Journal of Thermal Analysis, Vol. 54 (1998) 305-309

THERMOCHEMISTRY OF HETEROATOMIC COMPOUNDS

X. The thermochemistry of solution and solvation of substituted alkylphosphonic derivatives*

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Abstract

The enthalpies of vaporization of different classes of phosphorylated alcohols and amines were determined from their enthalpies of solution in hexane and carbon tetrachloride. The enthalpies of specific (hydrogen-bond) interaction with the solvents (chloroform and pyridine) of derivatives containing X–H groups (X=O or N) in the α-position to the P=O group were detemined. The results were explained in terms of the spatial structure of such compounds.

Keywords: enthalpy of solution, enthalpy of solvation, enthalpy of specific interaction with solvent, enthalpy of vaporization, phosphonic derivatives

Introduction

Phosphonic acid and its cyclic and acyclic ethers form a large group of organic compounds of phosphorus. Many phosphonic derivatives have biological activity and are used as pesticides [2, 3].

Despite the great practical importance of derivatives of phosphonic acid, their thermochemistry and thermodynamics have been relatively poorly investigated: there are no more than ten publications on this theme in the literature [4].

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1418-2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

A new method of estimating the enthalpies of vaporization of organic substances, based on their molar refractions and heats of solution in hexane or similar inert solvents, such as carbon tetrachloride or *p*-xylene, was recently proposed [5, 6] (Eqs (1)–(3)):

$$\Delta H_{\mathrm{vap}}/\mathrm{kJ\ mol^{-1}} = \Delta H_{\mathrm{soln}}(\mathrm{hexane}) + 4.39 + 1.05(\mathrm{MR_D} - \alpha) \tag{1}$$

$$\Delta H_{\mathrm{vap}}/\mathrm{kJ\ mol^{-1}} = \Delta H_{\mathrm{soln}}(\mathrm{CCl_4}) + 13.0 + 1.02(\mathrm{MR_D} - \alpha) \tag{2}$$

$$\Delta H_{\mathrm{vap}}/\mathrm{kJ\ mol^{-1}} = \Delta H_{\mathrm{soln}}(\mathrm{xylene}) + 11.7 + 1.08(\mathrm{MR_D} - \alpha) \tag{3}$$

where α is the correction factor for branched carbon atoms.

Further, a new approach to the analysis of the solvation enthalpy values, consisting of the sums of non-specific solvation and the specific interaction of the solute with solvents, for organic and heteroatomic compounds has been suggested via the use of Eqs (4)–(6) [5, 6]:

$$\Delta H_{\mathrm{solv}}(\mathrm{obs.}) = \Delta H_{\mathrm{soln}} - \Delta H_{\mathrm{vap}} \tag{4}$$

$$\Delta H_{\mathrm{solv}}(\mathrm{non{-}spec.}) = a_s + b_s\mathrm{MR_D} \tag{5}$$

$$\Delta H_{\mathrm{solv}}(\mathrm{obs.}) = \Delta H_{\mathrm{soln}}(\mathrm{non{-}spec.}) + \Delta H(\mathrm{spec.\ int.}) \tag{6}$$

The solvation enthalpies are determined by using the solution and vaporization enthalpies in different solvents

Experimental

The enthalpies of solution of the examined compounds were measured at 295–298 K in a differential calorimeter constructed according to the Arnett-Rogers scheme. The methods of measurement were described previously [6]. The results of 3–4 experiments were averaged. All substances were synthesized by reported methods [7, 8] and had physical constants in accordance with the literature values. Solvents were dried and purified by standard methods [9].

Results and discussion

Thermochemical studies were carried out on the behaviour in non-aqueous media (hexane, carbon tetrachloride, chloroform and pyridine) of the following derivatives of methylphosphonic acid $(\mathrm{R_1O})_2\mathrm{P(O)R}$ (1)–(11), containing an X–H group (*X*=O or N) with a mobile hydrogen atom in the α-position to the P=O group:

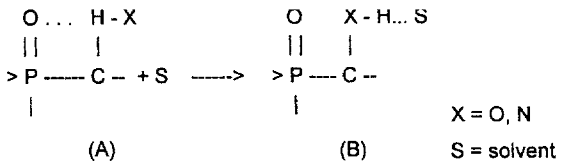
(1) R_1=Et, R_2=CH_2OH, (2) R_1=Pr, R_2=CH_2OH, (3) R_1=i-Pr, R_2=CH_2OH,
(4) R_1=Et, R_2 =CH(Me)OH, (5) R_1=Et, R_2=CH(Et)OH,
(6) R_1=Et, R_2=CH(Ph)OH, (7) R_1=Pr, R_2=CH(Ph)NHMe,
(8) R_1= i-Pr, R_2=CH(Ph)NHMe, (9) R_1=Am, R_2=C(c-hexylene)$NHCH_2Ph$,
(10) R_1=Et, R_2=$C(Me)_2NHCH_2Ph$, (11) R_1=Et, R_2=$C(Me)_2NHPr$-i.

The heats of solution of all these compounds in hexane and the molar refractions were used as in Eq. (1) to obtain the vaporization enthalpy values. Phosphorylated amines (9) and (10) are very poorly soluble in hexane, and their vaporization enthalpies were therefore determined via Eq. (2) with the use of ΔH_{soln} in carbon tetrachloride. All results are listed in Table 1.

Table 1 Enthalpies of solution and vaporization of phosphorylated alcohols and amines (1)–(11) in various solvents

Compound no.	ΔH_{soln}/kJ mol^{-1}					ΔH_{vap}/ kJ mol^{-1}
	C_6H_{14}	CCl_4	$CHCl_3$	C_5H_5N	MR_D	
(1)	4.3	-3.0	-5.2	-2.1	37.7	48.3
(2)	4.6	-2.4	-5.6	-3.3	46.9	58.2
(3)	2.6	-4.5	-7.1	-2.7	46.9	52.8
(4)	3.7	-3.0	-6.5	-4.0	42.3	50.8
(5)	3.9	-2.8	-7.0	-4.2	46.9	55.8
(6)	7.5	0.9	-7.2	-4.5	61.9	75.1
(7)	12.8	-2.2	-17.6	-0.5	78.0	97.1
(8)	12.9	-2.2	-18.0	-0.6	78.0	94.5
(9)	–	16.0	-18.8	-9.5	117.0	143.4
(10)	–	15.8	-18.4	-8.4	77.7	103.2
(11)	16.4	9.5	-20.1	-2.6	62.8	80.0

As demonstrated previously [7], phosphorylated alcohols and amines can exist in high diluting solvents as some form with internal and external hydrogen-bonds (structures A and B)



(A) (B)

Such a situation could be reflected in the solvation enthalpies of these compounds. The next stage of our investigation was therefore connected with the determination of the enthalpies of solvation of compounds (1)–(11) in the above solvents according to Eq. (4) (Table 1). The enthalpies of non-specific solvation were calculated by using Eq. (5), where coefficients a_s and b_s for CCl_4 and Py are –13.0, –1.02 and –17.0, –1.01, respectively [6]. The enthalpies of specific interaction between the solute and the solvents were found as differences: for chloroform: $\Delta H_{solv}(CHCl_3)-\Delta H_{solv}(CCl_4)$, and for pyridine: ΔH_{solv}(obs.)–ΔH_{solv}(calculated by using Eqs (5) and (6)).

Table 2 Enthalpies of solvation and specific interaction of phosphorylated alcohols and amines (1)–(11) in various solvents

Comp. no.	ΔH_{solv}/kJ mol^{-1}						$\Delta H_{spec.int.}$/ kJ mol^{-1}	
	C_6H_{14}	CCl_4		$CHCl_3$	C_5H_5N			
	calc.	obs.	calc.		obs.	calc.	$CHCl_3$	$C5H_5N$
(1)	40.0	51.3	51.5	53.5	50.4	55.1	2.2	–4.7
(2)	53.6	60.6	60.8	63.8	61.7	64.4	3.2	–2.7
(3)	50.3	57.3	57.6	59.9	55.5	61.1	2.6	–5.6
(4)	47.1	53.8	54.5	57.3	54.8	58.1	3.5	–3.3
(5)	52.0	58.6	59.2	62.8	60.0	62.7	4.2	–2.7
(6)	67.6	74.2	74.4	82.0	79.6	77.8	7.8	1.8
(7)	84.6	99.6	90.9	115.0	97.9	94.2	15.4	3.7
(8)	81.2	96.3	87.7	112.1	94.7	90.9	15.8	3.8
(9)	122.2	127.4	127.4	162.2	152.9	130.3	34.8	22.6
(10)	80.9	87.4	87.4	121.6	111.6	90.6	34.2	21.0
(11)	63.6	70.5	70.5	100.1	82.6	73.9	29.6	8.7

It follows from the data in Table 2 that the phosphorylated alcohols (1)–(6) participated in weak specific interactions with chloroform; there was practically no interaction with pyridine. The phosphorylated amines (7)–(11) underwent stronger interactions with both solvents, especially compounds (9)–(11).

These results are in good agreement with previous conclusions [7] concerning the strong internal hydrogen-bonds for α-hydroxyphosphonates (form A). The explanation for this situation is probably to be found in the spatial structure of phosphorylated alcohols and amines.

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This work was supported by a grant of St. Petersburg University.

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