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The Application of the Hammett Equation with the Constants σ^{ph} in the Chemistry of Organophosphorus Compounds

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The review deals with the application of the Hammett equation to organophosphorus reactions and equilibria using the constants σ^{ph}. As far as possible a complete list of the constants σ^{ph} is given. Analysis of the application of the constants σ^{ph} shows that linear correlations between the rate and equilibrium constants for organophosphorus reactions are usually obtained when the phosphorus atom is not a reaction centre.
For reactions involving phosphorus directly, linear correlations are achieved with the aid of the inductive (σ_I^{ph}) and resonance (σ_R^{ph}) constants, namely: $\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$. A method of calculation of the constants σ_I^{ph} and σ_R^{ph} is described and as far as possible a complete list of these constants is given for various groups attached to the phosphorus atom.
It has been demonstrated on 124 reaction series as examples the function $\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$ makes it possible to construct a universal system for the $\sigma\rho$ analysis of reactions, equilibria, and certain physical constants in the chemistry of organophosphorus compounds on the basis of the equation $\lg K = \lg K^0 + \rho\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$ with high correlation coefficients.
The relation between the constants α and ρ on the one hand and the type of reaction and its mechanism on the other is discussed.
The bibliography includes 117 references.

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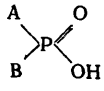
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1. INTRODUCTION

A characteristic feature of studies on the reactivity of organophosphorus compounds in recent years consists in the measurement of a large number of rate and equilibrium constants and the application of correlation equations to them. The first Hammett equation[1]:

$$\log \frac{K}{K^0} = \rho\sigma \qquad (1)$$

with the constants σ_p and σ_m^2 was applied to organophosphorus compounds in 1953 by Jaffé et al.[3] for the ionisation of aromatic phosphonic acids. In 1956 Kabachnik[4] showed that the Hammett equation is applicable to a wide variety of phosphorus acids:



and not only to aromatic acids provided that one uses the constants σ^{ph} specific to substituents linked to the phosphorus atom:

$$pK = pK^0 - \rho\Sigma\sigma^{\Phi}. \qquad (2)$$

In order to determine the constants σ^{ph}, about 150 ionisation constants of phosphorus acids in water and in 50% aqueous alcohol were employed in the calculation and the first 57 constants σ^{ph} were obtained. The use of these constants resulted in entirely satisfactory correlations between the ionisation constants (pK_a) of the acids (Table 2, series No. 1, 5, 12, 13).

2. THE CONSTANTS σ^{ph} FOR SUBSTITUENTS AT THE PHOSPHORUS ATOM

In recent years numerous quantitative data have accumulated on equilibrium and rate constants for reactions of organophosphorus compounds. Part of these data were used to determine new constants σ^{ph}. Thus, Kabachnik, Mastryukova, Melent'eva, and Shipov[5-7] determined the constants σ^{ph} for the C_6H_5O, p-$CH_3C_6H_4O$, cyclo-C_5H_9, and $CH_2{=}CH$ groups and Kabachnik, Balueva, and coworkers[8,9] determined the constants for the cyclo-C_6H_{11}, NC–CH_2CH_2, and $C_6H_{13}O$ groups. Ryss and Tul'chinksii[10] determined the constants σ^{ph} for fluorine directly linked to phosphorus, etc. However, the majority of the quantitative data have not been interpreted from this standpoint although their use would permit the determination of many new values of σ^{ph}.

Column 3 of Table 1 gives a complete compilation of the constants σ^{ph} published previously and calculated by the present authors from the literature data. Many of these constants were obtained as averages from several measurements in different reaction media and were then successfully used in various correlations. These constants are fairly reliable and have been printed in bold type in Table 1. The less reliable constants are printed in the usual type; the least reliable values are quoted with only one figure after the decimal point.

3. CORRELATIONS BETWEEN THE EQUILIBRIUM AND RATE CONSTANTS FOR REACTIONS AND THE CONSTANTS σ^{ph}

The constants σ^{ph} were found to be applicable in all those cases where the reaction does not involve directly the phosphorus atom, i.e. when the phosphorus atom is not subject to direct attack and hence σ-bonds involving phosphorus are not dissociated and new ones are not formed.

Table 1. The constants σ*, σ^{ph}, σ_I^{ph}, and σ_R^{ph} for substituents.

R	σ*	σ^{ph}	σ_I^{ph}	σ_R^{ph}	References	
					σ*	σ^{ph}
1	2	3	4	5	6	7
H	0.49	0	0	0	11	4
CH_3	0	−0.96	−0.96	0	11	4
C_2H_5	−0.100	−0.10	−1.10	0	11	4
C_3H_7	−0.115	−1.18	−1.18	0	11	4
iso-C_3H_7	−0.190	−1.30	−1.30	0	11	4
C_4H_9	−0.130	−1.22	−1.22	0	11	4
iso-C_4H_9	−0.125	−1.30	−1.30	0	11	4
s-C_4H_9	−0.210	−1.36	−1.36	0	11	4
t-C_4H_9	−0.300	−1.55	−1.55	0	11	4
C_5H_{11}	−0.162	−1.21	−1.21	0	11	12*
iso-C_5H_{11}	−0.162	−1.27	−1.27	0	11	12*
neo-C_5H_{11}	−0.165	−1.44	−1.44	0	11	13*
t-C_5H_{11}		−1.54	−1.54	0		13*
C_6H_{13}		−1.21	−1.21	0		12*
		−1.19	−1.19	0		13*
iso-C_6H_{13}		−1.21	−1.21	0		12*
C_8H_{17}		−1.11	−1.11	0		8
$C_{12}H_{25}$		−1.24	−1.24	0		13*
cyclo-C_5H_9	−0.200	−1.25	−1.25	0	11	6
cyclo-C_6H_{11}	−0.17	−1.19	−1.19	0	14	8
$CH_2{=}CH$	0.59	−0.68	0.22	−0.90	15	16
$CH_2{=}CH{-}CH_2$	0.23	−0.83	−0.50	−0.33	15*	13*
$C_6H_5CH_2$	0.215	−0.69	−0.53	−0.16	11	13*
$C_6H_5CH_2CH_2$	0.08	−1.06	−0.80	−0.26	11	17*
$(C_6H_5)_2CH$	0.405	−0.73	−0.15	−0.58	11	17*
$(C_6H_5)_3C$		−1.02				13*
$C_6H_5CH{=}CH$	0.41	−0.58	−0.14	−0.44	11	13*
$C_6H_5C{\equiv}C$	1.35	0.28	1.72	−1.44	11	17*
$HOCH_2$	0.555	−0.55	0.14	−0.69	11	4
$ClCH_2$	1.05	−0.05	1.13	−1.18	11	18
$BrCH_2$	1.00	0.0	1.0	−1.0	11	4
ICH_2	0.85	−0.1	0.7	−0.8	11	4
$C_6H_5OCH_2$	0.85	−0.2	0.7	−0.9	11	17*
$(CH_3)_3SiCH_2$	−0.26	−1.6	−1.5	−0.1	11	13*
Cl_2CH	1.94	0.27	2.90	−2.63	11	4
Cl_3C	2.61	0.3	4.2	−3.9	15	4
F_3C	2.49	0.7	4.0	−3.3	15	4[a]
$BrCH_2CH_2$	0.26	−0.8	−0.4	−0.4	11	13*
	0.40	−0.8	−0.2	−0.6	15	13*
$C_6H_5OCH_2CH_2$	0.27	−0.77	−0.42	−0.35	15*	12*
$NCCH_2CH_2$	0.80	−0.6	0.6	−1.2	11	8
	0.49	−0.6	0.0	−0.6	15*	8
$ClCH_2CH_2CH_2$	0.16	−0.72	−0.65	−0.07	15*	12*
^{-}O		0				4
HO	1.31	−0.39	1.65	−2.04	15	4
CH_3O	1.73	−0.12	2.48	−2.61	19*	4
C_2H_5O	1.64	−0.21	2.30	−2.52	19*, 20*	4
C_3H_7O	1.57	−0.32	2.16	−2.48	19*, 20*	4
iso-C_3H_7O	1.51	−0.29	2.04	−2.34	19*, 20*	4
C_4H_9O	1.55	−0.41	2.13	−2.54	19*, 20*	4
iso-C_4H_9O	1.52	−0.30	2.06	−2.36	19*, 20*	4
$C_5H_{11}O$	1.52	−0.39	2.06	−2.45		21*
iso-$C_5H_{11}O$	1.52	−0.38	2.06	−2.45		22*
neo-$C_5H_{11}O$	1.51	−0.29	2.04	−2.33		21
$C_6H_{13}O$		−0.32				9
	1.51	−0.40	2.04	−2.44		21*
$(CH_3)_2C{-}CH(CH_3)O$	1.46	−0.5	1.95	−2.45		21; σ_R^{ph} 23*
$ClCH_2CH_2O$		0.03			from σ^{ph} and σ_R^{ph}	9*
cyclo-$C_6H_{11}O$		−0.35				24*
C_6H_5O	2.24				15	
	1.91[b]	−0.06	2.83	−2.89		5
p-$CH_3C_6H_4O$		−0.14				5
CH_3S	1.47	0.15	1.96	−1.81	25*	26*
C_2H_5S	1.44	0.09	1.90	−1.81	27*	26*, 28*
C_3H_7S	1.38	−0.06	1.78	−1.84	27*	26*
iso-C_3H_7S	1.47	−0.06	1.96	−2.02	27*	26*
$(CH_3)_2N$	0.62	−1.22	0.27	−1.49	29*	30*
$(C_2H_5)_2N$	0.39	−1.54	−0.18	−1.36		31*, σ_R^{ph} 32*
p-$CH_3C_6H_4NH$		−1.7				33*
F	3.10	0.56	5.21	−4.65	15	10
Cl	2.68	0.93	4.37	−3.44	15	9*
C_6H_5	0.62	−0.48	0.27	−0.76	15	4
		−0.59[c]				6
C_6F_5	4.07	−0.02	7.13	−7.15	39*	39*

Table 1 (continued)

Aromatic Groups

R	σ^{ph}	Refs.	R	σ^{ph}	Refs.
m-$CH_3\overset{+}{N}H_2C_6H_4$	0.3	4	p-$CH_3C_6H_4$	−0.60	4
				−0.72[c]	16
p-$(CH_3)_2\overset{+}{N}HC_6H_4$	0.3	4	m-$C_6H_5NHC_6H_4$	−0.62	4
			p-HOC_6H_4	−0.65	4
m-$C_6H_5\overset{+}{N}H_2C_6H_4$	0.3	4	m-$CH_3NHC_6H_4$	−0.65	4
p-$NO_2C_6H_4$	0.13	4	p-$C_6H_5OC_6H_4$	−0.66	4
m-$NO_2C_6H_4$	0.10	4	m-$C_6H_5NHC_6H_4$	−0.67	4
p-$NH_2SO_2C_6H_4$	0.00	4	p-$(CH_3)_2NC_6H_4$	−0.68	4
p-CNC_6H_4	−0.04	34*		−0.91	41*
p-$HOCOC_6H_4$	−0.14	4		−1.17[c]	38*
m-$HOCOC_6H_4$	−0.18	4	p-$NH_2C_6H_4$	−0.78	4
m-ClC_6H_4	−0.22	4	p-$NH_2NHC_6H_4$	−0.79	4
m-BrC_6H_4	−0.23	4	p-$CH_3NHC_6H_4$	−0.81	4
p-$CH_3OCOC_6H_4$	−0.24	35*	p, m-$CH_2O_2C_6H_3$	−0.55	4
p-BrC_6H_4	−0.25	4	p-$C_6H_5COOC_6H_4$	−0.02	40*
p-ClC_6H_4	−0.29	4			
m-HOC_6H_4	−0.32	4			
m-$^{-}OCOC_6H_4$	−0.42	4			
p-$^{-}OCOC_6H_4$	−0.42	4			
m-$CH_3OC_6H_4$	−0.45[c]	36*, 37			
m-$NH_2NHC_6H_4$	−0.46	4			
p-$CH_3CONHC_6H_4$	−0.49	4			
p-$C_6H_5SC_6H_4$	−0.50	4			
m-$CH_3C_6H_4$	−0.55[c]	37*			
m-$NH_2C_6H_4$	−0.56	4			
p-$CH_3OC_6H_4$	−0.59	4			
	−0.74[c]	16			

[a] There was a misprint in the original: 0.50 was printed instead of 0.7 for σ^{ph}.
[b] Derived as the mean from numerous correlations for reactions of organophosphorus compounds.
[c] For two and more aryl groups at the phosphorus atom.
*Studies the data from which we employed in the calculation of the corresponding values of σ are denoted by an asterisk.

Table 2 presents the results for the correlations between the ionisation constants (pK_a) of organophosphorus acids in various media. Evidently the ionisation constants of acids of different types—phosphoric and phosphonic (first and second ionisations), phosphinic, phosphonous, and thioic, selenoic, and dithioic phosphorus acids—as well as the ionisation constants for phosphonium salts treated as acids show a satisfactory linear correlation with $\Sigma\sigma^{ph}$ regardless of the nature of the groups attached to phosphorus: alkyl and cycloalkyl groups, alkyl groups with electronegative substituents, aryl groups with different substituents, and also alkoxy-, aryloxy-, and other groups (see Figs. 1–3). It should be noted that such universal correlation is not always observed with other σ constants (σ*, σ^0, σ_p, σ_m, etc.). Whereas a satisfactory correlation is observed with the constants σ* for alkyl substituents[51] and the constants σ^0 [51] and σ [52] for aryl substituents, alkoxy-substituents remain outside the correlations. Here, of course, a unique correlation is not attainable.

Many of the acid ionisation constants listed in Table 2 are due to the authors of the review and others were taken from the literature. They were correlated in most cases by the present authors.

Table 3 presents the correlation of the protolysis constants (pK_p) of phosphorus acids in non-aqueous media using Hexamethoxy-Red as the base indicator.

Table 4 shows the relation between the basicity constants (pK_a) of phosphines, phosphine oxides, iminophosphoranes, and other substances and the constants σ^{ph}.

Table 2. Correlation of the ionisation constants of phosphorus acids in aqueous alcohol with the constants σ^{ph} ($pK = pK^0 - \rho\Sigma\sigma^{ph}$; $\alpha = 1.00$).

No. of series	Acid	Temp., °C	Alcohol content, %	No. of points n	pK_a^0	$\rho \pm S_\rho$	r	Standard deviation S	Refs.
1	ABPOOH		0	58	1.00	0.99±0.03	0.976		4
2	ABPOOH	20	0	8	0.98	1.06±0.12	0.965	0.27	42*
3	ABPOOH	20	0	5	1.05	0.95±0.10	0.982	0.21	43*
4	ABPOOH	20	7	20	1.02	1.04±0.02	0.995	0.07	44
5	ABPOOH		50	17	2.01	1.31±0.04	0.993		4
6	ABPOOH	20	50	16	2.05	1.24±0.03	0.995	0.07	44
7	ABPOOH	22	75	19	2.41	1.49±0.12	0.950	0.30	24*
8	ABPOOH	20	80	23	2.70	1.22±0.03	0.993	0.03	44
9	ABPOOH	22	95	17[a]	2.90	1.58±0.14	0.953	0.33	24*
10	ABPOOH	20	100	6[b]	6.70	0.91±0.09	0.982	0.15	43*
11	Ar_2POOH	23	THF 60	10	2.17	1.49±0.05	0.995	0.05	45*
12	AP (O) (O^-) OH		0	47	6.13	1.79±0.08	0.955		4
13	AP (O) (O^-) OH		50	19	7.59	1.36±0.04	0.992		4
14	ArP (H) OOH	25	0	6	1.14	1.20±0.14	0.974	0.06	34*
15	ABPSOH	20	7	8	0.70	0.92±0.02	0.995	0.07	46
16	ABPSOH	20	80	23	2.06	1.31±0.02	0.995	0.06	46
17	ABPSOH	20	100	5	6.79	0.70±0.10	0.945	0.10	43*
18	ABPSeOH	20	7	6	0.56	0.88±0.02	0.999	0.03	47
19	ABPSeOH	20	80	6	1.77	1.34±0.03	0.992	0.11	47
20	ABPSSH	20	7	17	1.74	−0.01±0.05	0.978[c]	0.12	48*
21	ABPSSH	20	80	17	2.64	−0.02±0.03	0.994[c]	0.06	48*
22	p-ABP(O)C_6H_4COOH	25	50	6	4.88	0.02±0.01	0.999[c]	0.02	49*
23	m-ABP(O)C_6H_4COOH	25	50	5	5.05	0.04±0.01	0.999[c]	0.02	49*
24	$[Ar_3\overset{+}{P}-CH_2COC_6H_5]\ X^-$[d]	20	50	5	3.29	1.79±0.19	0.983	0.12	36*
25	$[Ar_3\overset{+}{P}-CH_2COC_6H_5]\ X^-$[d]	20	80	6	3.27	1.58±0.16	0.979	0.17	36*
26	$[R_3\overset{+}{P}-CH_2COC_6H_5]\ X^-$[d]	20	95	4	2.54	2.11±0.11	0.997	0.12	50*
27	$\left[Ar_3\overset{+}{P}-CH(C_6H_4\text{-}o)(C_6H_4\text{-}o)\right]\ Br^-$		95	9	6.22	2.02±0.21	0.964	0.23	37*

[a] The point corresponding to $(C_6H_5O)_2POOH$ was excluded.
[b] The points corresponding to $(ArO)_2POOH$ and $(ClCH_2)(ArO)POOH$ were excluded.
[c] The correlation coefficient was calculated after rotating the coordinate axes by 45°.
[d] X = Cl or Br.
*Studies the data from which were used for the correlations.

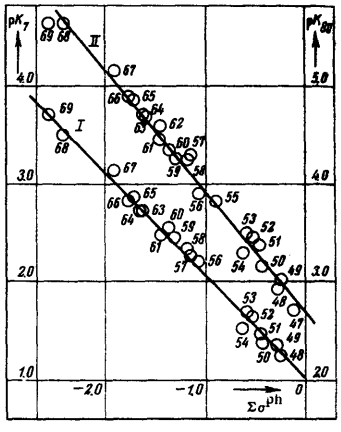


Figure 1. Variation of the ionisation constants (pK_a) of phosphorus acids of the type ABPOOH with $\Sigma\sigma^{ph}$ in 7% (I) and 80% (II) aqueous alcohol (see Table 2, series 4 and 8). The numbers of the points and the substituents A and B for the acids are indicated: 47) C_6H_5O, C_6H_5O; 48) CH_3O, CH_3O; 49) p-$CH_3C_6H_4O$, p-$CH_3C_6H_4O$; 50) C_2H_5O, C_2H_5O; 51) C_6H_5O, OH; 52) p-$CH_3C_6H_4O$, OH; 53) p-ClC_6H_4, p-ClC_6H_4; 54) C_3H_7O, C_3H_7O; 55) CH_2=CH, C_2H_5O; 56) CH_2=CH, OH; 57) CH_2=CH, C_6H_5; 58) C_6H_5, C_6H_5; 59) C_6H_5, p-$CH_3C_6H_4$; 60) CH_2=CH, CH_2=CH; 61) p-$CH_3C_6H_4$, p-$CH_3C_6H_4$; 62) p-$CH_3OC_6H_4$, p-$CH_3OC_6H_4$; 63) cyclo-C_5H_9, OH; 64) C_3H_7, C_6H_5; 65) cyclo-C_5H_9, C_6H_5; 66) iso-C_3H_7, C_6H_5; 67) CH_3, CH_3; 68) C_4H_9, C_4H_9; 69) iso-C_4H_9, iso-C_4H_9.

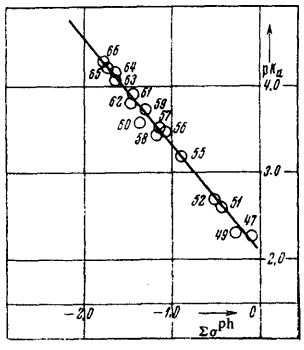


Figure 2. Variation of the ionisation constants (pK_a) of phosphorus acids of the type ABPOOH with $\Sigma\sigma^{ph}$ in 50% aqueous alcohol (see Table 2, series 6; the legend is the same as in Fig. 1).

These data were obtained mainly in nitromethane and are due to different investigators. Here too satisfactory correlation coefficients have been obtained (see also Figs. 4 and 5).

The attempt by Henderson and Streuli[61] to correlate the pK_a for phosphines with the inductive constants σ^* should be noted. They obtained a pronounced scatter of points which they interpreted as three parallel straight lines with relatively satisfactory correlation for primary, secondary,

and tertiary phosphines. When the constants σ^{ph} are employed, a single correlation is achieved for phosphines of all types with a better correlation coefficient.

Table 5 presents the correlations between the rate constants for certain reactions of organophosphorus compounds. These are alkylation of salts of dithioic phosphorus acids with benzyl chloride, bromination of the double bonds in vinyl derivatives of phosphorus, Pishchimuka rearrangement, etc. (Figs. 6 and 7). It should be noted that unfortunately the reaction mechanisms have not always been established[65], which makes $\sigma\rho$ analysis difficult.

Nikolaev et al.[66] showed that the constants σ^{ph} are applicable to the correlation of the quantitative data on the extraction of actinide salts by organophosphorus extracting agents from nitric acid media into organic solvents. It was found that linear correlations hold not only for the effective extraction constants ($\bar{k}$) or the stability constants of the complexes but also for the partition coefficients (K_p); the relevant data are presented in Table 6.

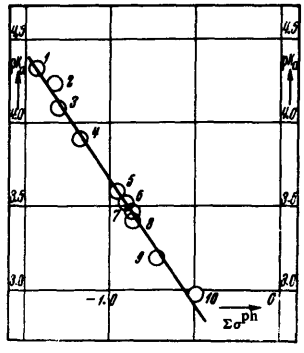


Figure 3. Variation of the ionisation constants (pK_a) of phosphorus acids of the type Ar_2POOH with $\Sigma\sigma^{ph}$ in 60% aqueous tetrahydrofuran (see Table 2, series 11): 1) p-$CH_3C_6H_4$, p-$CH_3C_6H_4$; 2) p-$CH_3OC_6H_4$, C_6H_5; 3) p-$CH_3C_6H_4$, C_6H_5; 4) C_6H_5, C_6H_5; 5) p-ClC_6H_4, C_6H_5; 6) p-BrC_6H_4, C_6H_5; 7) m-BrC_6H_4, C_6H_5; 8) m-ClC_6H_4, C_6H_5; 9) p-ClC_6H_4, p-ClC_6H_4; 10) p-$NO_2C_6H_4$, C_6H_5.

Table 3. Correlation of the protolysis constants for phosphorus acids at 20°C in non-aqueous media using Hexamethoxy-Red as the indicator base ($pK_p = pK_p^0 - \rho\Sigma\sigma^{ph}$; $\alpha = 1.00$).

No. of series	Acid	Medium	n	pK_p^0	$\rho \pm S_\rho$	r	S	Refs.
1	ABPOOH	C_6H_6	4	−2.89	6.11±0.08	0.982	0.19	18
2	ABPOOH	C_6H_5Cl	4	−3.51	7.02±0.05	0.994	0.12	18
3	ABPSOH	C_6H_6	7	−2.12	1.00±0.05	0.994	0.05	18
4	ABPSOH	C_6H_5Cl	7	−2.53	1.06±0.04	0.997	0.04	18
5	ABPSSH	C_6H_6	4	−1.29	0.89±0.08	0.992	0.05	18
6	ABPSSH	C_6H_5Cl	4	−2.20	0.96±0.07	0.990	0.05	18

*Studies the data from which were used for the correlations.

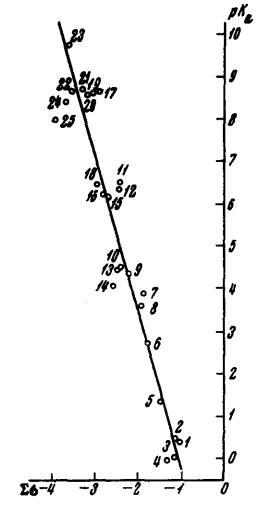


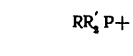
Figure 4. Variation of the basicity constants (pK_a) of phosphines of the type R′R″R‴P with $\Sigma\sigma^{ph}$ in nitromethane (see Table 4, series 3): 1) $CNCH_2CH_2$, $CHCH_2CH_2$, H; 2) C_8H_{17}, H, H; 3) C_6H_5, C_6H_5, H; 4) iso-C_4H_9, H, H; 5) $CNCH_2CH_2$, $CNCH_2CH_2$, $CNCH_2CH_2$; 6) C_6H_5, C_6H_5, C_6H_5; 7) CH_3, CH_3, H; 8) CH_3, $CNCH_2CH_2$, $CNCH_2CH_2$; 9) C_8H_{17}, C_8H_{17}, H; 10) cyclo-C_6H_{11}, cyclo-C_6H_{11}, H; 11) CH_3, CH_3, C_6H_5; 12) CH_3, CH_3, $CNCH_2CH_2$; 13) C_4H_9, C_4H_9, H; 14) iso-C_4H_9, iso-C_4H_9, H; 15) C_2H_5, C_2H_5, C_6H_5; 16) C_8H_{17}, C_8H_{17}, $CNCH_2CH_2$; 17) CH_3, CH_3, CH_3; 18) C_4H_9, C_4H_9, $CNCH_2CH_2$; 19) CH_3, CH_3, C_2H_5; 20) C_2H_5, C_2H_5, CH_3; 21) C_2H_5, C_2H_5, C_2H_5; 22) C_3H_7, C_3H_7, C_3H_7; 23) cyclo-C_6H_{11}, cyclo-C_6H_{11}, cyclo-C_6H_{11}; 24) C_4H_9, C_4H_9, C_4H_9; 25) iso-C_4H_9, iso-C_4H_9, iso-C_4H_9.

Table 4. Correlation of the basicity constants (pK_a) of organophosphorus bases with the constants σ^{ph} ($pK_a = pK_a^0 - \rho\Sigma\sigma^{ph}$; $\alpha = 1.00$).

No. of series	Formula	Medium	n	pK_a^0	$\rho \pm S_\rho$	r	S	Refs.
1	Ar_3P, 20°	80% C_2H_5OH	6[a]	0.26	1.90±0.25	0.968	0.12	53*
2	R_3P	C_2H_5OH	10	0.93	2.11±0.56	0.802	1.05	54*
3	R_3P	CH_3NO_2	25	−3.45	3.42	0.950		8
4	$XC_6H_4P(C_6H_5)_2$	CH_3NO_2	6	4.23	4.61±0.26	0.994	0.14	41*
5	R_3PO	CH_3NO_2	7	2.40	1.69±0.19	0.970	0.22	35*
6	$R_2P(O)—CH_2—P(O)R_2$	CH_3NO_2	10	4.59	0.79±0.22	0.985	0.25	55
7	$Ar_3P{=}NC_6H_5$	95% C_2H_5OH	4	2.82	3.41±0.12	0.989	0.25	56*
8	ABCP=NC_6H_5	CH_3NO_2	9	13.17	1.90±0.13	0.981	0.24	57
9	ABCP=NC_6H_4F-p	CH_3NO_2	8	12.78	1.89±0.15	0.982	0.26	57
10	$XC_6H_4P(C_6H_5){=}NC_6H_4NO_2$-$p$	CH_3NO_2	6	14.34	2.49±0.16	0.992	0.12	58*
11	ABP (=NR) (NHR′)	CH_3NO_2	10	13.02	1.68	0.981	0.30	59
12	cyclo-$(R_2PN)_3$	CH_3NO_2	10	2.49	1.24±0.11	0.971	0.97	60*

[a] The point corresponding to $(p\text{-}ClC_6H_4)_3P$ was excluded (see Ref. 53).
*Studies the data from which were used for the correlations.

Table 5. Correlation of the rate and equilibrium constants for certain reactions of organophosphorus compounds with the constants σ^{ph} ($\lg K = \lg K^0 - \rho\Sigma\sigma^{ph}$; $\alpha = 1.00$).

No. of series	Reaction	Temp., °C	Medium	n	$\lg K^0$	$\rho \pm S_\rho$	r	S	Refs.
1	ABPSSNA+$C_6H_5CH_2Cl$	25	96% C_2H_5OH	12	−3.87	−0.236	0.964		48
2	ABP (S) OC_2H_5+C_3H_7I	105	C_3H_7I	6	−5.53	−0.40±0.02	0.995	0.05	33*
3	ABP (=NC_6H_5) OC_2H_5+C_2H_5I	50	CH_3CN	6	−3.44	−0.60±0.06	0.984	0.08	62
4	RR'_2P+ 	35	C_6H_6	5	−4.13	−1.78±0.62	0.856	0.23	63*
5	ditto	40	C_6H_6	4	−4.35	−2.45±0.65	0.935	0.19	63*
6	»	45	C_6H_6	4	−4.23	−2.42±0.80	0.907	0.23	63*
7	$Ar_3P+N_3C_6H_5 \underset{k_2}{\overset{k_1}{\rightleftarrows}} Ar_3P{=}N{-}N{=}NC_6H_5$	25	C_6H_6	5	−2.64	−1.01±0.24	0.922	0.15	38*
8		25	C_6H_6	5	−1.06	0.38±0.06	0.969	0.03	38*
9	$Ar_3PN_3C_6H_5 \xrightarrow{k_3} Ar_3P{=}NC_6H_5+N_2$	25	C_6H_6	5	−1.07	0.40±0.15	0.838	0.09	38*
10	Ar_3P+S	25	C_6H_6	5	−7.09	−2.71±0.19	0.992	0.17	64*
11	ABP (O) $CH{=}CH_2+Br_2$, $k_{1/2}$	15	CCl_4	14	−3.38	−0.78±0.07	0.950	0.12	9
12	$Ar_3P{=}NC_6H_5+C_6H_5CHO$	45.5	C_2H_5OH	4	−0.79	−0.24±0.04	0.976	0.03	56*
13	ABP (S) OH ⇄ ABP (O) SH	20	7% C_2H_5OH	9	0.80	1.32±0.13	0.964	0.13	46
14	ABP (S) OH ⇄ ABP (O) SH	20	80% C_2H_5OH	7	0.90	2.51±0.38	0.947	0.17	46

*Studies the data from which were used for the correlations.

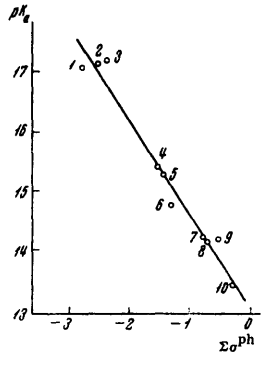


Figure 5. Variation of the basicity constants (pK_a) of phosphamidines of the type ABP(=NR)NHR′ with $\Sigma\sigma^{ph}$ in nitromethane (see Table 4, series 11). The numbers of the points and the substituents A and B are indicated for constant R = p-$CF_3C_6H_4$ and R′ = p-$CH_3OC_6H_4$: 1) iso-C_4H_9, iso-C_4H_9; 2) C_3H_7, C_3H_7; 3) C_2H_5, C_2H_5; 4) C_2H_5, iso-C_3H_7O; 5) C_2H_5, C_2H_5O; 6) C_6H_5, C_6H_5; 7) C_6H_5, C_2H_5O; 8) C_3H_7O, C_3H_7O; 9) C_2H_5O, C_2H_5O; 10) CH_3O, CH_3O.

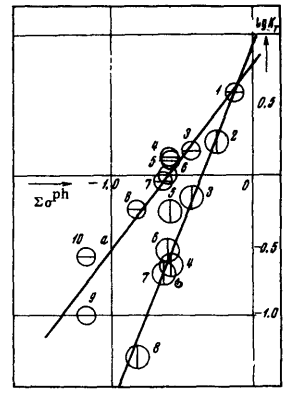


Figure 7. Variation of the tautomeric equilibrium constants ($\lg K_T$) for monothioic phosphorus acids of the type ABPSOH with $\Sigma\sigma^{ph}$ in 7% (*a*) and 80% (*b*) aqueous alcohol (see Table 5, series 13 and 14): 1) C_6H_5O, C_6H_5O; 2) CH_3O, CH_3O; 3) C_2H_5O, C_2H_5O; 4) iso-C_3H_7O, iso-C_3H_7O; 5) ClC_6H_4; ClC_6H_4; 6) iso-C_4H_9O, iso-C_4H_9O; 7) C_3H_7O, C_3H_7O; 8) C_4H_9O, C_4H_9O; 9) CH_3, C_2H_5O; 10) C_6H_5, C_6H_5.

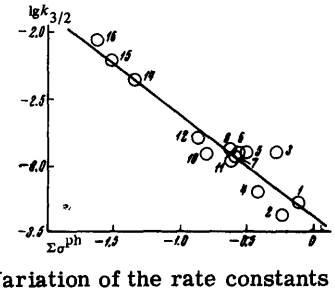


Figure 6. Variation of the rate constants ($\lg k_{3/2}$) for the bromination of derivatives of the type ABP(O)$CH{=}CH_2$ in carbon tetrachloride (see Table 5, series 11): 1) C_6H_5O, C_6H_5O; 2) CH_3O, CH_3O; 3) p-$CH_3C_6H_4O$, p-$CH_3C_6H_4O$; 4) C_2H_5O, C_2H_5O; 5) C_2H_5O, C_3H_7O; 6) iso-C_3H_7O, iso-C_3H_7O; 7) iso-C_4H_9O, iso-C_4H_9O; 8) C_3H_7O, C_3H_7O; 10) C_4H_9O, C_4H_9O; 11) $C_6H_{13}O$, $C_6H_{13}O$; 12) C_6H_5, C_4H_9O; 14) CH_3, C_4H_9O; 15) C_2H_5, C_4H_9O; 16) C_4H_9, C_4H_9O.

4. SEPARATION OF THE CONSTANTS σ^{ph} INTO INDUCTIVE AND RESONANCE COMPONENTS

The application of the constants σ^{ph} to reactions in which the phosphorus atom participates directly and to the physical properties of organophosphorus compounds proved to be more complicated. Numerous examples are known where the correlation with the aid of the constant σ^{ph} does not yield satisfactory results. Thus, in the attempt to correlate the rate constants for the alkaline hydrolysis of compounds of the type ABP(O)X, where X is fluorine or the p-nitrophenyl group (Maklyaev et al.[67]) it was found that the linear relation embraces only groups of similar substances: the data for phosphonates lie on one line and those for phosphates, as it were, lie on another (Fig. 8*a*). Similarly the data of Henderson and Buckler[68] for the rate constants for the alkylation of phosphines with ethyl iodide in acetone

are not correlated with the constants σ^{ph}. The points corresponding to different phosphines in Fig. 9 are distributed in a most peculiar fashion. At the same time the basicities of these phosphines show a satisfactory linear correlation between pK_a (in nitromethane) and $\Sigma\sigma^{ph}$ (Table 4, series 3)[8].

It is noteworthy that in both these and other known cases, where there is no correlation with the σ^{ph}, it is also impossible to achieve a linear correlation with any other known σ constants, for example, σ^* (Fig. 8*b*), σ^0, and others.

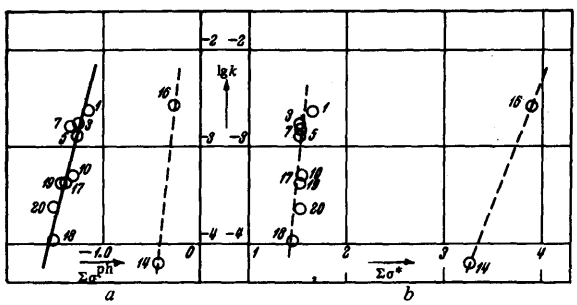


Figure 8. Correlation between the rate constants for alkaline hydrolysis ($\lg k$) of phosphorofluoridates and phosphonofluoridates of the type ABPOF: *a*) with $\Sigma\sigma^{ph}$; *b*) with $\Sigma\sigma^*$: 1) CH_3, C_2H_5O; 3) CH_3, iso-C_3H_7O; 5) CH_3, iso-C_4H_9O; 7) CH_3, iso-$C_5H_{11}O$; 10) C_2H_5, C_2H_5O; 14) C_2H_5O, C_2H_5O; 16) C_2H_5O, C_3H_7O; 17) C_3H_7, C_2H_5O; 18) iso-C_3H_7, C_2H_5O; 19) C_4H_9, C_2H_5O; 20) iso-C_4H_9, C_2H_5O.

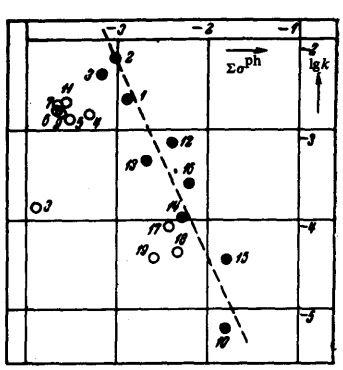


Figure 9. Correlation of the rate constants ($\lg k$) for the alkylation of phosphines of the type R′R″R‴P (according to the data of Henderson and Buckler[68]) with $\Sigma\sigma^{ph}$. The numbers of the points and the substituents R′, R″, and R‴ are indicated: 1) CH_3, CH_3, CH_3; 2) CH_3, CH_3, C_2H_5; 3) CH_3, C_2H_5, C_2H_5; 4) C_2H_5, C_2H_5, C_2H_5; 5) C_3H_7, C_3H_7, C_3H_7; 6) C_4H_9, C_4H_9, C_4H_9; 7) C_4H_9, C_4H_9, C_4H_9 [the second value of $\lg k$ quoted by the authors for $(C_4H_9)_3P$ was employed]; 8) iso-C_4H_9, iso-C_4H_9, iso-C_4H_9; 9) C_5H_{11}, C_5H_{11}, C_5H_{11}; 10) $CNCH_2CH_2$, $CNCH_2CH_2$, $CNCH_2CH_2$; 11) cyclo-C_6H_{11}; cyclo-C_6H_{11}, cyclo-C_6H_{11}; 12) CH_3, CH_3, C_6H_5; 13) C_2H_5, C_2H_5, C_6H_5, 14) C_2H_5, C_6H_5, C_6H_5; 15) C_6H_5, C_6H_5, C_6H_5; 16) *p*-$CH_3OC_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$CH_3OC_6H_4$; 17) C_4H_9, C_4H_9, H; 18) C_8H_{17}, C_8H_{17}, H; 19) iso-C_4H_9, iso-C_4H_9, H.

The complexity of the application of $\sigma\rho$ analysis to organophosphorus reactions of this type and the consequent apparent failure of the universality of the constants σ^{ph} gave rise to a number of papers in which other methods for the correlation analysis of organophosphorus compounds are proposed. These include the correlation of Peppard et al.[24] embracing the carboxylic and phosphonic acid series, the correlation between the NMR chemical shifts of ^{31}P with special constants[69], the constants σ_X^{ph} derived by Knunyants et al.[22] specifically for the hydrolysis of phosphorochloridates, phosphorofluoridates, and *p*-nitrophenyl phosphates, another set of constants for the hydrolysis of the corresponding phosphonates, and a third set for phosphonochlorido-thiolates[26], the correlation of Rozen and coworkers[70] between the extraction constants and the electronegativities of the substituents at the phosphorus atom, the multiparameter correlation of Pal'm et al.[71], etc. All these attempts at correlation in the chemistry of organophosphorus compounds were not developed further, since the constants proposed were not universal and could be applied only to a very limited range of substances and reaction series.

Table 6. Correlation of data[86] for the extraction of actinide salts with the constants σ^{ph} ($\alpha = 1.00$).

No. of series	Extraction	Medium	*n*	$\lg K_e^0$	$\rho+S_\rho$	*r*	*S*
1	$UO_2(NO_3)_2$+R′R″R‴PO[a]	H_2O/C_6H_6	12	−2.16	−1.06	0.973	0.23
2	ditto	$2M$ HNO_3/C_6H_6	15	−0.51	−0.96	0.968	0.22
3	»	$4M$ HNO_3/C_6H_6	13	−0.04	−0.73	0.976	0.16
4	»	$6M$ HNO_3/C_6H_6	15	0.10	−0.61	0.968	0.14
5	»	$8M$ HNO_3/C_6H_6	15	0.10	−0.48	0.907	0.14
6	»	HNO_3/C_6H_6, according to K_e	13	0.12	−0.81	0.975	0.18
7	»[b]	$0.5M$ HNO_3/CCl_4	15	−1.62	−1.32	0.987	0.17
8	»	$1M$ HNO_3/CCl_4	12	−1.11	−1.21	0.981	0.19
9	»	$2M$ HNO_3/CCl_4	14	−0.96	−1.42	0.961	0.21
10	»[c]	H_2O/CCl_4	13	−1.58	−0.80	0.976	0.17
11	»[d]	$0.5M$ HNO_3/C_6H_6	6	−1.89	−1.30	0.986	0.29
12	»[e]	$1M$ HNO_3/CCl_4	8	−0.39	−0.89	0.970	0.26
13	»	$3M$ HNO_3/CCl_4	8	0.74	−0.56	0.924	0.27
14	»[f]	$5M$ HNO_3/CCl_4	8	1.06	−0.41	0.885	0.26
15	»	HNO_3/CCl_4, according to K_e	8	1.00	−0.49	0.932	0.22
16	$Pu(NO_3)_4$+R′R″R‴PO[g]	$0.5M$ HNO_3/CCl_4	14	−1.61	−1.11	0.936	0.32
17	ditto	$1M$ HNO_3/CCl_4	11	−0.89	−0.94	0.921	0.32
18	»	$2M$ HNO_3/CCl_4	14	0.64	−0.27	0.706	0.27
19	»[h]	$2M$ HNO_3/CCl_4	5	−1.24	−1.29	0.966	0.29
20	»	$2M$ HNO_3/CCl_4	5	−1.26	−1.20	0.977	0.26
21	$UO_2(NO_3)_2$+R′R″R‴PO	C_6H_6	10	(log K^0) −2.36		0.994	0.26

[a] $c_{UO_2(NO_3)_2} = 0.1$ M; [b] $c_{UO_2(NO_3)_2} = 50$ g litre^{-1}; [c] $c_{UO_2(NO_3)_2} = 0.2$ M; [d] $c_{UO_2(NO_3)_2} = 8.4 \times 10^{-4}$ M; [e] $c_{UO_2(NO_3)_2} = 0.01$ M; [f] On further increase of the concentration of nitric acid, the correlation became greatly impaired; [g] $c_{Pu(NO_3)_4} = 1$ g litre^{-1}; [h] $c_{Pu(NO_3)_4} = 0.9$ g litre^{-1}.

At the same time, the extensive experience gained in the application of the constants σ^{ph} gave rise to the hope that it might be possible to develop correlation methods with the aid of σ^{ph} constants which would be universal and would permit $\sigma\rho$ analysis of the rate and equilibrium constants for a wide variety of organophosphorus compounds in which the phosphorus atom does and does not participate directly.

In order to develop such a system, it was necessary to elucidate first the nature of the electronic effects characterised by the constants σ^{ph}. In the paper quoted above[4], Kabachnik does not deal with the problem of the nature of the constants σ^{ph} at all; this was done for the first time by Pal'm[51], who established two linear relations: between the constants σ^0 of the *meta*-, and *para*-substituents in phenyl groups and the corresponding (for the substituted phenyl groups) constants σ^{ph}:

$$\sigma^{ph} = -0.48 + 0.78\sigma^0 \quad (3)$$

and between the constants σ^{ph} for alkyl substituents and Taft's inductive constants σ^*:

$$\sigma^{ph} = -0.965 + 1.97\sigma^*. \quad (4)$$

Hence Pal'm concluded that the constants σ^{ph} refer to inductive effects. At the same time he took into account the fact that numerous σ^{ph} constants for substituted alkyl, alkoxy-, and many other groups cannot be related by any simple procedure to the known constants σ. He suggested that in the case of such groups one is dealing with a "field effect"—the electrostatic interaction between the charge of the phosphonate or phosphate anion and the dipole of the substituent, which contributes to the constant σ^{ph}. However, this explanation, on which, incidentally, Pal'm does not insist, contradicts many experimental data. Firstly, there are reaction series, readily susceptible to correlation with the constant σ^{ph} in which there are no ionic centres either in the ground or in the transition state. For example, the radical bromination of vinyl derivatives of phosphorus[9], the order of which is 3/2, is a reaction of this type. Secondly, it is difficult to postulate powerful ion–dipole interaction for groups such as phenyl or vinyl, which nevertheless deviate from the linear relation between σ^{ph} and σ^*.

Finally, recently Mastryukova and Kabachnik[52] established that the constants σ^{ph} for aromatic groups are well correlated not only with Taft's σ^0 constants, characterising the inductive effect of the substituents in a phenyl group, but also with the usual σ constants, which include both the inductive and resonance components:

$$\sigma^{ph} = -0.415 + 0.634\sigma. \quad (5)$$

The correlation in the latter case is just as satisfactory. The the concept of the purely inductive nature of the constants σ^{ph} is found not to hold even after corrections for the "field effect".

On the other hand, there are convincing data indicating that the electronic effect of substituents at the phosphorus includes a resonance component. Thus in many studies the concept of d_π–p_π conjugation was invoked by the authors in the discussion of the results of chemical investigations or physical measurements. In their study on the kinetics of the hydrolysis of substituted phosphinyl chlorides, Dostrovsky and Halman[72] attribute the effect of substituents in the phosphinyl group on the rate of hydrolysis to inductive and resonance effects. Other investigators of the kinetics of the substitution reactions (solvolysis, hydrolysis) at a saturated phosphorus atom (Heat[73], Larsson[30], Hudson[74], Maklyaev and coworkers[23,67,75], Bel'skii and coworkers[76,77], etc.) also developed this point of view. In 1962 Kabachnik et al.[6] showed that the constants σ^{ph} of aryl groups can vary under the influence of steric hindrance to conjugation. A systematic description of the evidence in favour of the resonance interaction of the phosphorus atom with the groups joined to it may be found in papers by Hudson[65], Kabachnik[78], Loshadkin[79], etc. At present there is no doubt that the generally adopted hypothesis is valid.

In this connection there arose the idea that the constants σ^{ph} be divided into inductive (σ_I^{ph}) and resonance (σ_R^{ph}) components and that their role in the correlation of the reactivities of organophosphorus compounds be elucidated. Mastryukova[80] reported such subdivision of the constants at the Fourth Conference on the Chemistry and Application of Organophosphorus Compounds at Kazan in January 1969.

In the series of organic phosphorus compounds it was of course impossible to apply the procedures for the subdivision of the constants σ^{ph} into σ_I^{ph} and σ_R^{ph} employed in the aromatic series. In the latter case several methods were used to divide the constants into the inductive and resonance components: the inductive constants were calculated from model reaction series such as ionisation of bicyclo[2,2,2] octane-1-carboxylic acid[81], from Taft's σ^* constants[82], from the ionisation constants of substituted acetic acids[83], or from the ionisation constants of substituted *p*-toluic acids[84] or they were evaluated by comparing the constants σ_p and σ_m put forward by Taft and Lewis[85] and modified by Roberts and Jaffé[86]. With organophosphorus compounds, it was of course impossible to employ any of these methods.

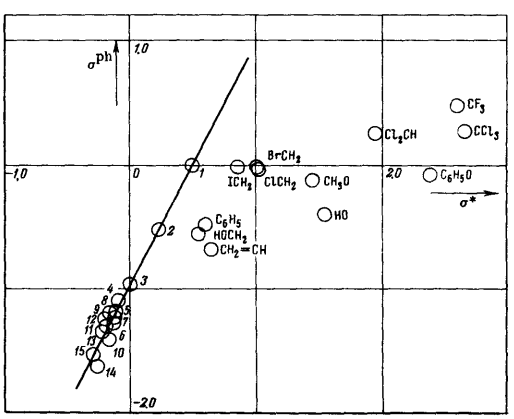


Figure 10. Relation between the constants σ^{ph} and Taft's σ^* constants for the substituents R. The numbers of the points and the substituents R are indicated: 1) H; 2) $C_6H_5CH_2$; 3) CH_3; 4) C_2H_5; 5) C_3H_7; 6) iso-C_4H_9; 7) C_4H_9; 8) cyclo-C_6H_{11}; 9) C_6H_{13}; 10) $(CH_3)_3CCH_2$; 11) iso-C_3H_7; 12) cyclo-C_5H_9; 13) s-C_4H_9; 14) $(CH_3)_3SiCH_2$; 15) $(CH_3)_3C$.

The subdivision of the constants σ^{ph} into σ_I^{ph} and σ_R^{ph} is based on the following considerations. It was noted above that the constants σ^{ph} for alkyl groups are linearly related to Taft's σ^* constants, i.e. they reflect only inductive effects. Fig. 10 shows the correlation between the constants σ^{ph} and σ^* for alkyl groups. Points corresponding to different substituents are also included. They do not lie on the straight line for the alkyl groups but are located to one side, in the direction of higher values of σ^*. It might have been supposed that the inductive effects of all these groups also follow the linear relation shown in Fig. 10 and the

deviations are due to resonance effects. Fig. 11 illustrates this hypothesis: for the points Q we have $OA = \sigma^*$, $AQ = \sigma^{ph}$, $BQ = \sigma_R^{ph}$, and $AB = \sigma_I^{ph}$. It follows from the above that the inductive components of the constants σ^{ph} for these substituents can also be calculated from the constants σ^* using the linear equation†

$$\sigma_I^{ph} = -0.960 + 1.99\,\sigma^* \qquad (6)$$

and the constants σ_R^{ph} can be found by difference

$$\sigma_R^{ph} = \sigma^{ph} - \sigma_I^{ph}.$$

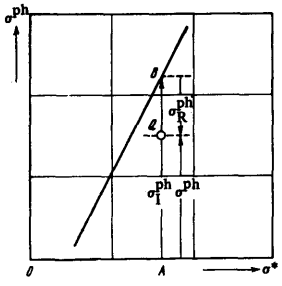


Figure 11. Relation between the constants σ^{ph}, σ_I^{ph}, and σ_R^{ph}.

Thus it has been arbitrarily assumed here that in the ionisation of acids the ratio $\sigma_I^{ph} : \sigma_R^{ph} = 1 : 1$ ($\alpha = 1$, see below).

One must of course bear in mind that the above treatment includes a number of arbitrary assumptions. For example, it is assumed that the inductive effects of alkyl groups follow the same relation as the inductive effects of substituted alkyl, aryl, alkoxy-, and other groups. Analysis of the constants for purely organic reaction series shows that this is not quite true, at least as regards the transmission of inductive effects along a saturated chain [87]. Probably the chemistry of phosphorus provides a better justification for the above hypothesis. This is evident if only from the existence of a unique correlation for all substituted and unsubstituted aromatic and aliphatic phosphorus acids.

The second assumption is that all the deviations from the linear relation (Fig. 10) have been attributed solely to resonance effects, without taking into account steric factors and hyperconjugation. The influence of steric factors on the reactivity of organophosphorus compounds will be discussed below. It is clearly shown only in a few cases. In most of the other cases the large bulk of the phosphorus atom ensures low steric hindrance due to the atoms and groups attached to it. At any rate, steric hindrance is in this case significantly lower than at the carbon atom. The effect of hyperconjugation is also probably slight (see below).

The above assumptions do not of course have a rigorous justification. However, they are no more arbitrary than those made in the separation of the inductive and resonance constants in the aromatic series, which does not preclude their fruitful employment.

† We revised the parameters of the equation, which differ somewhat from those quoted by Pal'm [51].

The constants σ^*, which are necessary in the calculation of inductive constants σ_I^{ph} by Eqn. (6), are presented in column 2 of Table 1. For electronegative substituents such as F, Cl, OH, CF_3, CCl_3, C_6H_5, CH_2=CH, and certain others, the constants σ^* were taken from Pal'm's book [15]; he calculated them from the ionisation constants of substituted acetic acids by the equation

$$\sigma^* = (2.623 - 0.552\,pK_a) \pm 0.034 \qquad (7)$$

using the conversion $\sigma^*_{XCH_2} = 0.388\sigma^*_X$. These constants differ somewhat from those quoted in "The Chemist's Handbook" [88] and are probably more accurate. The constants σ^* for CH_2=$CHCH_2$, $ClCH_2CH_2CH_2$, and other XCH_2 groups were calculated from the corresponding constants for the groups X by multiplying the latter by 0.388. [15]

Table 7. The constants σ^* for RO groups calculated from the ionisation constants of alkoxyacetic acids ($ROCH_2COOH$). [19]

R	pK_a	$\sigma^*_{ROCH_2}$	σ^*_{RO}	σ^*_{RO} calc. from σ_I	
				according to Taft (Ref.29)	according to Charton (Ref.83)
CH_3	3.53	0.67	1.73[a]	1.56; 1.87	—
C_2H_5	3.60	0.64	1.64	1.68	1.68
C_3H_7	3.65	0.61	1.57	1.74	1.68
iso-C_3H_7	3.69	0.59	1.51	—	1.62
C_4H_9	3.66	0.60	1.55	1.93	1.68
iso-C_4H_9	3.67	0.60	1.52	—	—
C_6H_5	3.17	0.87	2.24	—	2.43

[a] $\sigma^* = 1.67 \pm 0.07$ according to Pal'm [15].

Table 8. The constants σ^* for RS groups calculated from the ionisation constants of alkylthioacetic acids ($RSCH_2COOH$). [25,27]

R	pK_a	$\sigma^*_{RSCH_2}$	σ^*_{RS}	σ^*_{RS} calc. from σ_I	
				according to Taft (Ref.29)	according to Charton (Ref.83)
CH_3	3.72	0.57	1.47[a]	1.56	1.56
C_2H_5	3.74	0.56	1.44	1.56	1.56
C_3H_7	3.78	0.54	1.38	1.50	1.50
iso-C_3H_7	3.72	0.57	1.47	1.56	1.56
C_4H_9	3.81	0.52	1.34	1.43	1.43

[a] $\sigma^* = 1.44 \pm 0.06$ according to Pal'm [15].

The constants σ^* of alkoxy- (RO) and alkylthio- (RS) groups were calculated by the authors of this review. In the first case Palomaa's data [19] were employed. The constants σ^* for $ROCH_2$ groups (Table 7) were evaluated by Eqn. (7) from the ionisation constants of alkoxyacetic acids $ROCH_2COOH$ determined conductimetrically in water at 25 °C and these yielded the corresponding constants for the RO groups on being divided by 0.388. The constants σ^* for $RSCH_2$ groups were evaluated similarly from the data of Ramberg [25] and Larsson [27] from the ionisation constants of alkylthioacetic acids $RSCH_2COOH$ and from them the values for the RS groups were calculated (Table 8). For comparison, Tables 7 and 8 include the values of σ^* for alkoxy- and alkylthio-groups calculated from the constants σ_I by the familiar relation $\sigma^* = 6.23\sigma_I$.

Among aromatic groups, the constants σ* have been reliably determined only for the phenyl group (0.62).[15] In the calculation of the constants σ* for phenyl groups, one resorts sometimes to the relation between σ* and σ^0:

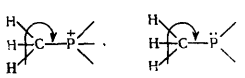
$$\sigma^*_{XC_6H_4} = \sigma^0_X + 0.600. \quad (8)$$

However, the applicability of this relation is very limited[87] and the use of the values of σ* thus obtained in the calculation of σ_I^{ph} gives rise to considerable doubts. Therefore Table 1 lists the constants σ*, σ^{ph}, σ_I^{ph}, and σ_R^{ph} only for the phenyl and pentafluorophenyl groups, the values for the latter having been calculated by an independent method from experimental NMR data[39] for ^{19}F. For the remaining aromatic groups, only the values of σ^{ph} are quoted. The literature sources from which the constants σ* were calculated or taken directly are indicated in column 6 of Table 1.

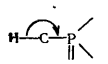
5. INDUCTIVE (σ_I^{ph}) AND RESONANCE (σ_R^{ph}) COMPONENTS OF THE CONSTANTS σ^{ph}

The constants σ_I^{ph} differ of course from the constants σ* by the choice of the starting point of the scale, i.e. the standard substituent: in the σ* scale the standard substituent is the CH_3 group ($\sigma^*_{CH_3} \equiv 0$), while hydrogen is employed as the standard in the σ^{ph} scale ($\sigma_H^{ph} \equiv 0$). Therefore Eqn. (6) contains a constant term of −0.960 equal to the constant σ^{ph} for the methyl group. The coefficient 1.99 in this equation characterises the relation between the σ^{ph} and σ* scales.

As stated in Table 1, the constants σ_R^{ph} for all alkyl groups are equated to zero. Formally this follows from the system employed in the calculation. The physical significance of this corresponds to the assumption that the hyperconjugation effects of the alkyl groups attached to phosphorus are negligible. An attempt to take into account the hyperconjugation effects in the hydrolysis of chlorophosphinates was made by Pal'm et al.[71], but they obtained the hyperconjugation component with the sign reversed, which is contrary to the known S_N2 mechanism of this reaction. Furthermore, the value of h obtained proved to be unusally high and without reasonable physical significance. Theoretically the greatest hyperconjugation effects might be expected in the reactions of organophosphorus compounds where the valence state of phosphorus changes. These include protonation and alkylation of phosphines[8,61,68]. Hyperconjugation, i.e. in this case σd conjugation, should stabilise to a greater extent the phosphonium compound



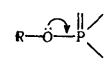
than the phosphine as a result of the contraction of the d orbitals when a positive charge appears[89]. A consequence of this should be an increase of the basicity of phosphines containing methyl groups. However, the basicity of trialkylphosphines decreases in the series $(CH_3)_2PC_2H_5 > (C_2H_5)_2PCH_3 > (CH_3)_3P >$ all remaining phosphines $> (iso\text{-}C_4H_9)P$.[61] In alkylation the same series is maintained. Hence Henderson and Buckler[68] concluded that combined hyperconjugation and steric effects operate. In reactions without change of the valence state of phosphorus, the problem of the possible hyperconjugation



is altogether obscure. In the literature there is no rigorous evidence indicating the existence of this phenomenon. It may be supposed that the hyperconjugation effects in these cases are small if they exist at all.

All the resonance constants of the groups attached to phosphorus are negative. This reflects the fact that phosphorus in its organic compounds behaves as an electron acceptor. For pentavelent (tetracoordinate) phosphorus this has been known for a long time[78,90] and is due both to the presence of an effective positive charge and to vacant low-lying higher atomic orbitals (3d and possibly 4s). It is interesting that in the trivalent state phosphorus also exhibits slight but definite acceptor properties (−M-effect, see Tsvetkov et al.[91] and Schiemenz[92]).

The resonance constants σ_R^{ph} of alkoxy-groups have high absolute magnitudes. This corresponds to a powerful effect of the type



in which the unshared electron pairs of the oxygen atoms partially fill the atomic d orbitals of phosphorus forming molecular $d_\pi - p_\pi$ orbitals‡.

With increase in the size of the alkoxy-group σ_R^{ph} decreases. The constants σ^{ph} for alkoxy-groups, which have small absolute magnitudes, consist of the sum of a large negative σ_R^{ph} and a somewhat smaller but still large positive σ_I^{ph}. Thus alkoxy-groups attached to phosphorus have large resonance and inductive effects acting in opposition. This is particularly characteristic of the phenoxy-group for which σ^{ph} is close to zero (−0.06), while $\sigma_R^{ph} = -2.89$ and $\sigma_I^{ph} = 2.83$.

The resonance constants of alkylthio-groups differ from those of alkoxy-groups by having smaller absolute magnitudes. In this case the relative influence of the inductive effects is greater and for the C_2H_5S group σ^{ph} is positive. Probably this is due to the smaller p-component of the atomic orbitals of sulphur compared with oxygen[93], as a result of which purely resonance interaction is weaker.

The inductive and resonance components of the constants σ^{ph} of halogens (fluorine and chlorine) attached to phosphorus have the greatest absolute magnitudes: $\sigma_I^{ph} = 5.21$ and $\sigma_R^{ph} = -4.65$ for fluorine and $\sigma_I^{ph} = 4.37$ and $\sigma_R^{ph} = -3.44$ for chlorine. This is evidence of intense electron withdrawal by an inductive effect and a somewhat weaker mesomeric effect. As a result σ^{ph} are large and positive.

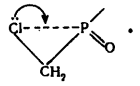
In general, it should be noted that there is a definite parallelism between the absolute values of σ_R^{ph} and σ_I^{ph} for the groups examined above: the greater the degree of withdrawal of electrons by the inductive effect the greater is the injection of electrons by the resonance effect. Possibly this is a consequence of the increase of the effective

‡ In all cases we are considering the participation of the atomic d orbitals of phosphorus following the concept generally adopted in the literature. The participation of atomic 4s or hybrid orbitals is disregarded. This problem is still not quite clear and requires special investigation.

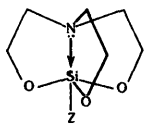
positive charge of the phosphorus by the inductive withdrawal of electrons. The atomic *d* orbitals of phosphorus then contract, which in turn leads to improved conditions for $d-p$ overlapping[89]. The parallel variation of the constants σ_I and σ_R has also been noted in the literature[94], particularly in those cases where the substituents compared have the same first atom, attached to the transmitting system. Then, for rigorously similar substituents, there is a linear relation between σ_R and σ_I.[95]

The resonance constants of the phenyl and vinyl groups have much smaller absolute values than those for alkoxy-groups. The π-electron system of the benzene ring or the double bond gives up its electrons to the *d* orbitals of phosphorus to only a slight degree. This is well known in view of the weak conjugation effects characteristic of aromatic and vinyl phosphorus compounds[78].

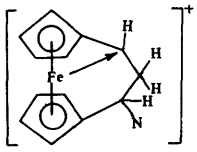
The fairly high values of σ_R^{ph} for groups such as $ClCH_2$, $BrCH_2$, Cl_2CH, and Cl_3C is striking. In the chemistry of aromatic compounds these groups are characterised by almost pure inductive effects. It may be supposed that resonance effects are in this case associated with the direct overlapping of the orbitals of the unshared electron pairs of chlorine with the *d* orbitals of phosphorus, forming a dative bond, which can be conventionally represented thus:



This effect is most characteristic of α-substituted derivatives; it is weaker for β-halogeno-derivatives and is virtually absent for γ-halogeno-derivatives. It is specific to phosphorus and probably to other elements with vacant *d* orbitals. Thus $p-d$ bonds of this type in organosilicon compounds have been discussed in the literature. As an example, one may quote the transannular $p-d$ bond in silatranes (triptychsiloxazolidines), first suggested by Frye et al.[96]:



It is interesting that a direct intramolecular donor-acceptor bond in ferrocene has been discussed by Richards and Hill[97] in connection with the stability of carbonium ions, for example:



This type of bond with phosphorus is probably present also in other groups with atoms having unshared electron pairs or π bonds in the α- or β-positions, formally separated from the phosphorus atoms by CH_2 groups. These include groups such as $CH_2OH(\sigma_R^{ph} = -0.69)$, $C_6H_5OCH_2$ $(\sigma_R^{ph} = -0.9)$, $C_2H_5OCH_2CH_2$ $(\sigma_R^{ph} = -0.35)$, $N{\equiv}CCH_2CH_2$ $(\sigma_R^{ph} = -1.22)$, $CH_2{=}CHCH_2$ $(\sigma_R^{ph} = -0.33)$, and even $C_6H_5CH_2$ $(\sigma_R^{ph} = -0.16)$.

6. CORRELATION BETWEEN THE RATE CONSTANTS FOR NUCLEOPHILIC SUBSTITUTION AT THE PHOSPHORUS ATOM

There is every reason to suppose that in nucleophilic substitution reactions at the phosphorus atom the relative contributions of the inductive and resonance components are different than in the ionisation of phosphorus acids. It has now been established that in the nucleophilic attack on phosphorus acid esters or esterified acid halides and similar compounds the transition state has the configuration of a trigonal bipyramid, and there is reason to believe that the *d* orbitals of phosphorus participate in its formation. If this model is correct, then substituents capable of $p-d$ conjugation (with a $+M$-effect) should sharply reduce the rate of nucleophilic substitution. In the estimation of their influence in $\sigma\rho$ analysis this should affect the contribution of the resonance σ_R^{ph} constant, namely it should increase it. Therefore it was to be expected that in the correlation of solvolysis and other nucleophilic substitution reactions the equation

$$\lg \frac{k}{k^0} = \rho\Sigma\,(\sigma_I^{ph} + \alpha\sigma_R^{ph}) \qquad (9)$$

would hold for $\alpha > 1$.

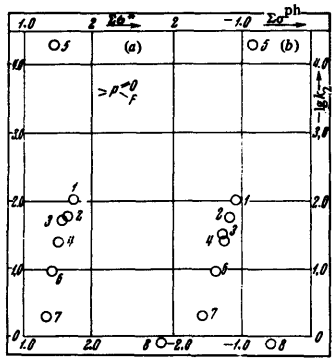


Figure 12. Correlation of the rate constants ($\lg k$) for the alkaline hydrolysis of the fluorides of phosphorus acids of the type ABPOF according to Larsson's data[30]: *a*) with Taft's σ^* constants; *b*) with the constants σ^{ph}. The substituents A and B for the acid fluorides are indicated: 1) CH_3, CH_3O; 2) CH_3, C_2H_5O; 3) CH_3, C_3H_7O; 4) CH_3, iso-C_3H_7O; 5) CH_3, C_2H_5S; 6) C_2H_5, iso-C_3H_7; 7) iso-C_3H_7, iso-C_3H_7O; 8) iso-C_3H_7O, iso-C_3H_7O.

Fig. 12 shows the correlation between the rate constants for the alkaline hydrolysis of phosphorus acid fluorides of the type APBOF on the basis of Larsson's experimental data[30]: two of the graphs (*a* and *b*) show the variation of $\lg k$ with $\Sigma\sigma^*$ and $\Sigma\sigma^{ph}$. Evidently there is no general correlation here, in agreement with previous findings. Fig. 13 shows the correlation between $\lg k$ and $\Sigma(\sigma_I^{ph} + 1.5\sigma_R^{ph})$. Here the points corresponding to di-isopropyl phosphorofluoridate (*8*), bis-(*NN*-dimethyl)phosphorodiamidic fluoride (*9*), (*NN*-dimethyl)methylphosphonamidic fluoride (*10*), and ethyl methylphosphonofluoridothiolate (*5*) together with

all the points for alkyl methylphosphonofluoridates fit very closely the linear relation. This means that in the $\sigma\rho$ analysis of the hydrolysis reactions of acid fluorides the resonance effects make a contribution 1.5 times as great ($\alpha = 1.5$) as in the ionisation of acids. The above corelation ($r = 0.95$, $S = 0.23$, $S_\rho = 0.13$) is remarkable, because here the rate constants vary by 8 powers of 10 ($\lg k$ varies from −4.26 to 4.29).

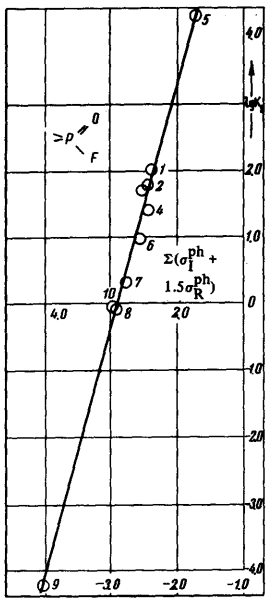


Figure 13. Variation of the rate constants ($\lg k$) for the alkaline hydrolysis of the fluorides of phosphorus acids of the type ABPOF according to Larsson's data [30] with $\Sigma(\sigma_I^{ph} + 1.5\sigma_R^{ph})$. For substances *1–8*, see Fig. 12; 9) $(CH_3)_2N$, $(CH_3)_2N$; 10) CH_3, $(CH_3)_2N$.

The coefficient $\alpha = 1.5$ is an optimum in this case, since poorer correlations are obtained with smaller and greater values of α. For all the reaction series discussed below, optimum values of α are also quoted.

Table 9 presents the results of the correlations between the rate constants for the solvolysis of compounds of the type ABP(O)X, where X = F, p-$NO_2C_6H_4O$, or Cl at different temperatures and in different media. In the hydrolysis of the acid fluorides and p-nitrophenyl esters the coefficient α varies in the range 1.5–1.55 (Table 9, series 1–8). In the solvolysis of acid chlorides in ethanol α = 1.30 (Table 9, series 13 and 14); for the hydrolysis of the chlorides in aqueous acetone, two values are quoted in Table 9—$\alpha = 1.5$ calculated from the experimental data of Hudson and Keay [74] (series 9) and $\alpha = 1.85$ calculated from the data of Neimysheva et al. [100] (series 10). The reason for this discrepancy is obscure. At any rate, it is evident that α depends not only on the type of reaction but probably also on the temperature and the medium.

Resonance effects play a major role in the hydrolysis of the chlorides of thionic acids of phosphorus (series 15 and 16); here $\alpha = 1.8$. The high contribution of the resonance component is in this case probably related to the high effective positive charge of the phosphorus atom [89], which leads to intensified d_π–p_π conjugation.

All the reaction series quoted in Table 9 are characterised by high positive values of the constants ρ, which is probably due to the high polarity of the transition states. Positive values of ρ correspond to an S_N2 mechanism. Substituents which increase the electron density at the phosphorus atom, i.e. with large negative values of $\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$ retard the reaction and conversely.

Table 10 presents data for the hydrolysis of the alkyl esters of phosphorus acids. Alkaline hydrolysis of ethylphosphonates at 59.2 °C is characterised by $\alpha = 1.6$ according to the data of Hudson et al. [99] (series 1), while according to the data of Bel'skii and coworkers [76,77] (series 3) the alkaline hydrolysis of ethylphosphinates at 80 °C is characterised by a lower value: $\alpha = 1.25$. Possibly this discrepancy is due to a difference in the experimental conditions. Both series have high values of ρ, which corresponds to nucleophilic attack by the hydroxide ion.

Table 9. Correlation of the rate constants for the solvolysis of compounds of the type ABP(Z)X with the constants σ_I^{ph} and σ_R^{ph}.

No. of series	Reaction	Temp., °C	Medium	n	α	$\lg k^0$	$\rho \pm S_\rho$	r	S	Refs
1	ABPOF+OH^-	25	H_2O	10	1.50	10.85	3.75±0.13	0.995	0.23	30
2	ABPOF+OH^-	25	H_2O	17[a]	1.55	6.09	1.72±0.18	0.923	0.30	22, 23
3	ABPO($OC_6H_4NO_2$-*p*)+OH^-	37.5	H_2O	12	1.50	4.34	2.90±0.19	0.979	0.21	12
4	ABPO($OC_6H_4NO_2$-*p*)+OH^-	25	H_2O	6	1.50	7.29	3.14±0.26	0.987	0.14	23
5	ABPO($OC_6H_4NO_2$-*p*)+OH^-	20	H_2O	7	1.50	8.08	3.51±0.61	0.932	0.24	22
6	ABPO($OC_6H_4NO_2$-*p*)+OH^-	25	H_2O	8	1.50	7.50	3.22±0.36	0.965	0.17	22
7	ABPO($OC_6H_4NO_2$-*p*)+OH^-	35	H_2O	8	1.50	7.45	3.11±0.36	0.962	0.17	22
8	ABPO($OC_6H_4NO_2$-*p*)+OH^-	45	H_2O	8	1.50	7.22	2.93±0.34	0.962	0.16	22
9	ABPOCl+H_2O	0	95% $(CH_3)_2CO$	11	1.50	10.22	4.64±0.74	0.901	0.35	74
10	ABPOCl+H_2O	0	95% $(CH_3)_2CO$	5	1.85	11.12	5.05±0.84	0.961	0.20	100
11	ABPOCl+H_2O	0	95% $(CH_3)_2CO$	9	(1.00)[b]	9.48	5.98±0.86	0.928	0.53	71
12	ABPOCl+H_2O	−40	95% $(CH_3)_2CO$	9	(1.00)[b]	12.65	7.05±1.18	0.914	0.51	71
13	ABPOCl+C_2H_5OH	25,2	C_2H_5OH	5	1.30	7.00	5.64±0.45	0.991	0.04	72
14	ABPOCl+C_2H_5OH	39,6	C_2H_5OH	5	1.30	6.86	5.34±0.68	0.976	0.19	72
15	ABPSCl+H_2O	0	95% $(CH_3)_2CO$	6	1.80	9.44	5.61±0.76	0.965	0.21	100
16	ABPSCl+H_2O	30	95% $(CH_3)_2CO$	6	1.80	13.73	7.26±0.77	0.978	0.21	100

[a] The point corresponding to di-isopropyl phosphorofluoridate was excluded.
[b] The coefficient α is unknown since the substituents varied exhibit only an inductive effect.
*Studies the data from which were used for the correlations.

On the other hand, neutral hydrolysis of alkylphosphinates (Table 10, series 4) has a low value of ρ (0.93), which is evidence of low polarity at the transition state. Here the rate of reaction is very low ($\lg k^0 = -5.27$) and $\alpha = 0.90$. Efremov et al.[101] recently established that in this case there is attack on the carbon of the alkyl group with subsequent dissociation of the alkyl–oxygen bond. Here too the S_N2 mechanism is reflected in a positive value of ρ.

Table 10. Correlation of the rate constants for the hydrolysis of phosphorus acid esters in an aqueous medium with the constants σ_I^{ph} and σ_R^{ph} [$\lg k = \lg k^0 + \rho\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$].

No. of series	Reaction	Temp., °C	n	α	$\lg k^0$	$\rho \pm S_\rho$	r	S	Refs.*
1	RPO $(OC_2H_5)_2$+OH^-	59.2	5	1.60	5.40	4.50±0.39	0.989	0.14	99,110
2	RPO(iso-$C_3H_7O)_2$+OH^-		5	(1.00)[a]	4.12	4.40±0.31	0.992	0.14	99,110
3	RR'PO (OC_2H_5)+OH^-	80	17	1.25	2.72	2.58±0.28	0.920	0.56	76,77
4	RR'PO (OC_2H_5)+H_2O	90	17	0.90	−5.27	0.93±0.06	0.971	0.18	76,77

[a] The coefficient α is unknown since the substituents varied only the inductive effect.
*Studies the data from which were used for the correlations.

An interesting reaction series, investigated by Neimysheva et al.[26], consists in the hydrolysis of alkyl phosphonochloridothiolates R(RS)POCl in 95% aqueous acetone and 0°C. The correlation data ($n = 11$, $\alpha = 1.65$, $\lg k^0 = 3.08$, $\rho = 1.82 \pm 0.27$, $r = 0.914$, and $S = 0.14$) indicate a profound difference between the hydrolysis of these compounds and that of other substances of the type ABPOCl.

Here ρ is unusually low for the hydrolysis of acid chlorides. It would probably be of interest to investigate this reaction in greater detail. There is no doubt that steric effects play a major role in it, as is in fact pointed out by the authors. Therefore the points corresponding to phosphonothiolates with isopropyl and s-butyl groups at the phosphorus atom were excluded in the calculation of the correlation parameters.

7. CORRELATION BETWEEN PHYSICOCHEMICAL DATA

Considerable interest attaches to the correlation between the equilibrium constants for the formation of complexes of various phosphoryl compounds with alcohols and phenols. The complexes are formed as a result of hydrogen bonding:

$$\rangle C{-}OH \ldots O{=}P\langle$$

These reactions were investigated by infrared spectroscopy mainly by Gramstad and coworkers[102-104].

On complete transfer of a proton, i.e. when an acid–base reaction takes place, the coefficient α is unity (Tables 2–4). It is reasonable to suppose that inductive effects play a major role in the formation of a hydrogen bond and therefore one may expect that the coefficient α will be less than unity. Indeed in all cases quoted in Table 11 α varies from 0.80 to 1.00. The lower is the acidity of the proton donor the smaller is α. Thus $\alpha = 0.80$ for the methanol complex, $\alpha = 0.90$ for the phenol and β-naphthol complexes, $\alpha = 0.95$ for the pentachlorophenol complex, and finally $\alpha = 1.00$ in the formation of a hydrogen bond with hydroxyphosphonium ions:

$$R_3P{=}O \ldots . HO{-}\overset{+}{P}R_3 .$$

All these reaction series are characterised by low negative values of ρ. A negative value of ρ shows that the equilibrium constant increases with increasing electron density at the phosphoryl oxygen atom. Electron-donor substituents of course increase the stability of the hydrogen bond. These effects are naturally small, in agreement with the low values of ρ.

Interesting complexes with iodine have been investigated by a similar method (series 10 and 11). Here the association constants are low ($\lg K^0 = 0.24$ at 20°C), but ρ is negative in this case too and consequently the iodine molecule adds as an electrophilic agent.

Table 11. Correlation of the association constants ($\lg K_{ass}$) in carbon tetrachloride determined from infrared spectra with the constants σ_I^{ph} and σ_R^{ph} [$\lg K_{ass} = \lg K_{ass}^0 + \rho\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$].

No. of series	Reaction	Temp., °C	n	α	$\lg K_{ass}^0$	$\rho \pm S_\rho$	r	S	Refs.*
	Formation of Hydrogen Bonds								
1	$CH_3OH \ldots O{=}P\langle$	20	13	0.80[a]	1.17	−0.16±0.01	0.968	0.06	102
2	$CH_3OH \ldots O{=}P\langle$	50	13	0.80[a]	0.87	−0.11±0.01	0.963	0.05	102
3	$C_6H_5OH \ldots O{=}P\langle$	20	13	0.90	2.32	−0.34±0.03	0.962	0.13	102
4	$C_6H_5OH \ldots O{=}P\langle$	50	13	0.90	1.95	−0.30±0.02	0.976	0.09	102
5	α-$C_{10}H_7OH \ldots O{=}P\langle$	20	14	0.90	2.36	−0.37±0.02	0.978	0.10	102
6	α-$C_{10}H_7OH \ldots O{=}P\langle$	50	14	0.90	1.96	−0.34±0.02	0.980	0.09	102
7	$C_6Cl_5OH \ldots O{=}P\langle$	20	14	0.95[b]	1.87	−0.44±0.03	0.973	0.12	102
8	$C_6Cl_5OH \ldots O{=}P\langle$	50	14	0.95[b]	1.54	−0.41±0.01	0.973	0.11	102
9	$\rangle\overset{+}{P}{-}OH \ldots O{=}P\langle$	C	7	1.00	2.34	−0.67±0.08	0.968	0.09	35
	Formation of Iodine Complexes								
10	$I_2 \cdot O{=}P\langle$	20	6	1.00[d]	0.24	−0.54±0.06	0.973	0.17	104
11	$I_2 \cdot O{=}P\langle$	50	6	0.95[d]	0.23	−0.44±0.04	0.984	0.12	104

[a] The authors correlate $\lg K_{ass}$ with $\Sigma\sigma^*$,[102] but in this case the correlation is much worse; at 20°C $r = 0.934$, $S = 0.09$, and $S_\rho = 0.01$ and at 50°C $r = 0.919$, $S = 0.08$, and $S_\rho = 0.01$.
[b] In the correlation of $\lg K_{ass}$ with $\Sigma\sigma^*$ at 20°C $r = 0.935$, $S = 0.19$, and $S_\rho = 0.03$ and at 50°C $r = 0.934$, $S = 0.17$, and $S_\rho = 0.03$.
[c] In nitromethane at room temperature.
[d] In the correlation of $\lg K_{ass}$ with $\Sigma\sigma^*$ at 20°C $r = 0.926$, $S = 0.28$, and $S_\rho = 0.06$ and at 50°C $r = 0.929$, $S = 0.25$, and $S_\rho = 0.05$.
*Studies the data of which were used for the correlations.

Gramstad and coworkers[102-104] correlated the association constants for the complexes of organophosphorus compounds with alcohols, phenols, and iodine with Taft's σ^* constants. Linear relations were observed, but the correlation coefficients were much lower than those in Table 11 (see the footnote to this Table).

Table 12. Correlation of half-wave potentials $E_{1/2}$ for the polarographic reduction of organophosphorus aldehydes and ketones with the constants σ_I^{ph} and σ_R^{ph} [$E_{1/2} = E^0_{1/2} + \rho\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$].

No. of series	Reaction	Temp., °C	Medium	n	α	$E^0_{1/2}$	$\rho \pm S_\rho$	r	S	Refs.*
1	R'R"P(O)CH_2CHO+e	20	H_2O	4	1.40	−0.90	0.28±0.03	0.987	0.01	105
2	R'(RO)P(O)$COCH_3$+e	20	DMF	8	1.40	−1.14	0.06±0.03	0.991[a]	0.03	106
3	R'(RO)P(O)COC_6H_5+e	20	DMF	12	1.25	−0.72	0.08±0.02	0.991[a]	0.02	107

[a] The correlation coefficient was calculated after rotating the coordinate axes by 45°.
*Studies the data from which were used for the correlations.

Razumov, Savicheva, and coworkers[105-107] investigated the polarographic reduction of organophosphorus oxo-compounds and observed a slight but nevertheless definite dependence of the half-wave potentials on the substituents at the phosphorus atom. Table 12 shows the correlation between the experimental data and the constants σ_I^{ph} and σ_R^{ph}. The positive values of the constant ρ indicate, as stated by the authors, that the potential-determining stage of the process consists in the addition of an electron to the molecule of the phosphorylated oxo-compound. Unexpectedly α proved to be greater than unity in these reactions, which undoubtedly indicates the participation of the phosphoryl group in the reduction process.

Table 13 lists data on the correlation between the chemical shifts in the ^{19}F NMR spectra of fluorine-containing organophosphorus compounds. In all cases α is close to unity and high correlation coefficients are obtained regardless of the type of compound.

There are literature data[111-113] for the ^{19}F NMR shifts in the spectra of phosphorus acid chlorides of the type ABPOF, i.e. compounds in which fluorine is linked directly to phosphorus. The attempts to correlate the chemical shifts in the ^{19}F NMR spectra of these compounds with the constants σ_I^{ph} and σ_R^{ph} and also with any other known σ constant were not successful.

A correlation between the ^{35}Cl NMR frequencies for compounds of the type $APOCl_2$ with the constants σ^{ph} was published by Tsvetkov et al.[114] Two linear relations were observed: one for the dichlorides of unsubstituted alkylphosphonic acids and another for the dichlorides of alkylphosphoric, vinylphosphonic, and arylphosphonic acids. When the constants σ_I^{ph} and σ_R^{ph} are used and the available data[114-116] for all substances of the type ABPOCl (where A and B can also be chlorine or fluorine atoms) are treated, then, with the exception of POF_2Cl, all the remaining data are satisfactorily correlated with $\Sigma(\sigma_I^{ph} + 1.20\sigma_R^{ph})$ (r = 0.970) (Table 13, series 10).

8. SPECIFICITY OF THE CONSTANTS σ^{ph}. STERIC EFFECTS

There is of course the problem of the relation between the constants σ^{ph}, σ_I^{ph}, and σ_R^{ph} on the one hand and the constants characterising the polar effects of substituents in the chemistry of carbon compounds: σ^*, σ_p, σ_m, σ^0, etc. Above it was noted that the inductive constants of the substituents σ_I^{ph} attached to phosphorus atoms differ from Taft's inductive constants σ^* only by the scale and the starting point adopted for their calculation. Thus the constants σ_I^{ph} can be derived from the constants σ^*. The constants σ^{ph} for aromatic groups can also be derived from the σ or σ^0 for the corresponding constituents in the aromatic ring[51,52]. Probably these two relations are the only ones between the constants σ^{ph} and other σ constants derived for purely organic compounds. The constants σ^{ph}

Table 13. Correlation of the ^{19}F and ^{35}Cl NMR data for organophosphorus compounds with the constants σ_I^{ph} and σ_R^{ph}.

No. of series	Compound	Medium	n	α	δ_0	$\rho \pm S_\rho$	r	S	Refs.*
	^{19}F-NMR								
1	$X_2PC_6H_4F$ δ_m	CCl_4, CCl_3F	7	0.85	−1.71	−0.97±0.15	0.947	0.52	108
2	$X_2PC_6H_4F$ δ_p	CCl_4, CCl_3F	8	1.10	−1.33	−2.21±0.21	0.974	1.10	108
3	$X_2PC_6F_5$ δ_m	CCl_3F	9[a]	0.85	−0.18	−0.69±0.04	0.990	0.21	39
4	$X_2PC_6F_5$ δ_p	CCl_3F	10	1.00	−4.23	−2.32±0.20	0.972	0.86	39
5	$X_2PC_6F_5$ δ_m	CCl_3F	12	0.80	0.02	−0.60±0.04	0.980	0.24	109
6	$X_2PC_6F_5$ δ_p	CCl_3F	12	0.90	−2.89	−1.84±0.15	0.967	0.83	109
7	$X_2P(O)C_6F_5$ Φ_m[b]	CCl_3F	4	1.00	158.7[c]	−1.06±0.14	0.984	0.23	109
8	$X_2P(O)C_6F_5$ Φ_p[b]	CCl_3F	4	0.90	147.2[c]	−3.36±0.11	0.999	0.18	109
9	XYZP=NC_6H_4F δ_p	CCl_4	12	1.00	13.50	0.90±0.06	0.982	0.20	31
10	^{35}Cl-NMR ABPOCl	—	28	1.20	27.89[d]	1.91±0.09	0.970	0.45	111, 115, 116

[a] The point corresponding to the PF_2 group was excluded (see Ref. 39).
[b] C_6F_6; Φ = 163.0 p.p.m.
[c] The values of Φ^0.
[d] The value of ν^0.
*Studies (with the exception of Ref. 31) the data from which were used for the correlations.

are compared in Fig. 14 with the constants σ_p for substituents in the aromatic ring. On the basis of this figure, it is difficult to arrive at any conclusion more definite than the statement that the constants agree as regards sign. Since the inductive components of the constants are linearly related, one may conclude that the reason for the differences lies in the resonance components.

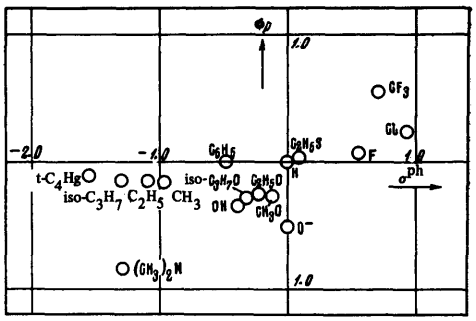


Figure 14. Relation between the constants σ^{ph} and σ_p for different substituents.

The resonance components of the constants σ^{ph} and σ_p, i.e. σ_R^{ph} and σ_R, are compared in Fig. 15. Evidently there is no simple relation between them. This is also found when the constants σ_R^0 are employed. Probably there are fundamental differences between the resonance effects in p_π–p_π conjugated systems and the conjugation effects in systems with a central phosphorus atom (d_π–p_π conjugation), associated with differences between the symmetries and other properties of atomic p and d orbitals. Thus σ^{ph} are specific constants.

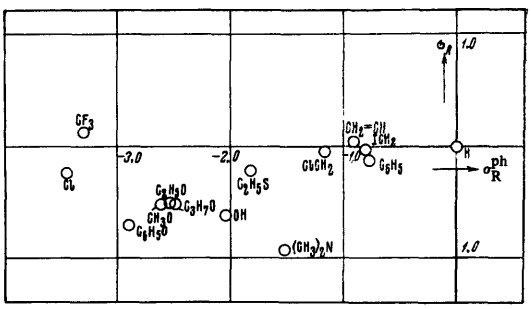


Figure 15. Relation between the constants σ_R^{ph} and σ_R for different substituents.

Rakshys et al.[108] successfully correlated the inductive and resonance constants σ_I and σ_R^0 for groups attached to trivalent phosphorus in phosphorylated fluorobenzene derivatives ($R_2PC_6H_4F$) and chemical shifts in the ^{19}F NMR spectra of these compounds. However, the principles of this correlation could not be extended to compounds of pentavalent (tetracoordinate) phosphorus.

We must now consider the effect of steric factors. This problem has been frequently discussed in the literature. The most pronounced effect of steric factors is observed in the alkylation of tertiary phosphines with alkyl halides. Henderson and Buckler[68] investigated the kinetics of the addition of ethyl iodide to tertiary aliphatic and aromatic phosphines. Although they did see a very limited dependence of the rate constants on the constants σ^*, only a few points in their graph fit a linear relation. The authors ascribe all the deviations to steric and hyperconjugation effects. In the correlation of the rate constants for the hydrolysis of dialkylphosphinic chloride in a neutral medium, Pal'm et al.[71] included Taft's E_S constants characterising steric effects and also the corresponding cross terms. Some workers, who have investigated the correlation of equilibrium or rate constants for reactions of organophosphorus compounds with the constants σ^*, σ^0, and σ_p and who observed deviations from linearity, attributed the latter to the effect of steric factors. Since in many cases these deviations are not observed when the constants σ^{ph} (or $\sigma_I^{ph} + \alpha\sigma_R^{ph}$) are employed, the conclusion that steric factors are responsible for these deviations must be treated with caution.

In general it may be supposed that, in reactions of organophosphorus compounds with participation of the phosphorus atom, steric effects play a smaller role than in the corresponding reactions of purely carbon compounds. This is related to the important fact that the phosphorus atom has a much greater radius than the carbon atom. Therefore for the tetrahedral structures of the initial or final compound and the trigonal bipyramid structure of the transition state, the difference between the hindering groups at the phosphorus atom is greater than at the carbon atom which means that the steric hindrance to the approach of the attacking agent is smaller.

It may be supposed that in all the correlations presented in Tables 2–6 the effect of steric factors is negligibly small. Nevertheless it must be noted that in the alkaline hydrolysis of *p*-nitrophenyl esters of phosphorus acids, investigated by Fukuto et al.[12,98], the point corresponding to compound with a t-butyl group at the phosphorus atom deviates from the linear relation (this point was disregarded in the correlation; Table 9, series 3). There is no doubt that the steric hindrance due to the bulky t-butyl group has an effect here. There is also no doubt that in the hydrolysis of phosphinic chlorides and even phosphonochloridates, investigated by Neimysheva et al.[71], the steric hindrance due to the isopropyl and isobutyl groups reduces the rate constant for S_N2 attack.

In Fig. 9 discussed above the filled circles correspond to tertiary phosphines containing only small alkyl groups or phenyl rings. These points are concentrated near the straight line drawn in the diagram. For these phosphines, the steric hindrance is least and there is a tendency towards a linear relation. All the substances containing higher alkyls (starting with propyl) markedly deviate towards lower rate constants. The deviations are particularly pronounced for tri-isobutylphosphine, the steric hindrance for which should be a maximum. At the same time, in the protonation of the same phosphines (Fig. 4 and Table 4, series 3), steric hindrance may in fact have an effect on the positions of the points near the straight line, but in this case the deviations are small and quite satisfactory correlation is observed ($r = 0.950$). In reactions of nitrogen compounds the greatest steric hindrance is observed in the alkylation of tertiary amines (the Menshutkin reaction) and in the formation of complexes with trimethyl-

boron[117]. In reactions of organophosphorus compounds steric hindrance is much less and yet it does have an effect in the alkylation of tertiary phosphines and in certain solvolysis reactions.

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All the correlations quoted above were calculated by least squares using Jaffé's method[2]. Tables 2–6 and 9–13 show that 124 reaction series were employed—for the equilibria and reactions of organophosphorus compounds.

Table 14.

Quality of correlation	r	Percentage of total number	
		This review	Jaffé's review (Ref.2)
Very good	>0.989	25	32.4
Good	0.970—0.989	37	24
Quite Satisfactory	0.950—0.970	20	13.7
Satisfactory	0.900—0.950	14	9.9
Poor	<0.900	4	20

These series include about 1300 individual constants. The statistical distribution of the correlation coefficients is shown in Table 14, according to which the number of very good and satisfactory correlations for organophosphorus compounds is somewhat greater (62%) than in Jaffé's compilation (56.4%), but the number of very good correlations is somewhat less and that of poor correlations is significantly less. It should be borne in mind that in many cases considerable experimental difficulties arise in the measurement of the rate constants for reactions of organophosphorus compounds and reduce the accuracy so that some of the σ^{ph} constants employed require revision. These revisions may alter the parameters of the individual correlations. However, there is no doubt about the wide applicability of correlation analysis to a wide variety of reactions and equilibria of organophosphorus compounds when the constants σ^{ph} or σ_I^{ph} and σ_R^{ph} (of different relative values) are employed.

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