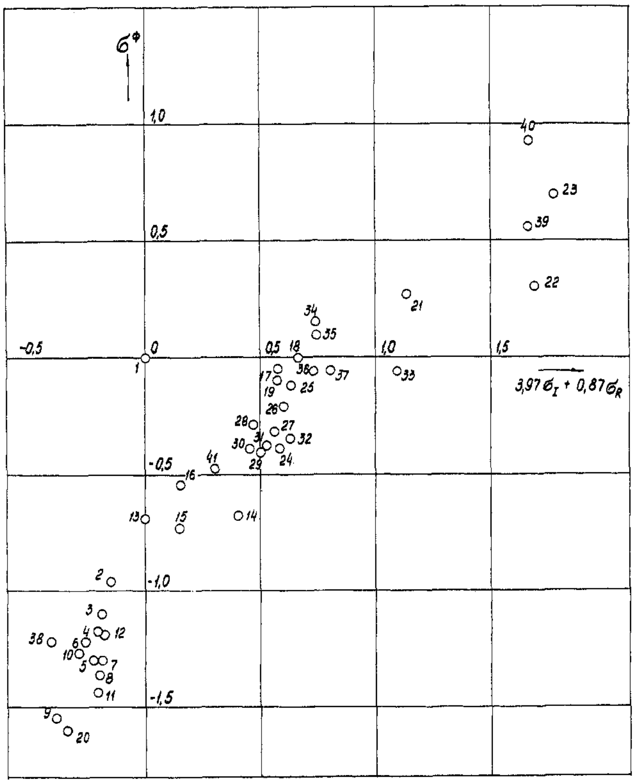

Figure 1.—σ^{Φ} constants *vs.* σ_I and σ_R constants.

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(20) Statistical analysis was performed as described in ref 21.

(21) L. M. Batuner and M. E. Pozin, "Matematicheskie metody v khimicheskoi tekhnike," Khimiya, Leningrad, 1968, p 689.

(22) The correlation coefficient becomes a little higher (0.957 compared with 0.931) by the exclusion of the value for h but it is still lower than that required for a good correlation.

(23) $\sigma_0^{\Phi} = -0.89$, $\rho = 1.000$, $r = 0.931$, $s = 0.24$, $s_\rho = 0.06$.

TABLE III

RESULTS OF CORRELATION WITH EQ 7

Set no.	$-\alpha$	$-\beta$	h	R	r_s	s_α	s_β	s_h	n
1	−3.97	−0.87	−0.89	0.931	0.372	0.25	0.06	0.24	41
2	6.83	3.02	2.31	0.919	0.983	0.81	0.35	0.16	15
3	13.30	−0.44	7.99	0.749	0.352	4.44	0.15	0.24	9
4	4.78	4.05	0.23	0.874	0.715	1.01	0.86	0.20	9
5	12.18	4.80	7.26	0.851	0.717	4.24	1.70	0.15	5
6	3.78	0.62	3.02	0.913	0.841	0.48	0.08	0.33	14
7	3.98	1.14	4.24	0.954	0.918	0.20	0.14	0.20	9
8	4.13	0.70	4.98	0.939	0.852	0.40	0.07	0.32	16
9	7.56	3.91	3.80	0.780	0.918	1.47	3.91	0.63	19
10	8.93	4.67	4.32	0.744	0.929	2.14	1.12	0.73	16
11	0.65	−0.08	−3.34	0.981	0.960	0.04	0.01	0.05	10

Thus alkyl substituents and hydrogen are likely to form a sharply inclined secondary band (no. 1–12). Partial linear correlation can be observed for the alkoxy- and alkylthio groups with normal chains (points 24–27, 29, 30, and 34–36). There are separate points corresponding to the strong electronegative substituents (CCl_3, CF_3, F, and Cl, no. 22, 23, 39, and 40). With an almost constant σ_{eff}, the value of σ^ϕ varies within 0.30–0.93.

In order to estimate both these correlation methods we have carried out a comparative correlation of the ionization constants (pK_a) of phosphorus acids using both methods. Table IV shows the reaction sets employed. Each of the sets relates to the data from a single paper, obtained by the same procedure and under analogous conditions. Use was made of all the constants published by the authors except in a very few cases when there were no literature data on the σ_I and σ_R[24] constants. The additivity principle was used in the correlation which was found to be very reasonable in the correlation analysis of organophosphorus reactions. Thus for acids of the type XYPOOH we used eq 7 for the correlations in accordance with

$$Q_X = \alpha\Sigma\sigma_I + \beta\Sigma\sigma_R + h \qquad (7)$$

Charton's method and eq 1 for the correlation with the σ^ϕ constants. In the calculations of correlation parameters from eq 7, when di- and tribasic acids were taken in the same set with monobasic ones, statistical factors of 0.30 and 0.48 pK_a unit have been used. No statistical factor was used in eq 1 since this has already been included in σ^ϕ of the hydroxy group. Table III (sets 2–10) shows the data of the correlations of ionization constants for organophosphorus acids with the σ_I and σ_R constants in accordance with the Charton procedure. Table V lists the results of the correlations of the same reaction sets with the σ^ϕ constants.

TABLE IV

THE REACTION SETS USED FOR CORRELATION

Set no.	Reaction set	pK	Conditions: Medium	Conditions: °C	Ref
1	Constants σ^ϕ		...	...	...
	Ionization Constants of XYPOOH				
2	Set of Crafts and Kosolapoff[a]	pK_1	H_2O	25	*b*
3	Set of Crafts and Kosolapoff[a]	pK_2	H_2O	25	*b*
4	Set of Kumler and Eiler	pK_1	H_2O	25	*c*
5	Set of Kumler and Eiler	pK_2	H_2O	25	*c*
6	Set of Mastryukova, *et al.*	pK_1	7% EtOH	20	*d*
7	Set of Mastryukova, *et al.*	pK_1	50% EtOH	20	*d*
8	Set of Mastryukova, *et al.*	pK_1	80% EtOH	20	*d*
9	Set of Peppard, *et al.*	pK_1	75% EtOH	22.5	*e*
10	Set of Peppard, *et al.*[f]	pK_1	95% EtOH	22.5	*e*
11	$XYPSSNa + C_6H_5CH_2Cl$		95.5% EtOH	25	*g*

[a] Data for *tert*-$C_5H_{11}P(O)(OH)_2$ are excluded since the authors assume that their acid obtained is not sufficiently pure. [b] P. C. Crofts and G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **75**, 3379 (1953). [c] W. D. Kumler and J. J. Eiler, *ibid.*, **65**, 2355 (1943). [d] T. A. Mastryukova, Doctoral Thesis, INEOS, Moscow, 1967 (autoreferate, 26). [e] D. F. Peppard, G. W. Mason, and C. M. Andreyasich, *J. Inorg. Nucl. Chem.*, **27**, 697 (1965). [f] Data for $(C_6H_5O)_2POOH$ are excluded since the pK_a value (1.91) is below that found in 75% alcohol (2.28); all other acids show the reverse relations. [g] M. I. Kabachnik, T. A. Mastryukova, G. A. Balueva, E. E. Kugucheva, A. E. Shipov, and T. A. Melentyeva, *Zh. Obshch. Khim.*, **31**, 140 (1961).

TABLE V

RESULTS OF CORRELATIONS WITH EQ 1

Set no.	ρ	pK^0	r	s_ρ	s	n
2	1.07	0.87	0.989	0.04	0.08	15
3	1.90	5.93	0.995	0.07	0.04	9
4	1.09	0.98	0.910	0.19	0.10	9
5	1.66	6.17	0.958	0.29	0.07	5
6	1.05	1.00	0.995	0.03	0.08	14
7	1.20	2.10	0.998	0.05	0.08	9
8	1.20	2.71	0.992	0.04	0.12	16
9	1.47	2.44	0.946	0.12	0.32	19
10	1.56	2.93	0.949	0.14	0.34	16
11[a]	−0.25	Log k^0 −3.91	0.990	0.01	0.04	10

[a] Calculated from the equation $\log k = \log k^0 + \rho\Sigma\sigma^\phi$.

Discussion

A comparison of Tables III and V shows that the use of the σ^ϕ constants for correlation of the ionization and rate constants of organophosphorus reactions is much more preferable than the use of σ_I and σ_R. The mean correlation coefficient in the first case was 0.972,[25]

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(24) The nine reaction sets presented in Table IV practically correspond to 19 reaction sets of Charton[14] and differ only in their compilation. Since Charton has separated the data of one set into several reaction sets, it is natural that he had a larger number of reaction sets than those in Table IV. For example, set 9 corresponds to the six sets of Charton (no. 5, 11, 13, 15, 17, and 19[14]) and set 10 to the five reaction sets (no. 12, 14, 16, 18, and 20[14]). The total number of the constants employed is approximately the same (122).

(25) It should be emphasized that the use of σ^ϕ provides high correlation coefficients not only for correlations with the ionization constants of XYPOOH acids but for many other reaction sets. Thus in our paper in *Uspekhi Khimii* we refer to 59 different reaction sets with an average correlation coefficient of 0.970.[11]

in the second 0.870. In accordance with Student's criterion a probability of the coincidence of these mean values is below 0.01. Moreover in the correlations employing σ^ϕ, the reaction sets of different authors under equivalent or very like conditions lead to the same correlation parameters. For example, sets 2, 4, and 6, respectively, yield ρ 1.07, 1.09, and 1.05 and $pK^0 = 0.87$, 0.98, and 1.00. Sets 3 and 5 give ρ 1.90 and 1.66, and $pK^0 = 5.93$ and 6.17. Differences in these values do not exceed the mean deviations. The correlation with Charton's method gives substantially different parameters. The sets 2, 4, and 6 give $h = 2.31$, 0.23, and 3.02, $\alpha = -6.83$, -4.78, and -3.78, $\beta = -3.02$, -4.05, and -0.62, respectively. The sets 3 and 5 give $h = 7.99$ and 7.26, $\alpha = -13.30$ and -12.18, $\beta = 0.44$ and -4.80. There is obviously no physical sense in these differences. Thus the Charton correlations, although giving satisfactory results, may lead to serious errors when analyzing the substituent effects on the properties of organophosphorus compounds. This danger may be avoided by using the σ^ϕ constants.

The correlation of σ^ϕ with σ_I and σ_R using eq 7 gives approximately linear dependence with the deviations mentioned above. Such a dependence shows that for organophosphorus compounds the substituent electronic effects are transmitted to the reaction center through inductive and mesomeric mechanisms. It may be assumed that the inductive mechanisms at phosphorus and carbon are in principle the same. This is confirmed by a good linear correlation between σ^ϕ values of alkyl groups and the σ^* Taft constants. As for the resonance effects, there is only a rough similarity between them for purely carbon and phosphorus compounds. For the aryl group bonded to phosphorus a contribution of the resonance component in σ^ϕ coincides with that of the aryl groups at carbon. For the RO, RS, and R_2N groups these contributions are different. For example, for the R_nX groups where X is an atom of the second row (N, O, or F; n varies, respectively, from 2 to 0), the two-parameter correlation of the σ^ϕ constants with σ_I and σ_R leads to the following results: $h = -0.46 \pm 0.08$, $\alpha = 2.69 \pm 0.16$, $\beta = 1.28 \pm 0.08$, $r_3 = 0.648$,[26] $R = 0.983$. However, one should not pay too much attention to this good correlation, but it does indicate that a contribution of the resonance component in the effective constant σ_{eff} is equal to 0.48.

Thus, the contribution of the resonance component to the σ^ϕ constants is determined essentially by the nature of the group attached. The overlap of p and π orbitals of a bonded group with the phosphorus d orbitals obviously differs from that with the π orbitals of benzene ring or some other purely carbon π system. Its dependence on the distances and angles is other than that for the p–p or p–π overlap, and this explains the different contribution of the resonance components to the substituent constants. Thus Charton's dependence of σ^ϕ on σ_I and σ_R is confirmed. In spite of the low correlation coefficient this dependence indicates a common similarity of the substituent effects at phosphorus and carbon. Certainly it would be tempting to employ the σ_I and σ_R constants in the correlation analysis of the organophosphorus reactions, but a more detailed discussion reveals specific differences in the resonance effects of groups at phosphorus and carbon. Certainly one cannot take into account such differences in the correlation with σ_I and σ_R, but this can be done by using the σ^ϕ constants. Therefore in correlation of the reaction rate and equilibrium constants of the organophosphorus compounds the results are better with the σ^ϕ constants. Thus it is the σ^ϕ constants that one should use in solving the correlation problems in the organophosphorus chemistry.

[26] Pair correlation coefficient for σ_R and σ_I.

Calculation of the pK_a Values of Alcohols from σ^* Constants and from the Carbonyl Frequencies of Their Esters

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As an alternative to direct measurement, the pK_a values of primary alcohols (RCH_2OH) may be calculated from σ^* constants by use of the equation pK_a (RCH_2OH) $= -1.316\sigma^*(R) + 15.74$ for alcohols in which C-2 is sp^3 or sp hybridized. For those alcohols in which C-2 is sp^2 hybridized, pK_a (RCH_2OH) $= -1.316\sigma^*(R) + 16.23$. Values of σ^* are based on pK_a data for the corresponding carboxylic acids (RCOOH) or on the carbonyl stretching frequencies of esters of RCH_2OH. Frequencies can be related to σ^* by bonding type: for C-2 (sp^3 or sp^2), $\sigma^*(R) = 0.08996\nu - 156.000$; for C-2 (sp), $\sigma^*(R) = 0.11757\nu - 203.991$; for C-2 ($sp^3$) but R = H or alkyl, $\sigma^*(R) = 0.10828\nu - 188.316$. For secondary alcohols, pK_a values can be calculated from $\Sigma\sigma^*$, the latter values being obtained by use of the additivity principle or from carbonyl frequencies of esters. Measurement of carbonyl frequency offers a novel and facile method for determination of σ^* values.

Aliphatic substituent constants (σ^* or σ_I) provide a measure of the relative effect of chain substituents on the electron density at a reactive atom or functional group. Originally, these constants were derived by Taft from ratios of the rates of acid and alkaline hydrolysis of esters and were shown, subsequently, to be applicable to a wide variety of reaction series, including the dissociation of carboxylic acids and alcohols.[2]

In connection with studies on alcohols as nucleophiles, reliable pK_a values were needed. The available

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[2] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.