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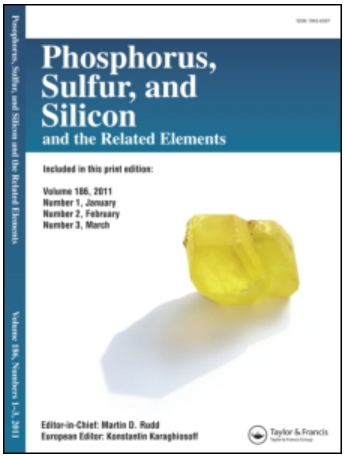

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ENTHALPIES OF FORMATION AND BOND ENERGIES OF P(III) AND As(III) COMPOUNDS

V.V.OVCHINNIKOV *, L.I.LAPTEVA, T.B.MAKEEVA, V.Yu.KUDRYAVTZEV, E.V.SAGADEEV and A.I.KONOVALOV

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Abstract The enthalpies of vaporization and formation of halogenides of P(III) and As(III) compounds of different cyclic and acyclic structure have been determined. The hydrolysis of mentioned compounds have been carried out and formation enthalpies in condensed state and gaseous phase have been calculated. The Cl_2P-, Cl_2As-, $ClP<$ and $ClAs<$ – group contributions in vaporization and formation enthalpies have been calculated on the basis of experimental data too. The appreciation of bond energies in chlorides of P(III) and As(III) has been given.

Key Words: *thermochemistry, vaporization, formation, phosphorus, arsenic, compound*

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INTRODUCTION

Thermochemistry of vaporization, solvation, reaction and formation of P(III)-organophosphorus and As(III)-organo-arsenic compounds have been not studied detail, however such data are very useful in understanding the reactivity of these substances. The development of research into thermochemistry and thermodynamics of the mentioned class of compounds is restricted to an extremely small number of

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works conserning of the vaporization enthalpy [1,2]. The vaporization enthalpy magnitudes, contrary to the heats of solution, have not been similarly easy obtained especially in the case of heteroatomic compounds.

B.Solomonov and A.Konovalov [3] suggested for the determination of this energetical term the Equation (1) with the use of molar refraction and solvation enthalpy of compound in alkane (hexane) (in kJ mol^{-1})

$$\Delta H_{vap} = \Delta H_{soln}(C_6H_{14}) + 4.39 + 1.05\ (MR_D - \alpha) \qquad (1),$$

where α is a molar refraction correction for branched carbon atoms.

Such approach allows us to extend considerably the library of thermochemical data and gives a basis for quantitative determination of formation enthalpy (ΔH_f^o) of P and As compounds in liquid (l), solid (s) state and gaseous phase (g) according to Equation (2)

$$\Delta H_f^o(\ g\ ) = \Delta H_f^o(\ l\ \text{or}\ s\ ) - \Delta H_{vap} \qquad (2)$$

RESULTS AND DISCUSSION

Among the three-coordinated organophosphorus and -arsenic compounds the halogenides are most reactive but thermochemistry of its reaction have not investigated systematically. In present work we report the previously published enthalpies of vaporization [4] and also measured now the hydrolysis and formation enthalpies of some P(III) and As(III)-halogenides of acyclic and cyclic structure; thermochemical data are summarized in Table I.

On the basis of additive scheme and using the contributions for organic groups of molecules in ΔH_f^o we

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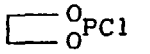
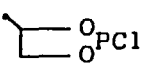
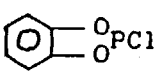
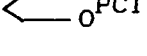
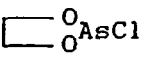
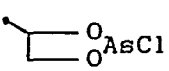
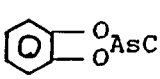
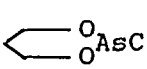
TABLE I Thermochemical data for some halogenides in kJ mol^{-1} at 298.15 K.

Formula	ΔH_{vap}	$-\Delta H_f^o$	
		(l or s)	(g)
$MeOPCl_2$	37.3	455.5	418.2±7.1
$PrOPCl_2$	45.2	532.7	487.5±7.0
$BuSPCl_2$	58.6	426.3	367.6±5.0 [a]
$(EtO)_2PCl$	48.5	683.2	634.7±8.4
$EtOAsCl_2$	47.1	558.7	511.6±9.8
$PrOAsCl_2$	52.2	574.0	521.8±10.5
$BuOAsCl_2$	55.7	590.8	535.1±12.0
	40.5	598.3	557.8±4.2
	41.4	630.2	588.8±5.4
	52.3	487.3 [b] 479.2	431.0±5.0 middle value
	44.5	655.6	611.1±7.5
	60.4	557.4	497.0±8.0
	59.8	588.7	528.9±7.3
	125.8	457.2	331.4±10.0
	62.0	565.4	503.4±8.3

[a] Calculated using the group contribution for $-PCl_2$.
[b] Reaction PCl_3 + catehol, see ref.[5].

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calculated the same parameters in the vaporization and formation enthalpies for Cl_2P-, ClP<, Cl_2As- and ClAs< fragments. The calculated values in ΔH_{vap} are 22.2±0.7, 17.9±0.8 and 29.0±1.0 kJ mol^{-1} for the first, second and third-fourth groups correspondingly. The calculated contributions in ΔH_f^o are -290.0+1.8, -321.3±1.1, -328.2±3.0 kJ mol^{-1} for Cl_2P-, ClP< and Cl_2As- groups; for five- and six-membered As(III)-containing cycles the same contributions represent themselves as -202.0±4.0 and -226.5±3.3 kJ mol^{-1} correspondingly.

The energies of P-Cl, As-Cl, P-O and As-O bonds (E_b) in molecules of $ROPCl_2$ and $ROAsCl_2$ types have been calculated using the computer programm for minimization of ΔH_{at}^o- values (eqn.3) which have been worked up by us on the basis of least-square mathematical method

$$\Delta H_{at}^o = \sum \Delta H_f^o \text{ (atoms)} - \Delta H_f^o \text{ (mol)} = \sum E_b \qquad (3).$$

The calculated bond energies (± 1.7%) of P-CL, As-Cl, P-O and As-O compose as 307.1±5.7, 313.8±1.7, 418.4±11.4 and 400.0±3.4 kJ mol^{-1}.

These observations are important when interpreting the chemical behaviour of trivalent organophosphorus and -arsenic compounds.

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