Correlation Analysis of Infrared, ^{31}P NMR, and Theoretical Data of Derivatives of Phosphoric and Thiophosphoric Acids

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Infrared and ^{31}P NMR spectra were measured for thirty-seven trisubstituted derivatives of phosphoric acids and potassium salts of disubstituted derivatives of thiophosphoric acids. Both, the IR $\tilde{\nu}(\nu(\text{P=O}))$ and NMR $\delta(^{31}\text{P})$ data correlate significantly mutually as well as with inductive σ^* substituent constants. The P=O bond orders and O charge densities calculated by AM1 approach provide also satisfactory linear correlations with infrared data. The considerably high slope of the $\Delta\tilde{\nu}(\nu(\text{P=O}))$ *vs.* $\overline{\sigma^*(\text{R})}$ correlation equation shows a marked substituent sensitivity of the phosphoryl group. From the results of the correlation analysis the value $\sigma^* = 1.53$ has been determined for sulfide anionic substituent, which is comparable to the electron-acceptor effect of alkoxy groups. The infrared and ^{31}P NMR data provide also satisfactory linear correlations with the P=O bond orders, O and P charge densities, respectively.

It is known that thio- and dithiophosphates exhibit significant pesticide activities [1]. These compounds are used for synthesis of systemic insecticides [2, 3] and defoliants [4]. "Imidan" having the structure of *O*,*O*-dimethyl *S*-phthalimidomethyl dithiophosphate is a well known insecticide [5]. The salts of organic thiophosphoric acids as nucleophilic agents are precursors of several biologically active compounds [6, 7]. Various salts of dialkylphosphoric acids with long alkyl chains belong to the group of anionic surfactants [8] and some of them show considerable antimicrobial effects [9—11]. One of us (F. G.), previously reported the synthesis and studied some biological activities of several heterocyclic derivatives of thio- and dithiophosphates [12] and salts of dialkylthiophosphoric acids [13].

In earlier works dependences of infrared spectral properties of the phosphoryl group on the relative masses and Pauling electronegativities of substituents were investigated [14—17]. The first systematic attempt to correlate the wavenumbers of the phosphoryl stretching vibration in a series of phosphonates with inductive effects of substituents was reported by *Griffin* [18]. Other similar correlations [19—22] were based on the introduction of specific substituent constants valid only for the phosphoryl group and had only a limited application to a wider range of substituents and compounds. Previously we have found [16, 23] significant linear correlations between the wavenumbers of the P=O stretching vibration and Taft inductive σ^* constant for several series of the thiophosphates containing structurally modified maleinimide moieties.

The ^{31}P NMR spectra of some derivatives of phosphoric and thiophosphoric acids showed [24, 25] that the chemical shifts of the phosphorus nuclei vary in a relatively wide region of values.

The present paper is focused on the study of linear correlations of the wavenumbers of infrared stretching vibrations, ^{31}P NMR chemical shifts, and theoretical parameters of the electronic structure of the phosphoryl group with substituent effects for series of simple derivatives of phosphoric and thiophosphoric acids. A special interest of us in this work was to study the infrared and NMR spectral properties of a series of potassium salts of *O*,*O*-disubstituted thiophosphoric acids, which have not been reported so far.

EXPERIMENTAL

Chlorides, dichlorides, and esters of organic phos-

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phoric acids were prepared by treating of phosphoryl trichloride with corresponding alcohols as described previously [26—29]. Potassium salts of organic thiophosphoric acids were synthesized by reaction of corresponding phosphites with sulfur and potassium alkoxide [13, 30—32] or by reacting phosphoryl chlorides with KOH [33]. The compounds were purified by distillation or crystallization prior to use for spectral measurements.

Spectral Measurements

The infrared spectra were measured in the $\tilde{\nu}$ region of 1100—1350 cm^{-1} at the room temperature using a Zeiss Specord M80 spectrometer. The measurements were carried out in solutions of compounds in acetonitrile employing KBr cells of 0.18 mm thicknesses. The acetonitrile was of spectral purity (Uvasol, Merck, Darmstadt, Germany). The concentrations of the solutions were chosen to reach maximal absorption 75—80 % for measured absorption bands. The maxima of the absorption bands were determined with an accuracy of ± 1 cm^{-1}.

The ^{31}P NMR spectra were measured at 25 °C on a Varian VXR 300 instrument operating at 121.421 MHz. Solutions in trichloromethane-*d* and cells of 5 mm pathlength were used. The chemical shifts were related to that of phosphoric acid.

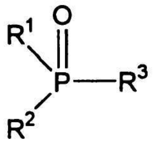
RESULTS AND DISCUSSION

Table 1. Infrared Spectral and Theoretical Data for Trisubstituted Derivatives of Phosphoric Acids

Compound	$\tilde{\nu}(\nu(P{=}O))/cm^{-1}$	$p(P{=}O)$	$-q(O)$
Ia	1248	1.1549	1.122
Ib	1252	1.1558	1.121
Ic	1257	1.1790	1.083
Id	1265	1.1736	1.083
Ie	1265	1.1685	1.092
If	1263	1.1616	1.092
Ig	1272	1.1733	1.082
Ih	1276	1.1821	1.078
Ii	1281	1.1855	1.075
Ij	1292	1.1916	1.073
Ik	1296	1.2109	1.056
Il	1298	1.2104	1.060
Im	1278	1.3344	0.948
In	1285	1.2334	1.016
Io	1285	1.2669	0.990
Ip	1288	1.3554	0.927
Iq	1295	1.3062	0.935
Ir	1294	1.3062	0.935
Is	1296	1.3060	0.935
It	1300	1.3102	0.930
Iu	1301	1.2745	0.989
Iv	1305	1.3369	0.912
Iz	1293	1.2378	1.012

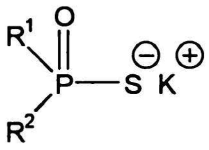
The intensive infrared absorption bands in the $\tilde{\nu}$ region of 1248—1305 cm^{-1} of trisubstituted derivatives of phosphoric acid (*I*) were assigned to the stretching vibration of the phosphoryl group in agreement with [18, 34—37] and are listed in Table 1. The difference between the absorption bands measured at the highest and lowest wavenumbers, $\Delta\tilde{\nu} = 57\ cm^{-1}$, indicates a significant sensitivity of the phosphoryl stretching vibration to the substituent effects.

The potassium salts of disubstituted derivatives of thiophosphoric acids (*II*) due to a strong mesomeric interaction between the P=O group and P-S^- anion exhibit the absorption bands of the phosphoryl stretching vibration in the $\tilde{\nu}$ region of 1139—



I

	R^1	R^2	R^3		R^1	R^2	R^3
a	OC_2H_5	OC_2H_5	CH_3	*m*	C_2H_5	Cl	Cl
b	OCH_3	OCH_3	CH_3	*n*	OC_3H_7	OC_3H_7	Cl
c	OC_3H_7-*i*	OC_3H_7-*i*	OC_3H_7-*i*	*o*	OC_2H_5	OC_2H_5	Cl
d	OC_4H_9	OC_4H_9	OC_4H_9	*p*	CH_2Cl	Cl	Cl
e	OC_3H_7	OC_3H_7	OC_3H_7	*q*	OC_4H_9	Cl	Cl
f	OC_2H_5	OC_2H_5	OC_2H_5	*r*	OC_3H_7	Cl	Cl
g	OCH_3	OCH_3	OCH_3	*s*	OC_2H_5	Cl	Cl
h	OC_2H_5	OC_2H_5	OC_6H_5	*t*	OCH_3	Cl	Cl
i	OCH_3	OCH_3	OC_6H_5	*u*	OC_6H_5	OC_6H_5	Cl
j	OC_2H_5	OC_6H_5	OC_6H_5	*v*	OC_6H_5	Cl	Cl
k	OCH_3	OC_6H_5	OC_6H_5	*z*	OCH_3	OCH_3	Cl
l	OC_6H_5	OC_6H_5	OC_6H_5				



II

	R^1	R^2		R^1	R^2
a	OCH_3	$N(CH_3)_2$	*h*	OC_3H_7	OC_3H_7
b	OC_4H_9-*s*	OC_4H_9-*s*	*i*	OC_2H_5	OC_3H_7
c	OC_3H_7-*i*	OC_3H_7-*i*	*j*	OC_2H_5	OC_2H_5
d	OC_6H_{13}	OC_6H_{13}	*k*	OCH_3	OC_2H_5
e	OC_5H_{11}	OC_5H_{11}	*l*	OCH_3	OCH_3
f	OC_4H_9-*i*	OC_4H_9-*i*	*m*	OC_6H_5	OC_2H_5
g	OC_4H_9	OC_4H_9	*n*	OC_6H_5	OC_6H_5

Table 2. Infrared, ^{31}P NMR, and Theoretical Data for Potassium Salts of Disubstituted Derivatives of Thiophosphoric Acids

Compound	$\tilde{\nu}(\nu(\text{P=O}))/\text{cm}^{-1}$	$\delta(^{31}\text{P})$	$p(\text{P=O})$	$-q(\text{O})$	$q(\text{P})$
IIa	1139		1.1536	1.126	2.680
IIb	1159	51.65	1.1882	1.086	2.564
IIc	1158	50.50	1.1535	1.116	2.573
IId	1158	52.80	1.1882	1.087	2.562
IIe	1159	59.92	1.1882	1.087	2.562
IIf	1158	52.44	1.1551	1.128	2.664
IIg	1162	52.86	1.1881	1.087	2.562
IIh	1153	52.86	1.1664	1.106	2.563
IIi	1159	–	1.1872	1.088	2.563
IIj	1159	52.98	1.1877	1.087	2.567
IIk	1164	56.07	1.1884	1.087	2.566
IIl	1167	56.25	1.1885	1.087	2.566
IIm	1176	62.07	1.2165	1.068	2.574
IIn	1185	–	1.2294	1.060	2.592

1185 cm^{-1}, which is by *ca.* 100 cm^{-1} lower than the $\tilde{\nu}(\nu(\text{P=O}))$ values for compounds *I*. The wavenumbers of the phosphoryl stretching vibration for series *II* are given in Table 2. In series *II* the substituents R^1 and R^2 are limited only to phenoxy and alkoxy groups and therefore their influence on the $\tilde{\nu}(\nu(\text{P=O}))$ wavenumbers is smaller than in the series *I* since $\Delta\tilde{\nu} = 46$ cm^{-1}.

The potassium salts of disubstituted derivatives of thiophosphoric acids (*II*) show ^{31}P NMR chemical shifts in the range of $\delta = 51.6$—62.1. The structural sensitivity of the $\delta(^{31}\text{P})$ is evident from Table 2 displaying a maximal change of about 12.

For the sake of comparison of data for compounds in series *I* and *II* we have defined the $\Delta\tilde{\nu}(\nu(\text{P=O}))$ wavenumber shifts relatively to the $\tilde{\nu}(\nu(\text{P=O}))$ wavenumbers of trimethyl phosphate (*Ig*) and potassium salt of *O*,*O*-dimethyl thiophosphate (*IIl*), respectively

$$\Delta\tilde{\nu}(\nu(\text{P=O}))^{I} = \tilde{\nu}(\nu(\text{P=O}))^{I} - \tilde{\nu}(\nu(\text{P=O}))^{Ig} \quad (1)$$

and

$$\Delta\tilde{\nu}(\nu(\text{P=O}))^{II} = \tilde{\nu}(\nu(\text{P=O}))^{II} - \tilde{\nu}(\nu(\text{P=O}))^{IIl} \quad (2)$$

The further requirement for such a comparison was to express for both series *I* and *II* the average $\overline{\sigma^*(\text{R})}$ values as the arithmetic means of the sum of Taft σ^* constants for substituents R^1, R^2, and R^3 [6, 21, 22, 38—40]

$$\overline{\sigma^*(\text{R})^{I}} = [\sigma^*(\text{R}^1) + \sigma^*(\text{R}^2) + \sigma^*(\text{R}^3)]/3 \quad (3)$$

and

$$\overline{\sigma^*(\text{R})^{II}} = [\sigma^*(\text{R}^1) + \sigma^*(\text{R}^2)]/2 \quad (4)$$

For all twenty-three compounds of series *I* and fourteen compounds of series *II* a significant joint correlation exists between the $\Delta\tilde{\nu}(\nu(\text{P=O}))$ wavenumber shifts and the average $\overline{\sigma^*(\text{R})}$ values. The statistical results of the correlation analysis are given in Table 3. It must be also noted that the use of any other specific substituent constants defined for the phosphoryl group [19—22] leads to statistically less significant results.

Table 3. Correlation Analysis for Spectral and Theoretical Data of Derivatives of Phosphoric and Thiophosphoric Acids

$$y = ax + b$$

Series	y	x	$a \pm s_a^a$	b	r^b	s^c	n^d	F^e
I and *II*	$\Delta\tilde{\nu}(\nu(\mathrm{P{=}O}))/\mathrm{cm}^{-1}$	$\overline{\sigma^*(\mathrm{R})}$	43.49 ± 1.67	−74.9	0.975	3.71	37	676
I	$\Delta\tilde{\nu}(\nu(\mathrm{P{=}O}))/\mathrm{cm}^{-1}$	$p(\mathrm{P{=}O})$	845.15 ± 69.25	−994.9	0.971	4.27	11^f	149
I	$\Delta\tilde{\nu}(\nu(\mathrm{P{=}O}))/\mathrm{cm}^{-1}$	$q(\mathrm{O})$	747.37 ± 95.90	811.9	0.933	6.42	11^f	61
II	$\Delta\tilde{\nu}(\nu(\mathrm{P{=}O}))/\mathrm{cm}^{-1}$	$p(\mathrm{P{=}O})$	563.99 ± 46.78	−676.0	0.967	3.02	12^g	145
II	$\Delta\tilde{\nu}(\nu(\mathrm{P{=}O}))/\mathrm{cm}^{-1}$	$q(\mathrm{O})$	660.56 ± 63.67	713.4	0.956	3.47	12^g	108
II	$\tilde{\nu}(\nu(\mathrm{P{=}O}))/\mathrm{cm}^{-1}$	$\delta(^{31}\mathrm{P})$	1.67 ± 0.16	1071.5	0.965	1.60	10^h	107
II	$\delta(^{31}\mathrm{P})$	$\overline{\sigma^*(\mathrm{R})}$	22.26 ± 2.15	18.2	0.961	0.93	11	107
II	$\delta(^{31}\mathrm{P})$	$q(\mathrm{P})$	747.44 ± 130.99	−1862.4	0.919	1.39	8^i	33

a) Standard deviation of the slope. *b*) Correlation coefficient. *c*) Standard deviation of the correlation. *d*) Number of compounds used in correlation. *e*) The value of Fisher—Snedecor test for parameters significant at 95 % level. *f*) Compounds *Ic* and *Im—Iz* omitted. *g*) Compounds *IIc* and *IIe* omitted. *h*) Compound *IIh* omitted as outlier. *i*) Compounds *IIb*, *IIc*, and *IIf* omitted.

The ^{13}P NMR chemical shifts for series *II* give also significant correlations with both, the empirical $\overline{\sigma^*(\mathrm{R})}$ values and the wavenumbers of the phosphoryl stretching vibration (Table 3), which indicates that the electron shielding and deshielding at the phosphorus nuclei is sufficiently altered by substituents R^1 and R^2.

The bond orders and charge densities at the phosphoryl group of compounds *I* and *II* were calculated using AM1 quantum-chemical method [41] with standard parametrization. These theoretical data are listed in Tables 1 and 2. The attempt to correlate the wavenumber shifts of the phosphoryl stretching vibration with theoretical characteristics, *i.e.* with P=O bond orders and oxygen charge densities shows that for series *I* the compounds containing $\mathrm{R}^2 = \mathrm{Cl}$ and $\mathrm{R}^3 = \mathrm{Cl}$ substituents must be omitted. On the other hand, for the series *II* the compounds with branched alkoxy substituent exhibit serious deviations from the linearity of correlations and must be excluded from the statistical treatment. Generally, the $\Delta\tilde{\nu}(\nu(\mathrm{P{=}O}))$ values give better correlations with bond orders, $(p(\mathrm{P{=}O}))$ compared to similar correlations with charge densities, $(q(\mathrm{O}))$ (Table 3). The $\delta(^{31}\mathrm{P})$ chemical shifts of all compounds of series *II* with linear alkoxy substituents exhibit a satisfactory linear correlation with phosphorus charge densities $(q(\mathrm{P}))$ (Table 3).

The statistically significant $\Delta\tilde{\nu}(\nu(\mathrm{P{=}O}))$ *vs.* $\overline{\sigma^*(\mathrm{R})}$ correlation equation enables to determine the Taft inductive σ^* constant for the S^- anionic substituent using the $\tilde{\nu}(\nu(\mathrm{P{=}O}))$ values for compounds of series *II* and the following equation

$$\sigma^*(\mathrm{S}^-) = 3[\Delta\tilde{\nu}(\nu(\mathrm{P{=}O})) - b]/a - 2\overline{\sigma^*(\mathrm{R})} \qquad (5)$$

The value of $\sigma^*(\mathrm{S}^-) = 1.53$ was determined as the arithmetic mean of values calculated from eqn (5) for all fourteen compounds of series *II*, which indicates that the sulfide anion has relatively strong electron-acceptor inductive effect comparable to that of the alkoxy substituents [42].

It can be concluded on the basis of the results of correlation analysis, that the phosphoryl group of derivatives of phosphoric and thiophosphoric acids is considerably sensitive to the substituent effects, which is reflected by both infrared and ^{31}P NMR spectral characteristics and demonstrated by theoretical parameters.

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