Thermochemistry of heteroatomic compounds
22.* Enthalpies of combustion and formation of alkyl(aryl)arsines and arsenites in the condensed and gaseous phases

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The enthalpies of combustion (ΔH_{comb}) of five primary, secondary, and tertiary alkyl(aryl)arsines in the condensed state were calculated using the equation $\Delta H_{comb} = -385.8 - 110.3N$, where N is the number of bond-forming electrons. The dependence presented is used for the calculation of the enthalpies of combustion of full esters and amidoesters of arsinous acid of noncyclic and cyclic structures.

Key words: arsines, arsenites, enthalpy of combustion, enthalpy of formation, enthalpy of vaporization.

Biological activity of arsines different in spatial structure has been known long ago, and some of them found use in therapy and veterinary medicine. For instance, tertiary arsines of the general formula $PhAs(C_nH_{n-1})_2$ at $n = 5—10$ possess fungicidal properties; their antibacterial activity depends on the length of the alkyl substituent at the arsenic atom.[2,3]

Nevertheless, published data on thermochemistry of vaporization, solvation, formation, and combustion of primary ($RAsH_2$), secondary (R_2AsH), and tertiary (R_3As) arsines are scarce.[4,5] We calculated the heats of formation ($\Delta H°_f$) of the above presented alkyl(aryl)arsines for the condensed and gaseous phases using three earlier found[5] values of the enthalpy of combustion (ΔH_{comb}/kJ mol^{-1}): -2779.0 ± 10.0 (trimethylarsine), -4846.3 ± 16.7 (triethylarsine), and -10082.6 ± 16.7 (triphenylarsine). It is known that the combustion of As^{III} derivatives in an oxygen atmosphere can be described by the equation

$$R_3As + n\,O_2 \longrightarrow x\,CO_2\,(g) + y\,H_2O\,(l) + z\,As_2O_3\,(s), \quad (1)$$

where n, x, y, and z are stoichiometric coefficients; R = Alk, Ar, AlkO, and R´$_2$N; g, l, and s indicate the gaseous, liquid and solid phases, respectively. The $\Delta H°_f$ values for CO_2 (g) (-395.5 kJ mol^{-1}), H_2O (l) (-285.8 kJ mol^{-1}), and As_2O_3 (s) (-656.9 kJ mol^{-1}) are given in the handbook.[5]

The enthalpy of combustion of organic[6] and organophosphorus[7] compounds in the liquid or solid state can be given by

$$\Delta H_{comb} = a + bN, \quad (2)$$

where N is the number of bond-forming (valent) electrons; a and b are coefficients.

Lone electron pairs (LEP) in a compound to be burned are ignored; one LEP is ignored in nitrogen (≡N:) and arsenic compounds (≡As:), and two LEP are ignored in oxygen-containing compounds. For example, the total number of bond-forming electrons for methylmercaptan Me—S—H is six; it was obtained by the summation of four electrons for carbon, four electrons for hydrogen, and two electrons for sulfur minus two LEP of the sulfur atom.[7]

Taking into account the above presented data on the enthalpies of combustion of trimethyl-, triethyl-, and triphenylarsines, we calculated the dependence similar to Eq. (2)

$$\Delta H_{comb} = (-385.8\pm70.6) - (110.3\pm1.2)N \quad (3)$$

$(r = 0.999, S_0 = 59.5, n = 3)$.

It turned out that the ΔH_{comb} values of the As^{III} derivatives can be described using the same parameter N that was suitable for organic or other heteroatomic compounds.[6,7]

The enthalpies of combustion of primary, secondary, and tertiary alkyl(aryl)arsines (**1—5**, Table 1) were calculated by Eq. (3) with the accepted error ±0.5% comparable with the errors of the experimental enthalpies of combustion of the As^{III} derivatives. The heats of combustion of organoarsenic compounds are necessary for the calculation of the enthalpies of their formation in the condensed state according to Eq. (1) and the Hess law[5]

$$\Delta H_{comb} = \Sigma\Delta H°_f\,(products) - \Sigma\Delta H°_f\,(reactants). \quad (4)$$

* For part 21, see Ref. 1.

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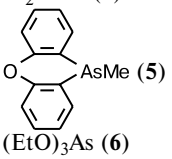
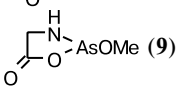
Table 1. Thermochemical characteristics (in kJ mol^{-1}) of selected primary, secondary, and tertiary alkylarsines and arsenites[a]

Compound	*N*	$-\Delta H_{comb}$ (±0.5%)	ΔH°_f[b]		ΔH_{vap}[c] (±5%)
			Condensed phase	Gaseous phase	
$MeAsH_2$ (**1**)	10	1488.8±7.4	52.3±7.4	75.7±8.6	23.4±1.2
$EtAsH_2$ (**2**)	16	2150.6±10.7	34.7±10.7	62.1±12.1	27.4±1.4
Me_2AsH (**3**)	16	2150.6±10.7	34.7±10.7	64.0±12.2	29.3±1.5
Et_2AsPh (**4**)	56	6562.6±32.8	155.3±32.8	224.3±36.2	69.0±3.4
 (**5**)	62	7224.4±36.1	208.3±36.1	290.1±40.2	81.8±4.1
$(EtO)_3As$ (**6**)	34	4136.0±20.7	−697.2±20.7	−637.3±23.7	59.9±3.0
$(PrO)_3As$ (**7**)	52	6121.4±30.6	−749.9±30.6	−675.1±34.3	74.8±3.7
 (**8**)	14	1930.0±9.6	−579.4±9.6	−533.6±11.9	45.7±2.3 [d]
 (**9**)	14	1930.0±9.6	−436.5±9.6	−387.7±12.0	48.8±2.4 [d]

[a] *N* is the number of bond-forming electrons; ΔH_{comb}, ΔH°_f, and ΔH_{vap} are the enthalpies of combustion, formation, and vaporization, respectively.
[b] Calculated by Eq. (4).
[c] Data of Refs 4 and 8.
[d] Calculated by the equation ΔH_{vap} (kJ mol^{-1}) = 4.26 + 9.37$^1\chi^s$ + 0.87$\mu^{2,7}$ where $^1\chi^s$ is the topological solvation index of the first order, and μ is the dipole moment of the compound.

In its turn, the knowledge of the enthalpies of vaporization (ΔH_{vap}) of alkyl(aryl)arsines determined by us earlier[8] made it possible to estimate the enthalpies of formation of all arsines in the gaseous phase.

To confirm a possibility of using Eq. (3) for the calculation of the enthalpies of combustion of derivatives of tricoordinate arsenic with both the As—C bonds and other bonds (As—O, As—N, or As—S), we calculated the thermochemical parameters of the arsinous acid derivatives $(EtO)_3As$ (**6**) and $(PrO)_3As$ (**7**) known in literature using Eqs (3) and (4). It turned out that for compounds **6** and **7** the enthalpies of formation (ΔH°_f) in the liquid state are equal to −697.2 and −749.9 kJ mol^{-1}, respectively, which differ from the values presented in the monograph[5] by 9.5 and 35.4 kJ mol^{-1}; the latter are in comparable accuracy with experimentally found values (reaction calorimetry) and our calculated values (see Table 1). This allows one to estimate the enthalpies of combustion and formation of biochemically important 2-methoxy-1,3,2-dioxaarsolane (**8**) and arsinated glycine, *viz.*, 2-methoxy-5-oxo-1,3,2-oxaazaarsolane (**9**), without direct calorimetric measurements.

The following can be concluded from the results presented in the work: if the direct determination of the enthalpies of combustion is impossible or substantially difficult, then the simple calculation of the ΔH_{comb} values of organoarsenic compounds within the 3—5% error can be carried out by correlation (3), which takes into account only the number of bond-forming electrons.

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