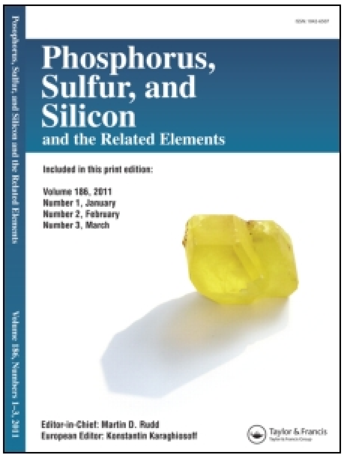

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Ovchinnikov, V. V. , Lapteva, L. I. , Khazieva, L. R. and Konovalov, A. I.(1999) 'Thermochemistry of Heteroatomic Compounds. Part 14 Enthalpies of Vaporization and Formation of Derivatives of Phosphoric and Phosphonic Acids', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 789 — 792

To link to this Article: DOI: 10.1080/10426509908546363

URL: http://dx.doi.org/10.1080/10426509908546363

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 789-792
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Thermochemistry of Heteroatomic Compounds. Part 14*. Enthalpies of Vaporization and Formation of Derivatives of Phosphoric and Phosphonic Acids

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The thermochemistry of phosphorylated derivatives of methylphosphonic acid have been systematically investigated. The vaporization and formation enthalpies about fifty derivatives of phosphoric and phosphonic acids were analysed and a number of contributions in the mentioned thrmochemical trems were created.

It was shown, that the specific interaction with chloroform and pyridine is expressed only at aminophosphonates but not at hydroxyphosphonates.

Keywords: thermochemistry; organophosphorus compounds; enthalpies of formation; vaporization; solvation

INTRODUCTION

The search of interrelation between chemical activity and thermochemical parameters and bond energies of heteroatomic compounds represents now an urgent problem, the work over which is executed in many thermochemical centres of the world. The derivatives of phosphoric and phosphonic acids are compounds with expressed reactivity however thermochemistry of such compounds is not practically investigated. The purpose of the present work is the study of thermochemistry of derivatives of phosphoric [>P(O)H] and alkylphosphonic [>P(O)R'] acids with α-functional groups OH, NH, Ph toward P=O bond: the study of enthalpic function of vaporization, solvation and formation in condensed and gas phases.

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* For Part 13 see ref [1].

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RESULTS AND DISCUSSION

The vaporization enthalpy (ΔH_{vap}), as well as the enthalpy of formation (ΔH_f^O), is one of major thermochemical parameters of organic and organophosphorus compounds. For these substances possible to use the method recently proposed by B.Solomonov and A.Konovalov [2] for the determination of enthalpy of vaporization of organic compounds, using the known refraction and heat solution in hexane (eq.1)

$$\Delta H_{vap}\,(\mathrm{kJ\ mol^{-1}}) = \Delta H_{solv}\,(C_6H_{14}) + 4.39 + 1.05\,MR_D \qquad (1).$$

In Table 1 are represented the vaporization enthalpy magnitudes for different types of derivatives of phosphoric and phosphonic acids, which have been measured with the use of eqn. (1).

Table 1 Experimental and calculated vaporization and formation enthalpies for condensed and gas phases of some phosphoric and phosphonic ethers (kJ mol^{-1})

Compound	ΔH_{vap}^{a}		$-\Delta H_f^o$		
			Gas phase		
	Exp	Calc	Exp	Calc	Condens phase
$(EtO)_2P(O)H$	49.5	45.7	877.4±4.2	883.0	926.9
$[(CH_2)_3]O_2P(O)H$	32.1	44.2	845.0±14.6	815.1	877.1
$[(CH_2)_2]O_2P(O)Me$	46.0	45.8	874.2±14.1	845.1	920.9
$[(CH_2)_3]O_2P(O)Me$	40.6	50.5	901.1±12.5	886.8	941.7
$(AmO)_2P(O)C(c\text{-}hex)NH$- -$CH_2Ph$	143.4	142.4	-	1025.5	1168.9
$(EtO)_2P(O)CMe_2NHCH_2Ph$	103.2	102.7	-	882.0	985.2
$(EtO)_2P(O)CH(morph)Pr$-i	88.4	89.5	1037.0±2.5	1023.4	1125.4
$(EtO)_2P(O)CH(Ph)OH$	75.1	75.5	-	992.9	1068.0

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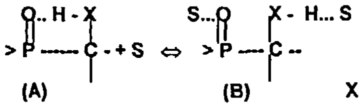
a Contributions:$C\text{-}P(O)(O\text{-})_2 = H\text{-}P(O)(O\text{-})_2$ 26.8 for phosphites and phosphonates and -5.6 kJ mol^{-1} for $C\text{-}P(O)(O\text{-})_2$ for phosphorylated alcohols.

The determination of this magnitude is connected with to large methodological difficulties, therefore it is very important to have a possibility for it theoretical calculation. On the basis of the analysis of our own and literary data on vaporization enthalpies have been calculated of a number of the group contributions in ΔH_{vap} for fragments, containing in structure P=O group; these data are represented under the Table 1. Such an approach allows to extend considerably of thermochemical data and gives a basis for quantitative determination of solvation enthalpy for organophosphorus compounds in any solvent according to equation (2)

$$\Delta H_{solv} = \Delta H_{soln} - \Delta H_{vap} \qquad (2).$$

Previously with the use of IR-investigations has been established that phosphorylated alkohols and amines form in condensed phase and solutions (S) the structures with the internal (A) and external (B) hydrogen bonds



X=O, N; S=$CHCl_3$, Py.

Taking into account such point of view we undertook the thermochemical research of substituted derivatives of methylphosphonic acid (12 compounds have been studied), having in α-position toward to P=O group X-H fragments with the mobil hydrogen atom in hexane, carbon tetrachloride, chloroform and pyridine (see Table 2). All phosphorylated alcohols practically do not display of specific interaction with pyridine and chloroform due to the strong internal hydrogen bond between P=O and OH groups. At the same time aminophosphonates display expressed specific interaction with both mentioned solvents.

Table 2 Enthalpies of specific interaction between of some phosphorylated amines and alcohols in pyridine and chloroform (kJ mol^{-1}, T 298 K)

Compound	Pyridin			$-\Delta H_{solv}$ [a]		$-\Delta H$ spec. Int.
	$-\Delta H_{solv}$		$-\Delta H$	CCl_4	$CHCl_3$	
	Exp	Calc [b]	spec.int.	Exp	Exp	$CHCl_3$
$(AmO)_2P(O)C(c\text{-}hex)$- $-CH_2Ph$	152.9	130.3	22.6	127.4	162.2	34.8

Table 2 (continued)

$(EtO)_2P(O)CMe_2NH$- $-CH_2Ph$	111.6	90.6	21.0	87.4	121.6	34.2
$(EtO)_2P(O)CH(Me)OH$	54.8	58.1	-3.3	53.8	57.3	3.5
$(EtO)_2P(O)CH(Ph)OH$	79.6	77.8	1.8	74.2	82.0	7.8

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[a] Calulated as a difference between of $\Delta H_{solv}(CHCl_3)$ and $\Delta H_{solv}(CCl_4)$.

[b] Calculated using the equation : ΔH_{solv}(non-spec.) = 17.0 + 1.01 MR_D

In the last part of this work we have studied the thermochemistry of hydrolysis reaction of alkylenechlorophosphites in the presence of triethylamine in dioxane and non-catalyzed Pudovik-reaction[3] (eqns. 3,4) :

$$\mathbf{RO_2PCl + H_2O + Et_3N \longrightarrow RO_2P(O)H + Et_3N \cdot HCl} \quad (3)$$

$$\mathbf{RO_2P(O)H + {>}C{=}CH\text{-}NR_2 \longrightarrow RO_2P(O)CH(NR_2)CH{<}} \quad (4).$$

Than, using the solvation enthalpies of reagents and products and enthalpies of processes in solution we calculated the rection enthalpies for the gas phase (eq. 5):

$$\mathbf{\Delta H_{reaction}\,(gas) = \Delta H_{reaction}\,(solution) - \Sigma\, \Delta H_{solv}\,(prods) + \Sigma\, \Delta H_{solv}\,(reags)} \quad (5).$$

All these thermochemical results are required for the calculation enthalpies of formation of ethers of phosphonic acid in the gas phase. Some of these data are listed in Table 1.

On the basis of the analysis literary and own experimental thermochemical data on formation enthalpies we calculated two group contributions for formation enthalpy in a gas phase for derivatives of phosphonic and phosphoric acids: -771.1 and -727.5 kJ mol^{-1} correspondingly. The calculated group contribution allow to predict the formation enthalpy values such difficult for thermochemical methods compounds as phosphorylated aminoalcohols, aminoacids, sugars, peptides or other substances with interesting and useful biological properties.

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