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THERMOCHEMISTRY OF HETEROATOMIC COMPOUNDS
VII. Enthalpies of solution, vaporization and solvation of three-coordinated arsenic derivatives*

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Abstract

The enthalpies of vaporization of different classes three-coordinated arsenic compounds have been determined according to their enthalpies of solution in hexane and molar refraction. The enthalpies of solvation of cyclic and acyclic As(III)-derivatives in hexane, carbon tetrachloride, *p*-xylene and pyridine are obtained and discussed.

Keywords: arsenic derivatives, enthalpy of solution, enthalpy of solvation, enthalpy of vaporization

Introduction

The enthalpies of solution, vaporization and solvation are known for the very small number of three-coordinated arsenic derivatives [2]. Although the values of the heats of solution can be determined relatively easily, the values of enthalpies of vaporization are difficult to determine and are thus poorly known for the overwhelming majority of heteroatomic compounds. We reported the data on the determination of the enthalpies of solution, vaporization and solvation of As(III)-derivatives of the different space structure.

Solomonov and Konovalov recently proposed a new method for estimating the enthalpy of vaporization of organic substances based on the data on their molar refraction and heats of solution in alkane (hexane) (Eq. (1)) [3].

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* Part 6, see Ref. [1].

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Table 1 Solution, vaporization and solvation enthalpies in kJ·mol^{-1} of As(III)-derivatives in solvents

Compound	ΔH_{soln}				MR_D	ΔH_{vap}	$-\Delta H_{solv}$			
No.	C_6H_{14}	CCl_4	*p*-xylene	pyridine			C_6H_{14}	CCl_4	*p*-xylene	pyridine
1	1.2	–2.7	0.1	0.1	77.4	86.9	85.7	89.6	86.8	86.8
2	2.6	–4.3	0.3	2.2	79.6	90.6	88.0	94.9	90.3	88.4
3	4.0	–5.2	–	–	57.7	69.0	65.0	74.2	–	–
4	5.8	–0.3	0.1	0.1	72.5	86.3	80.5	86.6	86.2	86.2
5	27.4	–	–	–	87.4	123.6[a]	96.2	–	–	–
6	5.4	0.9	–	–	47.7	59.9[b]	54.5	58.9	–	–
7	5.7	1.9	–	–	61.6	74.8[c]	69.1	72.9	–	–
8	6.2	2.6	–	–	75.4	89.8	83.6	87.2	–	–
9	8.0	3.0	–	–	70.6	86.5	78.5	83.3	–	–
10	5.2	–	–	–	35.7	47.1	41.9	–	–	–
11	6.8	–	–	–	40.3	52.2	45.4	–	–	–
12	4.1	–	–	–	44.9	55.7	51.6	–	–	–
13	6.4	–2.1	0.1	0.4	67.6	81.8	75.4	83.9	81.7	81.4
14	5.9	–4.1	0.1	1.5	81.2	95.6	89.7	100.2	95.5	94.1
15	6.9	–2.5	0.2	1.8	90.4	106.2	99.3	108.7	106.0	104.4
16	3.9	–2.7	0.2	2.6	99.7	113.0	109.1	115.7	112.8	110.4

[a] $\Delta H_{vap} = 98.3 \pm 8.4$ kJ·mol^{-1} [2], [b] $\Delta H_{vap} = 50.6 \pm 4.2$ kJ·mol^{-1} [2], [c] $\Delta H_{vap} = 58.6 \pm 8.4$ kJ·mol^{-1} [2]

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

where α is correction for the branched carbon atoms.

It should be noted that this method was used for the determination of vaporization enthalpy of different classes of tetra-coordinated phosphorus compounds [4]. Using this method we determined vaporization enthalpies of three-coordinated arsenic derivatives (Table 1). Enthalpy of solvation is the difference between the heats of solution and vaporization (Eq. (2))

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

Using the solution and vaporization enthalpies in hexane, carbon tetrachloride, *p*-xylene and pyridine we determine the solvation enthalpy values.

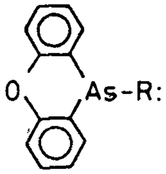
Experimental

Enthalpies of solution of compounds were measured at 295–298 K in a differential calorimeter constructed according to the Arnett-Rogers scheme. Methods of measurement have been previously described [5]. The ranges of concentration were $5\cdot10^{-3}$–$5\cdot10^{-2}$ mol^{-1} for liquid substances and 1–$5\cdot10^{-3}$ mol^{-1} for solids. The measured values have a magnitude which accurate to within 0.1–0.7 kJ·mol^{-1} for liquid and 0.5–2.0 kJ·mol^{-1} for solid products. This is taken as a result of the average of 3–4 experiments. All substances were synthesized by the previously reported methods [6] and have a physical constant in accord with the literature values. Solvents were dried and purified by standard methods [7].

Results and discussion

In the present work we determine enthalpies of solution in organic solvents of three-coordinated arsenic derivatives of acyclic (1–12) and cyclic (13–16) types, where R_3As:

(1) R = Et,*i*-Bu$_2$, (2) R = *i*-Am$_3$, (3) R = Et$_2$, Ph, (4) R = Et, Ph$_2$,
(5) R = Ph$_3$, (6) R = (EtO)$_3$, (7) R = (PrO)$_3$, (8) R = (BuO)$_3$,
(9) R = (i-BuO)$_3$, (10) R = EtO, Cl$_2$, (11) R = PrO, Cl$_2$,
(12) R = BuO, Cl$_2$,



(13) R = Me, (14) R = Bu, (15) R = Hex, (16) R = Oct.

Using the heats of solution of all compounds in hexane and molar refraction according to Eq. (1) we obtained the values of the enthalpies of vaporization (Table 1). Obtained by us the data of vaporization enthalpies of compounds (6–8) are slightly higher than the same values in work [2]. The difference between the enthalpies of vaporization for $(EtO)_3As$ and $(PrO)_3As$ can be about 14 kJ·mol^{-1} [2] (4.3 kJ·mol^{-1} on each CH_2-group). In work [2] this difference is only 3.3 kJ·mol^{-1}; according to our investigations this difference is 14.9 kJ·mol^{-1}. It should be noted there is a good correspondence between enthalpies of solution for Ph_3As in alcohol, acetonitrile [9] and obtained by us the values of enthalpy of solution in present work but enthalpy of vaporization is more than 98.3 kJ·mol^{-1} which have been represented in Ref. [2].

The next stage of our investigation is connected with the determination of enthalpies of solvation of some As(III)-derivatives (1–9, 13–16) in organic solvents according to Eq. (2) (Table 1). The observed enthalpy of solvation of any substances (A_i) in the solvent (S) consists from the sum of contributions of non-specific and specific interaction of the solute with the solvent (Eq. 3). It has been established that ΔH_{solv} (non-specific):

$$\Delta H^{A_i/S}_{solv}(\text{obs.}) = \Delta H^{A_i/S}(\text{non–spec.}) + \Delta H^{A_i/S}(\text{spec. int.}) \quad (3)$$

is dependent direct upon the molar refraction of solute (Eq. (4)) [3]

$$\Delta H_{solv}(\text{non–spec.}) = a_s + b_s MR_D \quad (4)$$

where a_s and b_s are coefficients.

Table 2 Parameters and characteristics of the equation ΔH_{solv} (non-spec.) = $a_s + b_s MR_D$ with correlation coefficients

Eq. No.	Solvent	a_s	b_s	r	S_o	No. of points n
5	CCl_4	–10.4±5.2	–1.06±0.07	0.980	3.300	12
6	*p*-xylene	–10.5±7.2	–1.03±0.09	0.981	2.348	7
7	pyridine	–15.3±7.4	–0.96±0.09	0.979	2.400	7

We have shown that the enthalpy of solvation As(III)-derivatives is in linear dependence on the magnitude of their molar refraction. The calculated correlation parameters for the Eqs (5–7) are represented in Table 2 and are similar to the same coefficients of Eq. (4) for P(III)-derivatives [1].

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Zusammenfassung — Entsprechend ihrer Lösungsenthalpien in Hexan und ihrer Molrefraktionen wurden die Verdampfungsenthalpien verschiedener Klassen trikoordinierter As(III)-verbindungen ermittelt. Die Solvatationsenthalpien von cyclischen und acyclischen As(III)-verbindungen in Hexan, Tetrachlorkohlenstoff, *p*-Xylol und Pyridin wurden ermittelt und diskutiert.