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# Thermochemistry of heteroatomic compounds. Part 6<sup>☆</sup>. Enthalpy of solvation and complex formation of some halides of three-coordinated phosphorus compounds in pyridine



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## Abstract

Using previously published values of the enthalpies of solvation of some derivatives of three-coordinated phosphorus compounds, the contributions of the non-specific solvation enthalpies in the general solvation effect in benzene, *p*-xylene, methanol and pyridine have been calculated. Taking into account the known possibility of intramolecular complex formation between halogenated derivatives of P<sup>III</sup> and pyridine, the magnitudes of specific interaction enthalpies for PCl<sub>3</sub>, PBr<sub>3</sub>, (EtO)<sub>2</sub>PCl,  PCl and  PBr were determined.

Thermodynamic parameters of complex formation between cyclic chlorophosphites and 1-dimethylamino-3,3-dimethyl-propan-2-one have been obtained and are discussed.

**Keywords:** Complexation; Enthalpy of solvation; Halide; Phosphorous; Pyridine

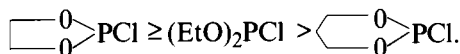
## 1. Introduction

As has been shown previously [2], the enthalpies of specific interaction between three-coordinated phosphorus derivatives and some hydrogen-donor solvents, such as chloroform, can serve to some extent as special indicators of the electron density distributions in molecules and the intramolecular interactions of the bonds. This is

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<sup>☆</sup> For Part 5, see Ref. [1].

done by comparison of the electron-donor ability of some chlorophosphites of different structure to chloroform [2], i.e.



At the same time it is well known that halides of  $\text{P}^{\text{III}}$  can be considered as acceptor molecules, able to form relative strong complexes with nitrogen compounds [3, 4]. With an interest in the investigation of different solvation factors, we report here some solvation enthalpies of halogenated species of three-coordinated phosphorus in pyridine and the thermodynamic characteristics of complex formation between cyclic chlorophosphites and  $\alpha$ -aminoketone.

## 2. Experimental

Enthalpies of solution of compounds were measured at 295–298 K in a differential calorimeter as described previously [1, 2].

The exothermic heats of interactions of chlorophosphites with aminoketone were measured at 298 K in chloroform in an automatic differential microcalorimeter DAC-1-1 of Calvet type, interfaced to a computer. The working volume of the glass vessels was  $3 \text{ cm}^3$ . The heats of dilution of all chlorophosphites ( $2 \text{ cm}^3$ ) are very small and were not considered; the exothermic heat of dilution of aminoketone ( $1 \text{ cm}^3$ ) in chloroform ( $q_{\text{dil}}$ ) was taken as  $0.00164 \text{ kJ}$  being the average value of several determinations. Some experimental data for the interaction of aminoketone (13) with 2-chloro-1,3,2-dioxaphosphorinane (18) are presented as an example in Table 1.

All halides of phosphorus were synthesized and purified by previously reported methods [2]. All preparations and measurements were carried out in dry argon atmosphere. Solvents were dried by standard methods [5].

## 3. Results and discussion

The measured enthalpy of solvation of any substances ( $A_i$ ) in a solvent (S) consists of the sum of non-specific and specific interactions

$$\Delta H_{\text{soliv}}^{A_i/S} (\text{obs}) = \Delta H^{A_i/S} (\text{non-spec.}) + \Delta H^{A_i/S} (\text{spec. int.}) \quad (1)$$

Table 1

Experimental data for the interaction between amino-ketone (13) and 2-chloro-1,3,2-dioxaphosphorinane (18)

$-Q_{\text{obs}}/\text{kJ}$	$C_0(13)/\text{mol dm}^{-3}$	$C_0(18)/\text{mol dm}^{-3}$
0.006498	0.02087	0.03926
0.007277	0.02981	0.03414
0.006044	0.02697	0.03076
0.008516	0.02783	0.27784

The first term is known for some solvents and is used in the form [6]

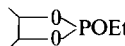
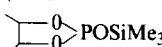
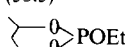
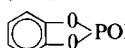
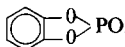
$$\Delta H_{\text{sol}}^{\text{A}_i/\text{S}}(\text{non-spec.}) = a_s + b_s(\text{MR}_D)^{A_i} \quad (2)$$

where  $a_s$  and  $b_s$  are coefficients, and  $(\text{MR}_D)$  is the molar refraction.

Eq. (2) was used previously for the determination of the contributions of non-specific solvation enthalpy in the general solvation effect for tetra-coordinated phosphorus compounds [1]. Taking into account this approach and using published data [2, 7, 8] (Table 2), we have analysed the enthalpies of solvation of three-coordinated phosphorus compounds with different structures (1–7) in benzene, *p*-xylene, methanol and pyridine.

The calculated coefficients of Eqs. (1) and (2) are shown in Table 3. Because the compounds with three-coordinated phosphorus listed in Table 2 do not form any detectable specific interactions with carbon tetrachloride, benzene, *p*-xylene or pyridine, the observed dependences, which reflect the non-specific solvation in common, are not unexpected. However, the results in Table 3 for methanol with similar correlative parameters are surprising. Probably in this case we have to consider the compen-

Table 2  
Enthalpies of solvation (in  $\text{kJ mol}^{-1}$ ) of some three-coordinated phosphorus compounds in solvents

Compound no.	Molecular formula $\text{MR}_D$	$-\Delta H_{\text{sol}}^{\text{a}}$			
		Benzene	<i>p</i> -Xylene	Methanol	Pyridine
1	$\text{Ph}_3\text{P}$ (85.0)	102.4	102.6	95.1	–
2	$(\text{EtO})_3\text{P}$ (42.8)	53.0	54.2	49.9	52.0
3	 POEt (40.6)	50.8	50.1	–	49.4
4	 POSiMe <sub>3</sub> (53.5)	–	62.0	–	–
5	 POEt (40.6)	51.7	50.5	48.1	50.7
6	 POEt (46.4)	–	56.9	54.8	57.2
7	 POBu- <i>t</i> (55.6)	–	–	–	62.4 <sup>b</sup>

<sup>a</sup> Data from Refs. [2, 7, 8]. <sup>b</sup> Enthalpies of solution in pyridine and vaporization are  $-0.5$  and  $61.9 \text{ kJ mol}^{-1}$ , respectively.

Table 3

Parameters and characteristics of the equation  $\Delta H_{\text{soln}}(\text{non-spec.}) = a_s + b_s(\text{MR}_D)$  with correlation coefficients

Solvent	$a_s$	$b_s$	$r$	$S_0$	No of points $n$
$\text{CCl}_4^a$	$-9.1 \pm 0.6$	$-1.08 \pm 0.01$	0.997	1.42	46
Benzene	$-7.8 \pm 2.8$	$-1.11 \pm 0.05$	0.998	2.00	4
<i>p</i> -Xylene	$-6.1 \pm 1.8$	$-1.13 \pm 0.03$	0.998	1.32	6
Methanol	$-6.4 \pm 1.7$	$-1.04 \pm 0.03$	0.999	1.09	4
Pyridine	$-12.6 \pm 5.1$	$-0.97 \pm 0.12$	0.978	1.29	5



<sup>a</sup> Data from Ref. [2].

sative effect: the exothermic formation of some hydrogen bonds between molecules of methanol and  $\text{P}^{\text{III}}$  compounds is compensated by an equal endothermic characteristic of the breaking of methanol–methanol molecular associations.

The next stage of our investigation was concerned with the determination of enthalpies of solvation of some halides of three-coordinated phosphorus compounds (8–12, Table 4) in pyridine. We determined the experimental solution enthalpies of phosphorus trichloride (8) and -bromide (9), diethylchlorophosphite (10), and cateolchloride (11) and -bromide (12) in pyridine. Taking into account the enthalpies of vaporization of all these compounds, calculated using their heats of solution in hexane

Table 4

Enthalpies of solution, vaporization, solvation and specific interaction (in  $\text{kJ mol}^{-1}$ ) of some halides of  $\text{P}^{\text{III}}$  with pyridine

Compound no.	Molecular formula ( $\text{MR}_D$ )	$\Delta H_{\text{soln}}$		$\Delta H_{\text{vap}}$	$-\Delta H_{\text{soln}}^{\text{A}_i/\text{Py}}$		$-\Delta H^c$ of specific interaction
		$\text{C}_6\text{H}_{14}$	$\text{C}_5\text{H}_5\text{N}$		Obs.	Calc. <sup>a</sup>	
8	$\text{PCl}_3$ (24.9)	1.6 <sup>b</sup>	-90.6	32.2 <sup>b</sup>	122.8	36.6	$86.2 \pm 6.8$
9	$\text{PBr}_3$ (33.3)	5.0	-141.5	44.3	185.8	44.8	$141.0 \pm 9.5$
10	$(\text{EtO})_2\text{PCl}$ (37.9)	4.3 <sup>b</sup>	-46.4	48.5 <sup>b</sup>	94.9	49.1	$45.8 \pm 3.7$
11	 $\text{PCl}$ (40.4)	5.5 <sup>b</sup>	-38.6	52.3 <sup>b</sup>	90.9	51.5	$39.4 \pm 3.5$
12	 $\text{PBr}$ (43.2)	7.9	-75.5	57.6	133.1	54.2	$78.9 \pm 6.5$

<sup>a</sup> Calculated using data for pyridine in Table 3. <sup>b</sup> Data from Ref. [2]. <sup>c</sup> The resulting error is the sum of the experimental determination and the standard deviation in the pyridine data and consists of no more than  $\pm 7$ –9%.

and their molar refractions according to Eq. (3), as shown previously [1, 6, 7], we obtained the values of the solvation enthalpies in pyridine, described as the observed values (Eq. (4))

$$\Delta H_{\text{vap}}/\text{kJ mol}^{-1} = \Delta H_{\text{soln}}(\text{C}_6\text{H}_{14}) + 4.39 + 1.05((\text{MR}_D) - \alpha) \quad (3)$$

where  $\alpha$  is the correction for the branched carbon atoms [1].

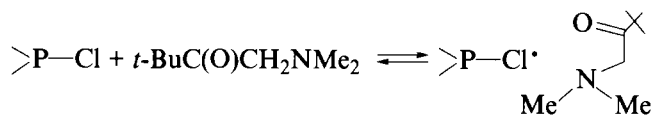
$$\Delta H_{\text{soln}}(\text{Obs}) = \Delta H_{\text{soln}}(\text{Py}) - \Delta H_{\text{vap}} \quad (4)$$

Due to the possibility of complex formation between halides (8–12) and pyridine, the observed enthalpies of solvation have large negative values. At the same time the enthalpies of non-specific solvation of compounds 8–12 in pyridine can be calculated using the values for pyridine in Table 3. In turn, the differences between the observed and calculated values of solvation enthalpies represent the enthalpies of specific interaction of the halides under investigation with pyridine.

It should be noted that the substitution of chlorine by a bromine atom in compounds 8, 9, 11 and 12 leads to stronger specific interactions, since the energy of the P–Br bond is less than that of the P–Cl bond. Probably this is largely responsible for the complex formation.

Comparing specific interaction enthalpies for compounds 10 and 11, acyclic chlorophosphite (10) reacts more exothermically with pyridine than the corresponding cyclic derivative (11). Perhaps, the intramolecular  $n, \sigma^*$ -hyperconjugative interaction between the lone electron pair of oxygens in alkoxy-radicals and the antibonding orbitals of the P–Cl bond is more pronounced in this case than the same effect in catecholchlorophosphite. Finally, it is necessary to note that the absolute values of the enthalpies of specific interaction of  $\text{PCl}_3$  or  $\text{PBr}_3$  with pyridine are greater than those of the cyclic and acyclic phosphite analogues. With pyridine as solvent, there will be acceptor molecules such as  $\text{PCl}_3$  and  $\text{PBr}_3$  that can form complexes of different structure in this medium, i.e.  $\text{PX}_3 \cdot \text{Py}$ ,  $\text{PX}_3 \cdot 2\text{Py}$  and  $\text{PX}_3 \cdot 3\text{Py}$ .

Because the values of the specific interaction enthalpies of chlorophosphites with pyridine obtained are large in comparison with those calculated [4] and found experimentally previously [3], further investigations of the acceptor ability of chlorophosphites in the process of complex formation with 1-dimethylamino-3,3-dimethylpropan-2-one ( $\alpha$ -aminoketone) (13) were undertaken. It is known that chlorophosphites form strong complexes with aminoketone in chloroform at 298 K by the absence of trialkylamine in reaction which serves as acceptor of HCl in the system [9]

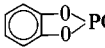
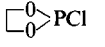
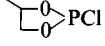
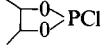
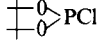
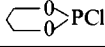


IR and NMR spectroscopic studies of the complex formation have shown that the lone pair of the nitrogen and the carbonyl-group of aminoketone (13) are involved; obviously a chelate is formed. This is supported by molecular orbital calculations of the aminoketone: the distance between the nitrogen and oxygen atoms is 2.7–2.8 Å.

The thermodynamic parameters of complex formation were studied using a calorimetric “entropy titration” method [11, 12] under the above conditions at different

Table 5

Calculated thermodynamic characteristics of the complex formation process<sup>a</sup> between aminoketone (13) and cyclic chlorophosphites (11, 14–18):  $\Delta G^0$  and  $\Delta H^0$  in  $\text{kJ mol}^{-1}$ ,  $\Delta S^0$  in  $\text{J mol}^{-1} \text{K}^{-1}$ , distance of P–Cl ( $l_{\text{P-Cl}}$ ) in Å

Compound no.	Formula	$\log K_{\text{eq}}$	$-\Delta G^0$	$-\Delta H^0$	$-\Delta S^0$	$l_{\text{P-Cl}}^{\text{b}}$
11		2.38	13.6	77.4	214	2.106
14		2.08	11.9	72.7	185	2.105
15		2.44	13.9	80.0	222	–
16		2.42	13.8	58.6	150	–
17		1.88	10.7	70.1	199	2.093
18		2.17	12.4	95.8	280	2.128

<sup>a</sup> The resulting error of the experimental and calculating determination of all parameters is no more than  $\pm 7$ –10%. <sup>b</sup> Data from Ref. [15].

ratios of donor to acceptor molecules (from 1:1 to 1:10). The observed exothermic effects ( $Q_{\text{Obs}}$ ) were analysed according to standard procedures calculated as multistage equilibria [11–14] (Table 5). The basis of these calculations involved known interrelations between the heat of complex formation ( $Q_{\text{Compl}} = Q_{\text{Obs}} - q_{\text{dil}}$ ) and the stability constant  $\beta_i$  [16]

$$Q_{\text{Compl}} = V \sum_{i=1}^{i=n} \beta_i [\text{M}] [\text{L}]^i \Delta H_i^0 \quad (5)$$

where  $V$  is volume of solution in l,  $\beta_i = K_1 K_2 \dots K_i$ ,  $[\text{M}]$  and  $[\text{L}]$  are concentrations of the complex and ligand, respectively,  $\Delta H_i^0$  is the enthalpy of complex formation, and  $i$  is the number of equilibrium stage.

Analysis was by least-squares procedure [12, 16]. The procedure was confirmed by determining the thermodynamic parameters of the system  $\text{AgNO}_3 + \text{C}_5\text{H}_5\text{N}$  using literature experimental data [12]. The following values were determined for the first stage:  $\log K_1 = 1.91 \pm 0.05$ ,  $\Delta H_1^0 = -21.8 \pm 0.5 \text{ kJ mol}^{-1}$ ; for the second stage:  $\log K_2 = 4.06 \pm 0.07$ ,  $\Delta H_2^0 = -47.0 \pm 1.1 \text{ kJ mol}^{-1}$ . The literature data are:  $\log K_1 = 1.99$ ,  $\log K_2 = 4.13$ ,  $\Delta H_1^0 = -19.2$ , and  $\Delta H_2^0 = -46.5 \text{ kJ mol}^{-1}$  [12].

As can be seen from the data listed in Table 5 there is good agreement between the magnitude of the enthalpy and entropy, which is consistent with the general mechanism of complex formation for chlorophosphites of different structure. Obviously the type of cyclic substituent (phenylenic or alkylenic) and the number of methyl groups on the five-membered rings (11–17) have a noticeable influence on the thermodynamic parameters. However, the values of enthalpy and entropy for six-membered ringed

compound (18) differ from those of other analogues within experimental errors (see the footnote to Table 5).

$$\Delta H^0 = (-17.9 \pm 5.4) + (0.28 \pm 0.02)\Delta S^0$$

$$r = 0.983, S_0 = 2.35, n = 6 \quad (6)$$

It is essential to note one other trend which is concerned with the sensitivity of the complex formation enthalpy to the size of the P–Cl bond in the chlorophosphites (Eq. (7)); the free energy of complex formation did not correlate with the P–Cl distance ( $r = 0.47$ )

$$\Delta H^0 = (1532 \pm 116) - (765 \pm 55)l_{\text{P-Cl}} \quad (7)$$

$$r = 0.970, S_0 = 1.40, n = 4$$

At the same time it is known that the energies (enthalpies) of bond formation in organic compounds often vary with bond lengths [17]. This should be taken as evidence that the energy of the P–Cl bond (or the energy of the antibonding orbital) is to a great degree responsible for the complex formation enthalpy.

#### 4. Conclusions

Taking into account the previously published results [2] on solvation factors of three-coordinated phosphorous compounds and the results of this work, certain features are apparent. It is obviously possible to calculate non-specific solvation enthalpies for these compounds in solvents such as carbon tetrachloride, benzene, *p*-xylene and pyridine using the molar refraction data and coefficients listed in Table 3.

Moreover, it is possible readily to determine the values of the specific interaction enthalpy of halides of P<sup>III</sup> in pyridine (or other nitrogen-containing solvents), which previously were difficult to obtain.

Finally, the thermodynamic parameters of complex formation of cyclic chlorophosphites with  $\alpha$ -aminoketone have been determined and serve as definite support for the strong acceptor ability of such compounds.

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