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Thermochemistry of heteroatomic compounds. Part 8[1]. Enthalpies of vaporization and solvation of three-coordinated organophosphorous halides

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Abstract

The enthalpies of vaporization and solvation of more than twenty acyclic and cyclic halides of three-coordinated organophosphorous compounds have been determined according to their enthalpies of solution in hexane and carbon tetrachloride. The Cl_2P- and $ClP<$ group contributions to the vaporization enthalpy for P(III) compounds of similar type have been calculated using experimental data.

Keywords: Enthalpy; Halides; Solvation; Vaporization

1. Introduction

The thermochemistry of vaporization, solvation and reaction of P(III) organophosphorus compounds has not been studied in any detail [2–4]; however such data are very useful in understanding the reactivity of these substances. Among three-coordinated organophosphorus compounds, halides are the most reactive but their enthalpies of vaporization, solvation and, especially, of reaction have not been investigated systematically. Previously, we reported the calorimetric determinations of the enthalpies of vaporization of P(III) derivatives of different space groups [2] and the Ramirez–Kukhtin cycloaddition reaction of some cyclic and acyclic ethers to benzyl [3].

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[1] For Part 7 see Ref. 1

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Subsequently, an analysis of the solvation enthalpies of cyclic P(III) ethers in CCl_4, benzene, *p*-xylene, methanol and pyridine was carried out [4]; the enthalpies of the specific interactions of halides of such compounds with pyridine, and the thermodynamic parameters of complex formation with α-aminoketone were also measured [4].

In this paper, we summarize the previously published work [2] and also measure the enthalpies of vaporization and solvation in hexane and carbon tetrachloride of the different three-coordinated phosphorus halides. Using this data, the group contributions to the vaporization enthalpy for $-PCl_2$ and $> PCl$ have been calculated.

2. Experimental

The enthalpies of solution of all compounds were measured at 298 K in a differential calorimeter, as previously reported [2, 5], as an average of 3–4 experiments. All halides of phosphorus were synthesized and purified by previously reported methods [2–5]. All operations in the preparation and synthesis, and in the thermochemical experiments, were carried out in dry argon atmosphere.

3. Results and discussion

It has been shown by us previously [5] that the enthalpies of vaporization of organophosphorus compounds can be determined with satisfactory accuracy using Eq. (1). This was first suggested by Solomonov and Konovalov [6] for the determination of the energetic terms of organic compounds using their known (or calculated) molar refraction and the enthalpy of solution in an alkane (hexane)

$$\Delta H_{\mathrm{vap}}(\mathrm{kJ\,mol^{-1}}) = \Delta H_{\mathrm{soln}}(C_6H_{14}) + 4.39 + 1.05(MR_D - \alpha) \quad (1)$$

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

Using this approach, the vaporization enthalpies of about twenty compounds containing a P(III) atom have been measured [2,5]. From this, it was possible to determine the magnitude of the solvation enthalpies for organophosphorus compounds in different solvents according to the equation

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

However, it has been established that the correlations between the solvation enthalpy and molar refraction of compounds which do not specifically interact with solvents such as carbon tetrachloride, *p*-xylene and benzene can be regarded as evidence of the non-specific character of their solvation [5]. This permits us to suggest some new equations (Eqs. (3)–(5)) for estimating vaporization enthalpy, similar to Eq. (1), i.e.

$$\Delta H_{\mathrm{vap}}, \mathrm{kJ\,mol^{-1}} = \Delta H_{\mathrm{soln}}(CCl_4) + 9.1 + 1.08(MR_D - \alpha) \quad (3)$$

$$\Delta H_{\mathrm{vap}}, \mathrm{kJ\,mol^{-1}} = \Delta H_{soln}(p\text{-}xyl) + 6.1 + 1.13(MR_D - \alpha) \quad (4)$$

$$\Delta H_{\mathrm{vap}}, \mathrm{kJ\,mol^{-1}} = \Delta H_{\mathrm{soln}}(C_6H_6) + 7.8 + 1.11(MR_D - \alpha) \quad (5)$$

Table 1
Solution, vaporization and solvation enthalpies in kJ mol^{-1} of P(III) halides

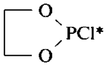
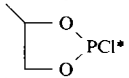
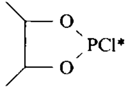
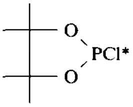
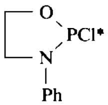
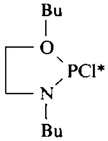
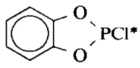
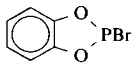
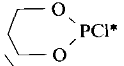
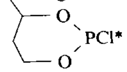
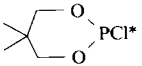
Compound no.	Formula	ΔH_{soln}		MR_D	ΔH_{vap}	$-\Delta H_{solv}$	
		C_6H_{14}	CCl_4			C_6H_{14}[c]	CCl_4
1	PCl_3[a]	1.6	0.3	24.9	32.2 32.6[b]	30.6	31.9
2	PBr_3	5.0		33.3	43.3 48.5[b]	39.3	45.1[d]
3	$MeOPCl_2$	4.7		26.9	37.3	32.6	38.2[d]
4	$EtOPCl_2$	2.4		32.0	40.4	38.0	43.7[d]
5	$PrOPCl_2$	2.7		36.3	45.2	42.5	48.3[d]
6	$BuOPCl_2$	1.3		41.2	48.9	47.6	53.6[d]
7	$PhOPCl_2$	4.2		46.5	57.4	53.2	59.3[d]
8	Et_2NPCl_2			42.5	48.7[e]	49.0	55.0[d]
9	$BuSPCl_2$	4.5		47.4	58.6 58.2[e] 58.3[g]	54.1	60.3[d]
10	$(EtO)_2PCl$[a]	4.3	0.0	37.9	48.5	44.2	48.5
11	$(Et_2N)_2PCl$	4.3		60.0	71.7 70.9[e] 71.3[g]	67.4	73.9[d]
12 	PCl[a]	8.7	4.2	26.1	40.5	31.8	36.3
13 	PCl[a]	7.2	3.3	30.0	41.4	34.2	38.1
14 	PCl[a]	7.3	2.3	34.8	44.9	37.6	42.6
15 	PCl[a]	7.5	2.4	44.0	48.0	40.5	45.6
16 	PCl[a]		18.4	51.8	83.4[f] 81.1[e] 82.1[g]	58.8	65.0[d]
17 	PCl[a]		−0.8	66.9	80.5[f] 83.7[e] 82.1[g]	74.6	81.3[d]
18 	PCl[a]	5.5	1.8	40.4	52.3	46.8	50.5
19 	PBr	7.9		43.2	57.6	49.7	55.8[d]

Table 1 (*Continued*)

Compound no.		Formula	ΔH_{soln}		MR_D	ΔH_{vap}	$-\Delta H_{solv}$	
			C_6H_{14}	CCl_4			C_6H_{14} [c]	CCl_4
20		PCl [a]	8.6	2.1	30.0	44.5	35.9	42.4
21		PCl [a]	7.7	2.5	34.8	47.1	39.4	44.6
22		PCl [a]	6.3	1.8	39.4	47.0	40.7	45.2

[a] ΔH_{soln} values for these compounds were obtained previously [2]; [b] Data from Ref. [7]; [c] Calculated using the equation $-\Delta H_{solv}(C_6H_{14}) = 4.39 + 1.05(MR_D - \alpha)$; [d] Calculated using the equation $-\Delta H_{solv}$ $(CCl_4) = 9.1 + 1.08\,(MR_D - \alpha)$ [4]; [e] Calculated using the group contributions in Table 2; [f] Calculated using Eq. (3); [g] A middle value.

In particular, Eqs. (3)–(5) can be used with crystalline substances or compounds with a high molecular weight which are not soluble in hexane.

The vaporization enthalpies for compounds 1–22 are listed in Table 1 as calculated using Eq. (1). For the two cyclic phosphorus- and nitrogen-containing compounds (16 and 17), Eq. (3) was adopted. It should be noted that the error in determining ΔH_{vap} from Eqs. (3)–(5) is no larger than that in using Eq. (1) and was about $\pm 3.0 - 4.5$ kJ mol^{-1}. In most cases, this is comparable to the uncertainties for other experimental methods [8]. But hydrolysis during these measurements makes these methods inoperable.

Because of this, group contributions for $-PCl_2$ and $> PCl$ fragments to ΔH_{vap} were calculated using the additive scheme (Eqn. 6)

$$\Delta H_{vap} = \sum_{i=1}^{n} n_i X_i \qquad (6)$$

where n is the number of the different fragments in a molecule, n_i is the number of i-type fragments in the molecule, X_i is the contribution to ΔH_{vap} of the i-type fragment.

This approach has been used successfully by Lebedev and Miroshnichenko [8] to calculate the vaporization enthalpy values of organic compounds with different structures. Some group contribution values [9] are presented in Table 2. Similarly, using the contributions of the non-phosphorus groups, we have calculated similar parameters X_i for Cl_2P- and $ClP <$ fragments using the ΔH_{vap} values for compounds (3–7) and for the second group of compounds (12–15, 20, 21). The calculated group contributions to ΔH_{vap} are shown in Table 2.

To verify the general applicability of both group contributions to the vaporization enthalpies of P(III)-halides, ΔH_{vap} was calculated for compounds 9, 11, 16 and 17. It can be seen from the data in Table 1 that there is good agreement between ΔH_{vap} values obtained by different methods. In addition, we calculated the vaporization enthalpies of some alkyldichlorophosphines (23–31) (Table 3) and compared the magnitude of these values with reported values [10]. Thus for compounds (24–26) only, there is good

Table 2
Some group contributions X_i for the calculation of vaporization enthalpy values in kJ mol^{-1}

Type of group	X_i
$C-(C)(H)_3$	6.4[a]
$C-(C)_2(O)(H)$	−1.1[a]
$C-(C)_2(H)_2$	4.8[a]
$C-(C)(S)(H)_2$	3.5[a]
$O-(C)_2$	7.8[a]
$S-(C)_2$	15.3[a]
$N-(C)_3$	4.2[a]
$C_\beta-(C_\beta)_2(H)$	5.3[a]
$C_\beta-(C_\beta)_2(N)$	8.6[a]
$\Delta_5 = \Delta_6$	6.4[a,b]
$Cl_2P-(C)$	22.2 ± 2.5, assigned
$Cl_2P-(O)$	
$Cl_2P-(N)$	
$Cl_2P-(S)$	
$ClP-(O)_2$	17.9 ± 2.0, assigned
$ClP-(N)_2$	
$ClP-(S)_2$	

[a] Data from Ref. [8].
[b] Correction for cyclic molecules.

agreement between the experimental and calculated values; probably, application of the vapour-pressure method to compounds with a high molecular weight leads to a substantial decrease in ΔH_{vap}. Comparison of vaporization enthalpies for the isosteric chloroalkanes $MeCHCl_2$ and $PrCHCl_2$ [8] with the corresponding values for the phosphorus-containing analogues was surprisingly close, see Table 3.

Table 3
The vaporization enthalpy values in kJ mol^{-1} for alkyldichlorophosphines

Compound no.	Formula	ΔH_{vap}		
		Expl.[c]	Calc.	|Diff|
23	$MePCl_2$[a]		28.6	
24	$EtPCl_2$	34.9	33.4	1.5
25	$PrPCl_2$[b]	39.2	38.2	1.0
26	$BuPCl_2$	42.1	43.0	0.9
27	$AmPCl_2$	42.2	47.8	5.7
28	$HexPCl_2$	45.3	52.6	7.3
29	$HeptPCl_2$	47.9	57.4	9.5
30	$OctPCl_2$	51.3	62.2	10.9
31	$PhPCl_2$		53.0	

[a] ΔH_{vap} for $MeCHCl_2$, 30.7 kJ mol^{-1} [8].
[b] ΔH_{vap} for $PrCHCl_2$, 39.3 kJ mol^{-1} [8].
[c] Data from Ref. [10].

4. Conclusion

Taking into account the above results, the group contributions of the Cl_2P-fragment have been evaluated and this allows the vaporization enthalpy to be calculated for compounds in which the phosphorus atom is attached directly to carbon, oxygen, nitrogen and sulphur. We have not been able to verify more widely the universality of group contribution in the vaporization enthalpy of ClP < fragments, but believe it is applicable in combination with oxygen or nitrogen atoms.

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