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Enthalpies of Specific Interaction of Heteroatom Derivatives of Three-Coordinate Phosphorus with Chloroform

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Abstract—The nature of hydrogen bonds formed by chloroform with three-coordinate phosphorus derivatives containing sulfur, silicon, and chlorine atoms and their carbon analogs was revealed by analysis of the experimental enthalpies of specific interactions. The main donor centers in the examined compounds were found to be oxygen atoms and π-electron systems of aromatic rings. Sulfur atoms give rise to weaker complexes as compared to oxygen. Phosphorus, chlorine, and silicon atoms are not involved directly in specific interactions with the solvent.

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Solvation effects on the reactivity of molecules are closely related to specific interactions between reagents and solvent. Just specific interactions including formation of donor–acceptor or H-complexes are more significant than nonspecific interactions between species in solution. However, analysis of solvation effects becomes difficult when solute molecules possess several possible coordination centers; in these cases, the experimentally measurable enthalpy of specific solvation reflects the overall effect, while practical application of such parameters requires separation of the overall effect into particular constituents.

The above stated fully applies to organophosphorus compounds having several active centers in their molecules (phosphorus atom, other heteroatoms possessing unshared electron pairs, π-electron systems). It is generally accepted [1–4] that donor–acceptor interactions of three-coordinate phosphorus compounds, e.g., with Lewis acids, involve the phosphorus atom. The question of reaction centers in organophosphorus compounds involved in hydrogen bonding remains a matter of discussions, primarily due to the lack of experimental data. In most cases, these centers are selected supposedly. It was presumed [5] that 2,2,3,3,4,4,5,5-octafluoropentanal with trialkyl phosphites forms H-complexes with participation of oxygen atoms in the latter. Analogous views on the nature of hydrogen bonds formed by trimethyl phosphite and bicyclic phosphites were reported in [6]. Nifant'ev et al. [7] noted that the principal center of coordination of neutral cyclic phosphites with monomeric alcohol molecules is the phosphorus atom. On the other hand, Epshtein et al. [8, 9] believed that interactions with phenol and ethanol involve both three-coordinate phosphorus atom and other electron-donor centers, such as oxygen atoms in triethyl phosphite, π-electron system of benzene rings in triphenylphosphine, etc. However, later studies have shown [10] that the absorption band in the IR spectrum of a triethyl phosphite–ethanol mixture, formerly assigned to $O\cdots H$ interaction, has a different origin: it is related to formation of triethyl phosphate as a result of oxidation of triethyl phosphite with atmospheric oxygen. Strong acids were shown to protonate phosphites at the phosphorus atom [11]. Nevertheless, it was found [12] that even compounds having a negatively charged three-coordinate phosphorus atom do not form hydrogen bonds with solvents. Thus the reactivity of three-coordinate phosphorus derivatives in hydrogen bonding strongly depends on both reactant nature and conditions, i.e., it cannot always be predicted *a priori*.

In the present study we made an attempt to reveal real centers for H-bonding with chloroform in some three-coordinated phosphorus derivatives containing chlorine, sulfur, and silicon atoms with a view to subsequently use the enthalpies of specific interaction as

Table 1. Enthalpies of specific interaction of $R^1R^2R^3X$ compounds with chloroform

Couple no.	R^1, R^2, R^3	$-\Delta H_{sp}$, kJ/mol	
		X = P	X = CH
I	$R^1 = R^2 = R^3 = Cl$	0	4[a]
II	$R^1 = R^2 = R^3 = Ph$	4.8	4.3
III	$R^1 = R^2 = R^3 = EtO$	8.1	14.4
IV	$R^1 = R^2 = EtO$, $R^3 = Ph$	7.1	8.4
V	$R^1 = R^2 = EtS$, Ph	4.8	6.2
VI	$R^1R^2 = OCH_2CMe_2CH_2O$, $R^3 = Ph$	10.2	10.9

[a] Enthalpy of self-association [13].

a quantitative parameter characterizing electron-donor power of organophosphorus compounds. In keeping with published data [13], the energy of hydrogen bonds formed by different electron donors is generally small: it ranges from –4 to –19 kJ/mol. Our previous study [14] on solvation with various solvents showed that chloroform (unlike, e.g., methanol whose self-associates do not always decompose due to interaction with dissolved substance; as a result, specific interaction effect considerably weakens) fairly efficiently solvates weak proton acceptors.

Table 2. Enthalpies of specific interaction of $[OR^1O]XR^2$ compounds with chloroform

Couple no.	R^1	X	R^2	$-\Delta H_{sp}$, kJ/mol
VII[a]	2Et	P	Cl	5.1*
	2Et	CH	Me	8.2
	2Et	P	OMe	8.1*
	2Et	P	OEt	8.1*
	2Et	P	OBu	8.1
VIII	$(CH_2)_3$	P	Cl	4.6**
	$(CH_2)_3$	P	OBu	8.1
IX	$MeCH(CH_2)_2$	P	Cl	5.0*
	$MeCH(CH_2)_2$	P	OMe	9.0*
X	$CH_2C(Me)_2CH_2$	P	Cl	4.4**
	$CH_2C(Me)_2CH_2$	CH	Me	9.8
	$CH_2C(Me)_2CH_2$	P	OMe	7.9
	$CH_2C(Me)_2CH_2$	P	OEt	8.0
XI	$(CH_2)_2$	P	Cl	5.3*, **
	$(CH_2)_2$	P	OMe	8.5*
XII	MeCHCHMe	P	Cl	5.3**
	MeCHCHMe	CH	Me	8.2
	MeCHCHMe	P	OEt	9.4
XIII	Me_2CCMe_2	P	Cl	6.6
	Me_2CCMe_2	CH	Me	10.2
	Me_2CCMe_2	P	OEt	8.6
XIV	o-C_6H_4	P	Cl	2.2
	o-C_6H_4	P	OEt[b]	3.5

[a] Acyclic compounds.

[b] R^2 = t-BuO: ΔH_{sp} = 5.5 kJ/mol.

The possibility for H-bonding between chloroform molecule and phosphorus atom was judged by the experimental enthalpies of specific interactions of several three-coordinate phosphorus derivatives and structurally related phosphorus-free compounds (Table 1). Among these couples, complete absence of interaction between chloroform and phosphorus trichloride should be noted, whereas the energy of self-association of chloroform (which is a carbon-containing analog of phosphorus trichloride) is –4 kJ/mol (couple **I**). Similar relations were found for the other compounds. The only exception was couple **II** in which the phosphorus analog turned out to be slightly stronger (but within the experimental error) electron-donor.

It is known [15] that basicity parameters correlate well with their ionization potentials (I); therefore, the latter may be used to predict the protonation center in molecules with several heteroatoms on a qualitative level [16]. We compared the ionization potentials of the lone electron pair on the phosphorus atom [15–18] in cyclic and acyclic trialkyl phosphited and dialkyl phosphorochloridites (total of 7 values) with the enthalpies of their specific interactions with chloroform (the ΔH_{sp} values in Table 2 are marked with an asterisk). The corresponding correlation coefficient was as poor as $r \approx 0.7$; i.e., we can speak about only parallel variation of these parameters. Extension of the compound series by inclusion of phosphoramidites, trithiophosphites, and tris(trimethylsilyl) phosphite further impairs the correlation ($r \approx 0.4$).

A satisfactory correlation was obtained between the enthalpies of specific interaction of the same seven phosphites and the sum of ionization potentials characterizing lone electron pairs on the heteroatoms neighboring to the phosphorus atom.

$$\Delta H_{sp} = -(78.0\pm7.2) + (2.19\pm0.22)\Sigma I_{O,Cl}; \qquad (1)$$

$$r = 0.975,\ S_0 = 0.50,\ n = 7.$$

The same correlation coefficient was found for ΔH_{sp} and a combination of parameters; here, the coefficient at the phosphorus term had a small value but a large bias.

$$\Delta H_{sp} = -(77.8\pm6.8) + (2.14\pm0.38)\Sigma I_{O,Cl} + (0.16\pm0.85)\Sigma I_P; \quad (2)$$
$$r = 0.975,\ S_0 = 0.56,\ n = 7.$$

Correlations (1) and (2), as well as the data in Table 1, indicate that either the three-coordinate phosphorus atom is not involved in specific interaction with chloroform or it forms very weak hydrogen bonds with an energy not exceeding 1 kJ/mol. Therefore, the donor centers in three-coordinate phosphorus compounds are other heteroatoms, while the donor centers in couples **II** and **IV**–**VI** are π-electron systems in the benzene rings. In particular, only the latter mode of H-bonding may be responsible for fairly effective interaction with chloroform of couple **II** compounds, provided that the phosphorus atom is inactive. In fact, comparison of the enthalpies of specific interactions for couples **XV**–**XIX** (Table 3) shows that benzaldehyde acetals always give stronger H-complexes with chloroform than do those derived from acetaldehyde, which may be due to additional participation of phenyl fragments in complex formation. The formation of hydrogen bonds between chloroform, on the one hand, and triphenylphosphine, triphenylmethane, and other related compounds, on the other, with participation of π electrons in the latter is very consistent with published data [19], according to which the enthalpy of mixing of chloroform with benzene is –0.75 kJ/mol (exothermic process).

H-Complexes formed by chloroform and P(III) acid halides are characterized by considerably lower energy of hydrogen bonds, as compared to the corresponding P(III) acid esters (Table 2). This means that the chlorine atom, as well as phosphorus, does not participate in specific interaction with chloroform or at least such interaction is extremely weak. According to [19], the enthalpy of hydrogen bond formation between chloroform and carbon tetrachloride is 0.2 kJ/mol (endothermic process), which is consistent with our data on the solvation of phosphorus trichloride with chloroform. On the other hand, apart from correlations (1) and (2), the series of phosphorochloridites gives rise to correlation (3) between the enthalpies of specific interaction and chlorine frequencies ν^{35} [20] in the NQR spectra (the corresponding ΔH_{sp} values in Table 2 are marked with a double asterisk, and ΔH_{sp} = –6.6 kJ/mol was used for 2-chloro-3-phenyl-1,3,2-oxazaphospholane).

$$\nu^{35} = 26.0 + 1.18\Delta H_{sp};\ r = 0.994,\ S_0 = 0.50,\ n = 5. \quad (3)$$

Table 3. Enthalpies of specific interaction of $R^1R^2CHR^3$ compounds with chloroform

Couple no.	R^1R^2	$-\Delta H_{sp}$, kJ/mol	
		R^3 = Ph	R^3 = Me
XV	$R^1 = R^2$ = EtO	8.4	8.2
XVI	$OCH_2CMe_2CH_2O$	10.9	9.8
XVII	OCHMeCHMeO	9.8	8.2
XVIII	$OCMe_2CMe_2O$	10.9	10.2
XIX	$R^1 = R^2$ = EtS	6.2	4.1[a]

[a] R^3 = *i*-Pr.

The above data are seemingly contradictory, unless we take into consideration the fact that the ^{35}Cl frequency in NQR spectra is determined primarily by the mechanism of hyperconjugation between substituents on the phosphorus atom and P–Cl bond. Therefore, the ν^{35} values change in parallel with the P–Cl bond length and its polarizability [20]. Obviously, just these factors affect the enthalpy of specific interaction, though direct H-bonding at the chlorine atom does not occur. The enthalpies of specific interaction between chloroform and acetals (Table 2) considerably exceed those found for phosphorochloridites, indicating a significant contribution of intramolecular electronic effects to hydrogen bonding. However, this aspect is the subject of special study.

Analogous conclusion may be drawn for silicon-containing phosphites. Like phosphorus trichloride, tris(trimethylsilyl) phosphite is not prone to H-bonding with chloroform. Comparison of the ΔH_{sp} values for couples **XX**–**XXII** (Table 4) shows that replacement of ethyl group in cyclic phosphites by trimethylsilyl group considerably reduces the enthalpy of H-complex formation. Similar relations were also observed in [21–23] while studying the strength of hydrogen bonds formed by chloroform with sulfur and silicon analogs of ethers and amines. Our results showed that, unlike triethylamine (ΔH_{sp} –9.3 kJ/mol), diethyl(trimethylsilyl)amine and hexamethyldisiloxane do not form

Table 4. Enthalpies of specific interaction of $R^1R^2POR^3$ compounds with chloroform

Couple no.	R^1R^2	$-\Delta H_{sp}$, kJ/mol	
		$R^3 = SiMe_3$	R^3 = Et
XX	$OCH_2CMe_2CH_2O$	5.7	7.9
XXI	OCHMeCHMeO	6.9	9.4
XXII	*o*-$C_6H_4O_2$	1.6	3.5

Table 5. Enthalpies of specific interactions of some oxygen and sulfur-containing derivatives with chloroform

Couple no.	Compound	$-\Delta H_{sp}$, kJ/mol	
		X = S	X = O
XXIII	$(EtX)_2CHAlk$	4.1[a]	8.2[b]
XXIV	$(EtX)_2PPh$	4.8	7.1
XXV	$(EtX)_3P$	5.3	8.1

[a] Alk = *i*-Pr.
[b] Alk = Me.

H-complexes with chloroform. likewise, no H-bonding was revealed between chloroform and tetramethylsilane. These data unambiguously indicate that silicon atom is not involved in specific interaction with chloroform, though the possibility for formation of $Si\cdots Cl$ bond was considered in [22].

A probable reason is that trimethylsilyl group creates steric hindrances to H-bonding with the neighboring atoms. However, Borisov et al. [24] previously showed that steric effect of alkyl substituent is not significant in complex formation between phenol and trialkylsiloxy group. We found that *tert*-butyl *o*-phenylene phosphite which is isosteric to *o*-phenylene trimethylsilyl phosphite gives rise to even stronger hydrogen bond than does the corresponding ethyl phosphite (Table 4; see also note [b] to Table 2).

Thus we have found that Period III elements such as silicon, phosphorus, and chlorine present in molecules of three-coordinate phosphorus compounds are not involved in H-complex formation with chloroform. The same does not apply to sulfur. On the other hand, the data in Table 5 show that H-complexes derived from chloroform and thiophosphites or dithioacetals are much weaker than those formed by their oxygen-containing analogs, which is consistent with published data on the donor power of oxygen- and sulfur-containing compounds [25]. On the whole, our results conform to the conclusion drawn previously [13] that the enthalpy of hydrogen bond decreases in going to elements of higher Periods due to increase in the diffuse character of orbitals, reduction of the *np*-electron density on the potential donor centers, and overriding donor ability of *np*-orbital of heteroelement responsible for the formation of $X\cdots H$ bond (Table 5) [26].

EXPERIMENTAL

The compounds examined in the present work were described in [14]. Their purity was additionally checked by GLC on a Chrom-4 chromatograph; 1-m column packed with 5% of DS 550 on Chromaton N-AW-DMCS (0.200–0.250 mm); carrier gas helium, flow rate $(1.0–1.7)\times 10^{-6}$ m^3/s.

The procedures for calorimetric experiments were described in [14, 27]. Liquid compounds were distilled just before measurements. Dissolution was carried out under dry argon. Chloroform was purified by successive distillations over phosphorus(V) oxide and calcium hydride. The enthalpies of specific interactions with chloroform were calculated according to the procedure described in [14] from the difference in the enthalpies of solvation in chloroform and carbon tetrachloride.

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