

## Thermochemistry of heteroatomic compounds. Part 5<sup>1</sup>. Enthalpies of vaporization and solvation of tetracoordinated phosphorous derivatives

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(Received 27 April 1993; accepted 10 June 1993)

### Abstract

The enthalpies of vaporization of different classes of tetracoordinated phosphorous compounds have been determined according to their enthalpies of solution in hexane and carbon tetrachloride. Good agreement of some values with literature data is established. The enthalpies of specific (hydrogen bond) interaction of derivatives having acid properties, with *p*-xylene, dioxan and acetone have been determined. The enthalpies of solvation of cyclic and acyclic derivatives of methylphosphonic acid in different solvents are analysed and discussed.

### INTRODUCTION

The chemical behaviour of organophosphorus compounds in many respects depends on the influence of the medium in which the processes occur. At the same time the influence of the solvent on the reaction is estimated in many cases by the change of equilibrium or rate constants. However, solvation factors of reactants and products are rarely analysed, even though such work is useful when studying mechanisms of reaction.

We have previously reported the calorimetric determination of the enthalpy of solvation [2, 3] and the (1 + 4)-cycloaddition reaction of three-coordinated phosphorus derivatives to benzyl compounds [1]. It was noted that the development of research into the thermodynamics of organophosphorus compounds, as well as other heteroatomic compounds, is restricted to an extremely small number of works concerning enthalpy of vaporization. However for organophosphorus compounds it may be possible to use the method recently proposed for the determination of

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<sup>1</sup> For Part 4 see ref. 1.

enthalpy of vaporization of organic compounds, using their known molar refraction and heat of solution in alkane (Y) [4]

$$\Delta H_{\text{vap}} + \text{kJ mol}^{-1} = \Delta H_{\text{soln}}(\text{Y}) + 4.39 + 1.05(\text{MR}_{\text{D}} - \alpha) \quad (1)$$

where  $\alpha$  is the molar refraction correction for branched carbon atoms:  $1.6 \text{ cm}^3 \text{ mol}^{-1}$  for  $\text{>CH}$  and  $4.8 \text{ cm}^3 \text{ mol}^{-1}$  for  $\text{>C}$ .

Such an approach allows us to extend considerably the library of thermochemical data and gives a basis for quantitative determination of solvation enthalpy for organophosphorus compounds in any solvent according to

$$\Delta H_{\text{solv}} = \Delta H_{\text{soln}} - \Delta H_{\text{vap}} \quad (2)$$

In the present work we determined enthalpies of solution and vaporization of different classes of tetracoordinated phosphorus compounds and we analysed their enthalpies of solvation in organic solvents.

## EXPERIMENTAL

Enthalpies of solution of compounds were measured at 295–298 K in a differential calorimeter constructed according to the Arnett–Rodgers scheme. Methods of measurement have been previously described [2, 3, 7]. The ranges of concentration were  $5 \times 10^{-3}$ – $5 \times 10^{-2} \text{ mol l}^{-1}$  for liquid substances and  $1$ – $5 \times 10^{-3} \text{ mol l}^{-1}$  for solids. The measured values have a magnitude which is accurate to within  $0.1$ – $0.7 \text{ kJ mol}^{-1}$  for liquids and  $0.5$ – $2.0 \text{ kJ mol}^{-1}$  for solid products. This is taken as a result of the average of 3–4 experiments. Variation of experimental values of solution enthalpies of solutes was observed only in the case of solutions of strongly associated derivatives of thio-acids of phosphorus (**36–38**); for the remaining products no change of enthalpy of solution in the indicated intervals of temperature and concentrations was observed.

All substances were synthesized by previously reported methods [7, 20–28] and have physical constants in accord with the literature values. Solvents were dried and purified by standard methods [29].

## RESULTS AND DISCUSSION

### *The solvation enthalpy in carbon tetrachloride*

Carbon tetrachloride is the most widely spread and applicable solvent which, like alkanes, is unable to enter into specific interaction with organophosphorus compounds. This solvent is most often used for spectral

TABLE 1

Solution, vaporization and non-specific solvation enthalpies in  $\text{kJ mol}^{-1}$  of various types of phosphorus compounds in hexane and carbon tetrachloride

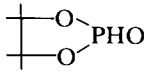
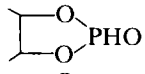
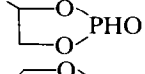
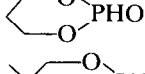
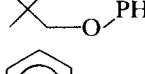
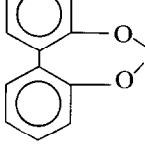
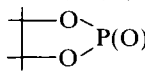
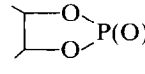
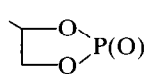
Com- pound no.	Formula	$\Delta H_{\text{soln}}^a$		$\text{MR}_D$	$\Delta H_{\text{vap}}$	$-\Delta H_{\text{solv}}$		
		$\text{C}_6\text{H}_{14}$ $\text{CCl}_4$				$\text{C}_6\text{H}_{14}^b$ $\text{CCl}_4$		
						Obs.	Calc. <sup>c</sup>	
<b>Phosphoric acids</b>								
1	$(\text{MeO})_2\text{PHO}$	11.5	4.4	22.5	39.5	28.0	35.1	
2	$(\text{EtO})_2\text{PHO}$	11.9	-0.2	31.6	49.5 <sup>d</sup>	37.6	49.7	
3	$(\text{PrO})_2\text{PHO}$	9.6		41.0	57.0	47.4		54.8
4	$(i\text{-PrO})_2\text{PHO}$	7.3	-1.5	40.9	51.3	44.0	52.8	
5	$(\text{PhO})_2\text{PHO}$		5.7	62.2	82.1 <sup>e</sup>	69.7		76.4
6	$(\text{ClCH}_2\text{CH}_2\text{O})_2\text{PHO}$		10.7	41.2	65.7 <sup>e</sup>	47.6		55.0
7		32.4	24.6	38.6	67.3	34.9	42.7	
8		10.5	5.9	30.1	43.1	32.6	37.2	
9			3.2	24.7	39.8 <sup>e</sup>	28.6		36.6
10			-6.1	24.7	32.1 <sup>e</sup>	30.3		38.2
11			17.5	34.0	60.3 <sup>e</sup>	35.0		42.8
12			22.6	59.1	95.9 <sup>e</sup>	66.0		73.3
<b>Phosphonates</b>								
13	$(\text{MeO})_2\text{P}(\text{O})\text{Me}$		2.7	26.2	42.4 <sup>e</sup>	31.9		39.7
14	$(\text{EtO})_2\text{P}(\text{O})\text{Me}$		3.0	35.5	52.2 <sup>e,f</sup>	41.7		49.2
15	$(\text{EtO})_2\text{P}(\text{O})\text{Et}$	9.0	4.9	40.6	56.0	47.0	51.1	
16	$(\text{PrO})_2\text{P}(\text{O})\text{Me}$	9.8	3.7	45.2	61.6	51.8	57.9	
17	$(\text{ClCH}_2\text{CH}_2\text{O})_2\text{P}(\text{O})\text{Me}$		7.6	45.9	67.4 <sup>e</sup>	52.6		59.8
18	$(\text{PhO})_2\text{P}(\text{O})\text{Me}$		4.0	65.9	84.2 <sup>e</sup>	73.6		80.2
19		14.8	5.7	42.7	53.9	39.1	48.2	
20			4.7	34.7	49.8 <sup>e</sup>	37.5		45.1
21			9.4	29.3	50.6 <sup>e</sup>	33.5		41.2

TABLE 1 (continued)

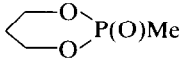
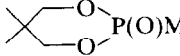
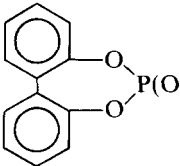
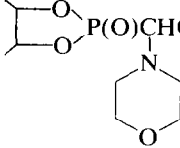
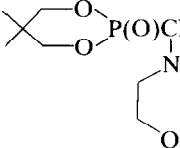
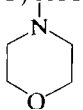
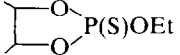
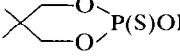
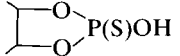
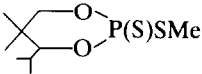
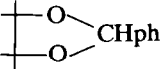
Com- pound no.	Formula	$\Delta H_{\text{soln}}^a$		MR <sub>D</sub>	$\Delta H_{\text{vap}}$	$-\Delta H_{\text{soln}}$		
		C <sub>6</sub> H <sub>14</sub> CCl <sub>4</sub>				C <sub>6</sub> H <sub>14</sub> <sup>b</sup> CCl <sub>4</sub>		
						Obs.	Calc. <sup>c</sup>	
22		-2.2	29.3	29.3	40.6 <sup>c</sup>	35.1	42.9	
23		24.5	38.6	38.6	72.0 <sup>c</sup>	39.9	47.5	
24		16.9	63.7	63.7	94.9 <sup>c</sup>	71.3	78.0	
25		28.5	69.6	69.6	99.2	70.7	77.5	
26		25.1	74.2	74.2	99.0	73.9	80.5	
27	(EtO) <sub>2</sub> P(O)CHCHMe <sub>2</sub> 	12.0	71.8	71.8	88.4	76.4	83.0	
Phosphates and thiophosphates								
28	Cl <sub>3</sub> PO	5.9	1.1 <sup>g</sup>	25.5	38.5 <sup>g</sup>	32.6	37.4	
29	(Me <sub>2</sub> N) <sub>3</sub> PO		-5.8 <sup>h</sup>	47.9	61.1 <sup>c</sup>	54.7	66.9	
30	(EtO) <sub>3</sub> PO	8.3	2.1	41.9	56.7 <sup>i</sup>	48.4	54.6	
31	(BuO) <sub>3</sub> PO	7.5	4.4	69.6	85.0 <sup>k</sup>	77.5	80.6	
32	i-PrO(EtO) <sub>2</sub> PO	11.4	0.9	46.5	62.9	51.5	62.0	
33	(EtO) <sub>3</sub> PS	7.1	-0.7	52.5	66.6	59.5	67.3	
34		12.4	2.9	50.3	66.2	53.8	63.3	
35		31.2	19.1	55.1	88.4	57.2	69.3	
36	(EtO) <sub>2</sub> P(S)OH		51.0 <sup>l</sup>	40.1	104.9 <sup>c</sup>	46.5	53.9	
37			78.2 <sup>l</sup>	37.9	126.6 <sup>c</sup>	40.8	48.4	

TABLE 1 (continued)

Com- pound no.	Formula	$\Delta H_{\text{soln}}^{\text{a}}$		MR <sub>D</sub>	$\Delta H_{\text{vap}}$	$-\Delta H_{\text{solv}}$	
		C <sub>6</sub> H <sub>14</sub>	CCl <sub>4</sub>			C <sub>6</sub> H <sub>14</sub> <sup>b</sup>	CCl <sub>4</sub>
						Obs.	Calc. <sup>c</sup>
38			70.3 <sup>1</sup>	42.6	121.8 <sup>c</sup>	44.1	51.5
39	(EtO) <sub>2</sub> P(S)SH	10.2	2.8	50.6	67.7	57.5	64.9
40	(i-PrO) <sub>2</sub> P(S)SH	8.0	0.0	56.9	68.8	60.8	65.9
41	(BuO) <sub>2</sub> P(S)SH	8.1		66.0	81.8	73.7	80.3
42	(i-BuO) <sub>2</sub> P(S)SH	7.5		66.0	77.8	70.3	77.1
43	(s-BuO) <sub>2</sub> P(S)SH	7.8		66.0	78.1	70.3	77.1
44		17.3	10.1	45.2	66.0	42.7	55.9
45			22.3	54.4	81.0 <sup>c</sup>	51.4	58.7
46		19.2	11.1	49.6	72.3	53.1	61.2
47			22.5	49.8	81.4 <sup>c</sup>	51.6	58.9
48			25.5	54.4	87.5 <sup>c</sup>	54.8	62.0
49			6.6	60.3	72.9 <sup>c</sup>	59.3	66.3
50	Et <sub>2</sub> P(S)SH		6.3	45.7	65.9 <sup>c</sup>	52.4	59.6
51	(EtO) <sub>2</sub> P(S)SEt	8.1	0.0	56.5	71.8	63.7	71.8
52	(i-PrO) <sub>2</sub> P(S)SMe		-1.0	61.5	71.5 <sup>c</sup>	65.6	72.5
53	(s-BuO) <sub>2</sub> P(S)SEt	4.9	-2.5	75.0	84.7	79.8	87.2
54	Et <sub>2</sub> P(S)SMe		-0.5	49.8	63.3 <sup>c</sup>	56.7	63.8
55		6.6	1.6	54.5	64.9	58.3	63.3
56			21.2	59.0	84.6 <sup>c</sup>	56.3	63.4
57		16.4	7.7	59.2	80.0	63.5	72.3
58			25.3	54.4	88.9 <sup>c</sup>	56.5	63.6
59			21.1	59.0	87.7 <sup>c</sup>	59.6	66.6

TABLE 1 (continued)

Com- pound no.	Formula	$\Delta H_{\text{soln}}^{\text{a}}$		$\text{MR}_{\text{D}}$	$\Delta H_{\text{vap}}$	$-\Delta H_{\text{solv}}$	
		$\text{C}_6\text{H}_{14}$ $\text{CCl}_4$				$\text{C}_6\text{H}_{14}^{\text{b}}$ $\text{CCl}_4$	
						Obs.	Calc. <sup>c</sup>
60		4.1	64.9	64.9	75.1 <sup>d</sup>	64.1	71.0
61		5.9	0.7	59.7	61.2	55.3	60.5
62	(PrO) <sub>2</sub> CHph	6.0	0.2	61.0	72.8	66.8	72.6

<sup>a</sup> Values of  $\Delta H_{\text{soln}}$  for some compounds were obtained previously [6, 7]. <sup>b</sup> Calculated using the equation  $-\Delta H_{\text{solv}}(\text{C}_6\text{H}_{14}) = 4.39 + 1.05(\text{MR}_{\text{D}} - \alpha)$ . <sup>c</sup> Calculated using eqn. (4). <sup>d</sup>  $\Delta H_{\text{vap}} = 49.3 \text{ kJ mol}^{-1}$  [8]. <sup>e</sup> Calculated using eqn. (4) and  $\Delta H_{\text{soln}}(\text{CCl}_4)$ . <sup>f</sup>  $\Delta H_{\text{vap}} = 56.5 \pm 4.0 \text{ kJ mol}^{-1}$  [9]. <sup>g</sup> Data from ref. 10. <sup>h</sup> Data from ref. 11. <sup>i</sup>  $\Delta H_{\text{vap}} = 57.3 \pm 4.0 \text{ kJ mol}^{-1}$  [9]. <sup>k</sup>  $\Delta H_{\text{vap}} = 72.0 \pm 5.0 \text{ kJ mol}^{-1}$  [9]. <sup>l</sup> Extrapolated to high dilution.

research on molecules, study of thermodynamic complex formation, determination of dipole moments, and synthesis of different compounds.

We have shown that the enthalpy of solvation of trivalent phosphorus compounds is in linear dependence on the magnitude of their molar refraction [3]

$$-\Delta H_{\text{solv}} = 9.08 + 1.08\text{MR}_{\text{D}} \quad (3)$$

In this paper we determined the solution enthalpies of different classes of organosphorus compounds with P<sup>IV</sup> in hexane and carbon tetrachloride (Table 1). Using eqn. (1) we calculated their enthalpies of vaporization and then in accordance with eqn. (2) we found solvation enthalpies for compounds (1, 2, 4, 7, 8, 15–17, 19, 28–35, 39, 44, 46, 51, 53, 55 and 57) in carbon tetrachloride. It was seen that the experimentally calculated non-specific solvation enthalpies of the mentioned acyclic and five-membered cyclic organophosphorus compounds are also found to be in good agreement with their molar refraction (eqn. (4)). Points corresponding to six-membered cyclic derivatives are not included in the calculation because their conformational transformation enthalpies have magnitudes of 5–10 kJ mol<sup>-1</sup> [5].

$$-\Delta H_{\text{solv}} = (13.0 \pm 1.9) + (1.02 \pm 0.04)\text{MR}_{\text{D}} \quad (4)$$

$$r = 0.985 \quad S_0 = 2.40, \quad n = 20$$

Parameters of eqn. (4) are found to be in good agreement with the coefficients shown above according to eqn. (3) and analogous equations describing the magnitudes  $\Delta H_{\text{sol}}(A_i/\text{CCl}_4)$  of organic molecules  $A_i$ , containing in their structure carbonylic, hydroxylic or nitro groups [4]. This shows that the enthalpies of non-specific solvation of organic compounds and organophosphorus derivatives in  $\text{CCl}_4$  are quantitatively similar and are mainly determined by the volume (or molar refraction) of the solute.

Combination of eqns. (2) and (4) may be used for determination of vaporization enthalpy of organophosphorus compounds having a tetra-coordinated phosphorus atom, since most are not soluble in alkanes. By combining eqns. (2) and (4), correcting for molar refraction on the branched carbon skeleton and taking into account the solution enthalpies in  $\text{CCl}_4$ , we determined vaporization enthalpies of phosphorus derivatives as shown in Table 1. It can be seen that there is good agreement of  $\Delta H_{\text{vap}}$  values for compound (14): calculated  $52.2 \pm 2.9 \text{ kJ mol}^{-1}$ , experimental  $56.5 \pm 4.0 \text{ kJ mol}^{-1}$  [9], respectively. The error in the determination of vaporization enthalpy of organophosphorus compounds according to eqns. (1), (2) and (4) is summed from the experimental error of solution enthalpy (see Experimental section) and the standard deviation in eqn. (4), and consists of  $\pm 2.5\text{--}4.0 \text{ kJ mol}^{-1}$  depending on the aggregate state of the dissolved product. It can be noted that the determination of  $\Delta H_{\text{vap}}$  for six-membered cyclic compounds is obviously accompanied by a larger error because this type of compound is found in conformational equilibrium.

#### *Enthalpy of non-specific solvation and specific interaction of organophosphorus compounds in p-xylene, nitrobenzene, dioxan and acetone*

The experimentally determined enthalpy of solvation according to eqn. (2) is the sum of the enthalpy of non-specific solvation and the specific interaction of the solute with the solvent. The problem of determination of  $\Delta H_{\text{sol}}$  (non-specific) for organic compounds ( $A_i$ ) in many solvents (S) has already been solved [4]; it has been established that this energetic term is found to depend direct upon the molar refraction of the solute

$$\Delta H_{\text{sol}}(\text{non-spec}) = a_s + b_s \text{MR}_D \quad (5)$$

where  $a_s$  and  $b_s$  are coefficients.

Verification of the applicability of the above conclusion to the analysis of enthalpy of solvation of organophosphorus compounds not only using the solvent carbon tetrachloride, but also for other solvents was carried out. To do so, the enthalpies of solution and solvation of different types of esters of tetra-coordinated phosphorus atom were determined in *p*-xylene (Table 2), nitrobenzene (Table 3), dioxan (Table 4) and acetone (Table 5). The calculated correlations (eqn. (6–9)), which are shown in Table 6 confirm

TABLE 2

Enthalpies in  $\text{kJ mol}^{-1}$  of solution, solvation and specific interaction of compounds in *p*-xylene

No. of compound in Table 1	$\Delta H_{\text{soln}}$	$-\Delta H_{\text{solv}}$		$-\Delta H$ of specific interaction
		Obs.	Calc. <sup>a</sup>	
2	2.3	47.2		
3	0.6	56.4		
7	24.0	43.3		
8	4.3	38.8		
19	6.0	47.9		
25	21.8	77.4		
27	0.0	88.4		
33	-0.5	67.1		
34	1.2	65.0		
51	-0.2	72.0		
55	-0.6	65.5		
36	20.4 <sup>b</sup>	84.5	55.0	29.5
37	42.0 <sup>b</sup>	84.6	49.2	35.4
38	43.8	78.0	52.5	25.5
39	0.4	67.3	66.3	1.0
40	0.0	70.6	69.7	0.9
41	-0.5	82.3	82.9	-0.6
42	-0.1	77.9	79.5	-1.6
43	-0.7	78.8	79.5	-0.7
44	3.8	62.2	57.3	4.9

<sup>a</sup> Calculated using eqn. (6) in Table 6. <sup>b</sup> Extrapolated to high dilution.

that the enthalpies of solvation of neutral organophosphorus compounds in the indicated solvents are of non-specific character.

Derivatives of phosphorus compounds having mobile hydrogen atoms are susceptible to specific interactions (hydrogen bonding) with solvents having a lone electron pair or  $\pi$ -system. The differences between the values

TABLE 3

Enthalpies in  $\text{kJ mol}^{-1}$  of solution and solvation of compounds in nitrobenzene

No. of compound in Table 1	$\Delta H_{\text{soln}}$	$-\Delta H_{\text{solv}}$
16	-1.9	63.5
19	0.9	53.0
28	0.4 <sup>a</sup>	38.1 <sup>a</sup>
52	1.6	69.9

<sup>a</sup> Data from ref. 10.



TABLE 4

Enthalpies in  $\text{kJ mol}^{-1}$  of solution, solvation and specific interaction of compounds in dioxane

No. of compound in Table 1	$\Delta H_{\text{soln}}$	$-\Delta H_{\text{solv}}$		$-\Delta H$ of specific interaction
		Obs.	Calc. <sup>a</sup>	
2	1.8	47.7		
3	1.9	55.1		
16	1.2	60.4		
19	2.6	51.3		
20	2.3	47.5		
51	2.2	69.6		
52	1.3	70.2		
53	4.3	80.4		
54	-0.9	64.2		
55	2.0	62.9		
56	22.7	61.9		
7	20.3	47.0	46.4	0.6
39	-1.9	69.6	63.9	5.7 <sup>b</sup>
40	-2.7	73.3	66.4	6.9 <sup>c</sup>
43	-0.4	78.5	73.8	4.7
44	-1.9	67.9	57.1	10.8 <sup>d</sup>
45	13.6	67.4	59.2	8.2 <sup>e</sup>
50	1.6	64.3	59.9	4.4 <sup>f</sup>

<sup>a</sup> Calculated using eqn. (9) in Table 6. <sup>b</sup> Values of  $\Delta H$  for hydrogen bonding are  $-6.6 \text{ kJ mol}^{-1}$  [7] and  $-8.8 \text{ kJ mol}^{-1}$  [13]. <sup>c</sup>  $\Delta H$  for hydrogen bonding is  $-7.9 \text{ kJ mol}^{-1}$  [7].

<sup>d</sup> Values of  $\Delta H$  for hydrogen bonding are  $-12.5 \text{ kJ mol}^{-1}$  [7] and  $-10.0 \text{ kJ mol}^{-1}$  [13]. <sup>e</sup>  $\Delta H$  for hydrogen bonding is  $-10.2 \text{ kJ mol}^{-1}$  [7]. <sup>f</sup>  $\Delta H$  for hydrogen bonding is  $-4.3 \text{ kJ mol}^{-1}$  [7].

of solvation enthalpies calculated using eqns. (6–9) and those found (see Tables 2, 4 and 5) constitute the enthalpies of specific interaction (or hydrogen bonding).

Hydrophosphorylic compounds of different spatial isomerism form almost no hydrogen bonds with *p*-xylene and dioxan, but show appreciable specific interaction with acetone. Here the values of enthalpy of specific interaction correspond quite well to the magnitudes of  $\Delta H$  of hydrogen bonds determined previously by the use of Arnett's "pure base" method [6]. Dithiophosphorus acids are effective H-donors in dioxan (Table 4) and the results are in good agreement with the calorimetric [7] and spectral [12] data. However, in *p*-xylene their proton-donor character is practically non-existent except for the derivative with the phospholoanic ring (44). The strongest hydrogen bonding with *p*-xylene is observed for thiophosphates (36–38) due to  $\text{OH} \cdots \pi$ -type bond formation.

TABLE 5

Enthalpies in  $\text{kJ mol}^{-1}$  of solution, solvation and specific interaction of compounds in acetone

No. of compound in Table 1	$\Delta H_{\text{soln}}$	$-\Delta H_{\text{solv}}$		$-\Delta H$ of specific interaction
		Obs.	Calc. <sup>a</sup>	
13	0.7	41.7		
14	0.1	52.1		
17	0.4	67.0		
18	-0.2	84.4		
19	-2.0	55.9		
20	-1.7	51.5		
21	0.7	49.9		
24	15.3	79.6		
5	-0.9	83.0	80.3	2.7 <sup>b</sup>
6	-0.4	66.1	60.3	5.8 <sup>c</sup>
7	1.6	65.7	48.7	17.0 <sup>d</sup>
8	-24.0	67.1	46.7	20.4 <sup>e</sup>
9	-22.0	61.7	43.1	18.6 <sup>f</sup>
12	15.8	80.1	77.3	2.8 <sup>g</sup>

<sup>a</sup> Calculated using eqn. (8) in Table 6. <sup>b</sup>  $\Delta H$  for hydrogen bonding is  $-2.4 \text{ kJ mol}^{-1}$  [6]. <sup>c</sup>  $\Delta H$  for hydrogen bonding is  $-3.9 \text{ kJ mol}^{-1}$  [6]. <sup>d</sup>  $\Delta H$  for hydrogen bonding is  $-15.3 \text{ kJ mol}^{-1}$  [6]. <sup>e</sup>  $\Delta H$  for hydrogen bonding is  $-23.5 \text{ kJ mol}^{-1}$  [6]. <sup>f</sup>  $\Delta H$  for hydrogen bonding is  $-16.4 \text{ kJ mol}^{-1}$  [6]. <sup>g</sup>  $\Delta H$  for hydrogen bonding is  $-5.2 \text{ kJ mol}^{-1}$  [6].

### Enthalpy of solvation of methylphosphonic acid derivatives in different solvents

Previously we reported [14] the solution and transfer enthalpies (cyclohexane was taken as a standard solvent) of phosphonates (**16** and **19**), pinacol- and dipropylacetals of benzaldehyde (**61** and **62** respectively) in different solvents. With the  $\Delta H_{\text{vap}}$  data for the indicated compounds it is now possible to determine enthalpies of their solvation in various solvents

TABLE 6

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

Equation no.	Solvent	$a_s$	$b_s$	$r$	$S_0$	No. of points $n$
4	$\text{CCl}_4$	$-13.0 \pm 1.9$	$-1.02 \pm 0.04$	0.985	2.40	20
6	<i>p</i> -Xylene	$-11.7 \pm 1.9$	$-1.08 \pm 0.04$	0.994	1.83	11
7	Nitrobenzene	$-18.6 \pm 8.3$	$-0.93 \pm 0.19$	0.958	4.90	4
8	Acetone	$-21.2 \pm 3.1$	$-0.95 \pm 0.07$	0.983	2.98	8
9	Dioxane	$-22.9 \pm 1.4$	$+0.81 \pm 0.03$	0.994	1.12	11

TABLE 7

Enthalpies of solvation in  $\text{kJ mol}^{-1}$  <sup>a</sup> of phosphonates (**16** and **19**) and acetals of benzaldehyde (**61** and **62**) in various solvents

Solvent no.	Solvent	$\pi^*$	$-\Delta H_{\text{solv}}$		$(\delta H_{\text{solv}})_{16}^{19}$	$-\Delta H_{\text{solv}}$		$(\delta H_{\text{solv}})_{62}^{61}$
			<b>19</b>	<b>16</b>		<b>61<sup>c</sup></b>	<b>62<sup>d</sup></b>	
1	Cyclohexane	0	39.1	51.8	12.7	55.3	66.8	11.5
2	$\text{CCl}_4$	0.28	48.2	57.9	9.7	60.5	72.6	12.1
3	Benzene	0.59	49.1	62.7	13.6	60.0	71.9	11.9
4	Dioxan	0.55	51.3	60.4	9.1	60.9	70.5	9.6
5	Chlorobenzene	0.71	52.3	65.1	12.8	62.3	73.7	11.4
6	Nitrobenzene	1.01	53.0	63.5	10.5	60.6	71.0	10.4
7	DMSO	1.00	54.1	59.6	5.5	57.7	65.2	7.5
8	Methanol	0.60	56.9	65.8	8.9	57.8	68.2	10.4
9	Ethanol	0.54	52.8	63.8	11.0	58.9	68.5	9.6
10	Propanol	0.51	51.7	62.0	10.3	58.0	68.0	10.0
11	Isobutanol	0.41 <sup>b</sup>	49.8	61.6	11.8	54.1	65.3	11.2
12	Acetic acid	0.64	61.0	72.4	11.4	61.4		
13	Propanol–water (1:1)	0.80 <sup>b</sup>	56.7	66.4	9.7	54.5	64.0	9.5
14	Dioxan–water (1:1)	0.82 <sup>b</sup>	60.1	66.7	6.6	59.3		
15	Chloroform	0.58	69.0	81.1	12.1	71.4	81.7	10.3

<sup>a</sup> Values of  $\Delta H_{\text{solv}}$  were reported in ref. 14. <sup>b</sup> Calculated using  $\pi^*$  constants for similar solvents.

<sup>c</sup>  $\text{MR}_D = 59.7 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\Delta H_{\text{vap}} = 61.2 \text{ kJ mol}^{-1}$ . <sup>d</sup>  $\text{MR}_D = 61.0 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\Delta H_{\text{vap}} = 72.8 \text{ kJ mol}^{-1}$ .

(Table 7). The differences in magnitudes  $\delta H_{\text{solv}}$  between phosphorus containing compounds and non-phosphorus compounds confirm that acyclic derivatives of both types are better solvated ( $8\text{--}13 \text{ kJ mol}^{-1}$ ) in inert, polar and H-donor solvents. Here a reasonable interrelation (eqn. (10) can be observed between the relative energetic terms indicated.

$$(\delta H_{\text{solv}})_{16}^{19} = (-6.6 \pm 1.8) + (1.67 \pm 0.18)(\delta H_{\text{solv}})_{62}^{61} \quad (10)$$

$$r = 0.933 \quad S_0 = 0.83 \quad n = 13$$

There is a certain interest in analyzing the gross enthalpy of solvation of derivatives of tetracoordinated phosphorus compounds, as far as they include in their composition both non-specific and specific solvations, particularly with H-donor solvents. One of the simplest examples of separating enthalpy of solvation in the indicated deposits is the “baseline” method suggested by Stephenson and Fuchs [15]. According to this method the difference in enthalpy of solvation of the compound to be investigated and the model compound is graphically compared with the  $\pi^*$ -constant values of series of solvents. Among the solvents selected were inert ones (alkanes, halogenated and aromatic hydrocarbons, ethers) and using corresponding points a graph was constructed which was then used as a

baseline. Deviation from the line point corresponding to the H-donor solvent; is regarded as a measure of the relative interaction of the investigated solute with the solvent.

When determining relative enthalpies of specific interaction of phosphonates (**16** and **19**) with H-donor solvents (Table 7), we used the values of  $\delta H_{\text{solv}}$  of the corresponding cyclic and acyclic acetals (**61** and **62**) as model compounds which had previously been standardized by dividing by coefficient 1.67 in eqn. (10); this results in the most correction to differences in the molar volumes (refractions). As can be seen, the differences in the enthalpies of solvation found for derivatives of cyclic  $(\delta H_{\text{solv}})_{61}^{19}$  and acyclic  $(\delta H_{\text{solv}})_{62}^{16}$  structures correlate satisfactorily with  $\pi^*$  constants of the first seven solvents in Table 7 (eqns. (11) and (12)).

$$(\delta H_{\text{solv}})_{61}^{19} = (-7.4 \pm 1.1) - (11.0 \pm 2.5)\pi^* \quad (11)$$

$$r = 0.946, \quad S_0 = 1.50, \quad n = 7$$

$$(\delta H_{\text{solv}})_{62}^{16} = (-12.5 \pm 2.7) - (9.3 \pm 1.3)\pi^* \quad (12)$$

$$r = 0.936, \quad S_0 = 1.56, \quad n = 7$$

Upon deviation from these lines, the points corresponding to H-donor associating solvents (alcohols, acid, organo-water mixtures) and weakly associated chloroform were taken to be the relative values of enthalpy of specific interaction for the compounds (**16** and **19**) (Table 8). In the case of model compounds (**61** and **62**) and phosphonates (**16** and **19**) which have identical alkoxylic and dioxyalkylenic fragments at the carbon and

TABLE 8

Relative values of enthalpies of solvation in  $\text{kJ mol}^{-1}$  of cyclic (**19**) and **61**) and acyclic (**16** and **62**) phosphonates and acetals, and enthalpies of specific interaction in  $\text{kJ mol}^{-1}$  of P=O groups with H-donor solvents

No. of solvent in Table 7	<b>19</b>			<b>16</b>		
	$-(\delta H_{\text{solv}})_{61}^{19}$		$-\Delta H_{\text{sp.int.}}$ P=O...H	$-(\delta H_{\text{solv}})_{62}^{16}$		$-\Delta H_{\text{sp.int.}}$ P=O...H
	Obs.	Calc. <sup>a</sup>		Obs.	Calc. <sup>b</sup>	
8	22.3	14.0	8.3	25.0	18.1	6.9
9	17.5	13.3	4.2	22.8	17.5	5.3
10	17.0	13.0	4.0	21.3	17.2	4.1
11	17.4	11.9	5.5	22.5	16.3	6.2
12	24.2	14.4	9.8			
13	24.1	16.2	7.9	28.1	19.9	8.2
14	24.6	16.4	8.2			
15	26.2	13.8	12.4	32.2	17.9	14.3

<sup>a</sup> Calculated using eqn. (11). <sup>b</sup> Calculated using eqn. (12).

phosphorus atoms, the obtained  $\Delta H$  values of specific interaction are responsible mainly for the formation of H-bonds between oxygen atoms in P=O groups and hydroxylic groups of alcohols, acid, water or the C–H bond in chloroform.

When we look at the values of specific interaction (P=O $\cdots$ H) it is possible to note that the energies of H-bond formation of the phosphoryl group with chloroform are in good agreement with the values determined for similar compounds by calorimetric [12] and spectroscopic [16, 17] methods. In the case of other proton donor solvents, enthalpies of specific interaction for P=O $\cdots$ H systems show lower values than those obtained for the enthalpies of H-complex formation of alkylphosphonic acid esters with alcohols ( $-17$  to  $-24$  kJ mol $^{-1}$ ) and organo-water mixtures ( $-14$  to  $-20$  kJ mol $^{-1}$ ) [17, 18]. This may be due to the following reasons. First, the determined values of specific interaction obtained using the baseline method contain considerable errors because there is an uncertainty in the choice of model compounds. The other relevant factor is that the investigated compounds are soluble in the corresponding solvents (energy of alcohol–alcohol hydrogen bond is about  $-19.7$  kJ mol $^{-1}$  [19]). In spite of the fact that phosphorylic compounds are relatively strong bases, the exothermic formation of hydrogen bond complexes between the molecules of phosphonates (**16** and **19**) and hydroxyl containing solvents are significantly compensated by endothermic processes of changes of associative equilibria in such solvents [19].

## CONCLUSIONS

Among the investigated enthalpies of solvation of tetra-coordinated phosphorus derivatives, one can see two features. The first is that heterocyclic derivatives differ from comparable compounds having identical volumes (or molar refractions); acyclic compounds have enthalpies of solvation which are, on average, 10 kJ mol $^{-1}$  lower.

The second feature which is apparent from the results obtained is the fact that there is a difference between the quantitative determination of specific interaction enthalpy of phosphoryl-containing molecules with associated solvent and a phosphorus compound—H-donor molecule system.

These observations are important when interpreting the chemical behaviour of organophosphorus compounds of different structure in various solvents.

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