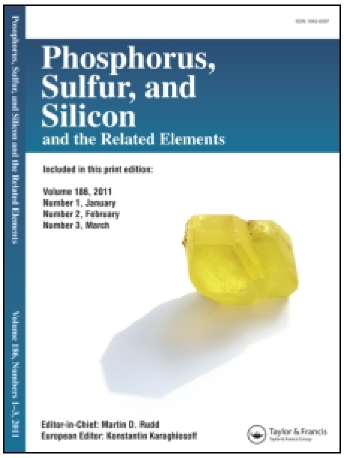

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THERMOCHEMISTRY OF HETEROATOMIC COMPOUNDS, XX. THEORETICAL CALCULATIONS OF THE VAPORIZATION ENTHALPIES OF ALKYLARSINES, STIBINES, AND BISMUTHINES

V. V. Ovchinnikov[a]; L. I. Lapteva[a]; M. G. Kireev[a]
[a] Kazan State Academy of Construction and Architecture, Kazan, Russia

To cite this Article Ovchinnikov, V. V. , Lapteva, L. I. and Kireev, M. G.(2004) 'THERMOCHEMISTRY OF HETEROATOMIC COMPOUNDS, XX. THEORETICAL CALCULATIONS OF THE VAPORIZATION ENTHALPIES OF ALKYLARSINES, STIBINES, AND BISMUTHINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 11, 2323 — 2328

To link to this Article: DOI: 10.1080/10426500490485039

URL: http://dx.doi.org/10.1080/10426500490485039

Phosphorus, Sulfur, and Silicon, 179:2323–2328, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490485039

THERMOCHEMISTRY OF HETEROATOMIC COMPOUNDS, XX. THEORETICAL CALCULATIONS OF THE VAPORIZATION ENTHALPIES OF ALKYLARSINES, STIBINES, AND BISMUTHINES

V. V. Ovchinnikov, L. I. Lapteva, and M. G. Kireev
Kazan State Academy of Construction and Architecture, Kazan, Russia

(Received May 12, 2003; accepted July 5, 2004)

The vaporization enthalpies (ΔH_{vap}) of 26 primary, secondary, and tertiary alkylarsines, stibines, and bismuthines were calculated using the Trouton and Wadso equations and the first-order topological solvation index, ${}^1\chi^S$. The contributions to vaporization enthalpy for $-AsH_2$ *(16.6 ± 0.2),* $>AsH$ *(16.7 ± 0.1) groups and As(III)-atom in* R_3As *(13.7 ± 1.0),* $-SbH_2$ *(22.0 ± [2.0]),* $>SbH$ *(19.0 ± [2.0]) groups and Sb(III)-atom in* R_3Sb *(12.7 ± 3.5),* $-BiH_2$ *(26.3 ± [2.2]),* $>BiH$ *(24.3 ± [2.2]) groups and Bi(III)-atom in* R_3Bi *(16.2 ± 3.1 kJ mol^{-1}) were calculated.*

Keywords: Arsines; bismuthines; molar refraction; stibines; topological solvation index; vaporization enthalpy

INTRODUCTION

The biological activity of arsines has been known for a long time. The tertiary arsines of general formula $RAs(C_nH_{n-1})_2$ (where R=H, Alk, Ar; $n = 5 \div 10$) show fungicide properties; the chemotherapy activity of some of them depends on the length of the carbon radicals at the arsenic atom.[2,3] It is necessary to note that the tertiary stibines and bismuthines of the above-mentioned formula also often reveal antibacterial properties.[3]

The experimental thermochemistry of organic arsines, stibines, and bismuthines has technical difficulties, mainly because of their

Address correspondence to V. V. Ovchinnikov, Kazan State Academy of Construction and Architecture, 420043 Kazan, Zelionaya Str. 1, Kazan, Russia. E-mail: ovchinnikov@ksaba.ru

nonstability and association on the air.[3] For this reason, at the present moment important thermochemical data such as the vaporization, formation, and solvation enthalpies are known in the literature no more than for 25 organic arsenic, stibium, and bismuth compounds. The last circumstances stimulated us to under research on the first above-mentioned energetic term (ΔH_{vap}) of organic arsine $RAsH_2$, R_2AsH, R_3As, and their Sb and Bi analogues of the akin structure.

RESULTS AND DISCUSSION

Usually the method of calculation of the ΔH_{vap} (in kJ mol^{-1}) of such compounds is founded on the use of the well-known Trouton and Wadso approaches (Equations (1) and (2)):[4–6]

$$\Delta H_{\text{vap}} = [0.00736\,T_b + 1.056] * 22 \tag{1}$$

where T_b is the boiling temperature and 22 is the Trouton constant,

$$\Delta H_{\text{vap}} = 0.172\,T_b + 20.9 \tag{2}$$

However, recently a new method of the ΔH_{vap} calculation has been suggested, which is based on the application of topological solvation index of the first order (${}^1\chi^{\text{S}}$) and the knowledge of the dipole moment (μ) of the evaporated compounds:[7,8]

$$\Delta H_{\text{vap}} = 4.26 + 9.37\,{}^1\chi^{\text{S}} + 0.87\mu^2 \tag{3}$$

Calculation Procedure of ΔH_{vap} Values of Arsines

We calculated the values of vaporization enthalpies using Equations (1)–(3) for some alkylarsines (Table I, compounds **1–18**) and compared some of them with the literature data. It is necessary to note that the experimental and calculated through the above-mentioned methods ΔH_{vap} values for compounds (**1**, **6**, **15** and **16**) correspond well with each other. Nevertheless, we must also mention the detectable difference in the same ΔH_{vap} magnitudes for arsines (**11** and **18**), especially when we applied the theoretic (Equation (3) and empirical approaches.

The experimental values of the dipole moments, which we used in Equation (3) for some arsines, were taken from Johnson and Pechukas[9] and Rosenbaum and Sandberg.[10] The magnitudes of the μ for the non-symmetric arsines (**12–15** and **17**) are not experimentally known and were calculated via the half-empirical PM3-quantum mechanic method. Accordingly, to the opinion of Antipin and Konovalov,[8] the assumption of the μ-value in the range 1.0–2.0 D is not connected with the large

TABLE I Thermochemical Characteristics of Arsines, Stibines, and Bismuthines in kJ mol^{-1}

						ΔH_{vap}				
No 1	Compound 2	$T_{b,}^{0,a}$ 3	MR$_{D,}^{b}$ cm^3 mol^{-1} 4	μ,D 5	$^1\chi^S$ 6	Exp. 7	Eq. 1 8	Eq. 2 9	Eq. 3 10	Average 11
Primary arsines										
(1)	$MeAsH_2$	2.3	19.5	1.10	2.000	22.6^c	23.6	23.1	24.1	23.4 ± 1.8
(2)	$EtAsH_2$	38.1	24.1	1.22	2.121		29.4	27.5	25.4	27.4 ± 2.0
(3)	Bu AsH_2	101	33.4	1.36	3.121		39.6	38.3	35.1	37.7 ± 2.3
(4)	TBu AsH_2	65–67	28.6	0.96	2.977		33.9	32.3	33.0	33.1 ± 0.8
(5)	$AmAsH_2$	125.4	38.0	0.99	3.621		43.5	42.5	39.0	41.7 ± 2.4
Secondary arsines										
(6)	Me_2AsH	36–37	24.4	1.23	2.828	27.6^c	29.8	27.8	32.1	29.3 ± 2.1
(7)	Me(Et)AsH	72.1	28.8	1.28	3.121		34.9	33.3	34.7	34.3 ± 0.9
(8)	Me(Pr)AsH	100.8	33.4	1.12	3.621		39.6	38.2	39.3	39.0 ± 0.7
(9)	Et_2AsH	100.8	33.4	1.40	3.414		39.6	38.2	38.0	38.6 ± 0.9
(10)	Pr_2AsH	157–159	42.6	1.19	4.414		48.8	48.1	46.9	47.9 ± 1.0
Tertiary arsines										
(11)	Me_3As	50.4	28.7	0.86	3.464	28.9^d 27.9^d 29.3^e	31.4	29.6	32.0	29.4 ± 1.9
(12)	$Me_2(Et)As$	85.6	33.4	0.74	3.833		37.1	36.6	41.0	38.2 ± 2.3
(13)	$Et_2(Me)As$	113.2	38.0	0.70	4.202		41.6	40.4	44.5	42.2 ± 2.1
(14)	Me(Et)(Pr)As	129	42.6	0.70	4.702		44.1	43.1	49.2	45.5 ± 2.3
(15)	$IBu_2(Et)As$	High boiling point	57.9	1.00	6.282	66.5^f			64.0	65.3 ± 1.8
(16)	iAm_3As		79.6	0.99	8.752	90.6^f			87.2	88.9 ± 2.4
(17)	$Me_2(i\text{Bu})As$	122–124	41.0	1.00	4.689		43.2	42.1	49.1	44.8 ± 3.7
(18)	Et_3As	146–148	42.5	1.10	4.571	43.1^g 38.1^i 41.8^j	46.9	46.2	48.0	44.0 ± 4.0
Stibines										
(19)	$MeSbH_2$	41				27.4^d	29.9	28.0		28.3 ± 0.9
(20)	Me_2SbH	60.7				30.8^d	33.1	31.3		31.7 ± 1.5
(21)	Me_3Sb	80.6				33.5^j 31.4^k	36.1	33.5		33.6 ± 2.2
(22)	Et_3Sb	149.9				38.5^j	47.5	46.7		44.2 ± 3.2
Bismuthines										
(23)	$MeBiH_2$	72				29.9^i	34.9	33.3		32.7 ± 2.2
(24)	Me_2BiH	103				32.7^i	38.6	39.9		37.0 ± 2.2
(25)	Me_3Bi	107.1				37.7^i 36.0^j	40.6	39.3		38.4 ± 2.4
(26)	Et_3Bi	150				46.0^j	47.5	46.7		46.7 ± 0.7

[a] Data of Dub.[3]

[b] The MR_D values were calculated on the additive scheme Equation (4).

[c] Data of Johnson and Pechukas.[9]

[d] Data of Rosenbaum and Sandberg[10] and Long and Sackman.[15]

[e] Data of Long and Sackman.[15]

[f] Data of Ovchinnikov et al.[14]

[g] Data of Lantsch et al.[16]

[i] Data of Lantsch et al.[17]

[j] Data of Cox and Pilcher.[6]

[k] Data of Baev et al.[18]

errors in the magnitudes of the vaporization enthalpy (no more than ± 2–4 kJ mol^{-1}).

In the column 11 of Table I are listed the average ΔH_{vap} values for all investigated As compounds, which have been calculated as middle values between the experimental and those received through Equations (1)–(3) with the standard deviations (0.5–3.2 kJ mol^{-1} with the t test distribution about 95% of the probability).[11]

The contribution of $-AsH_2$, $>AsH$ groups, and ≡As-atom into vaporization enthalpy of the similar-type compounds has been appreciated from the calculated values of ΔH_{vap} (Table I, column 11) according to the additive scheme.

$$\Delta H_{vap} = \sum n_i X_i \tag{4}$$

where n is the number of different groups in molecule, n_i is the number of the fragments of i-type in molecule, and X_i is a contribution of the i fragment. The corresponding symbols and magnitudes of the group contributions for alkyl substituents at the arsenic atom were taken from the literature[12] (6.36 ± 0.05, 4.77 ± 0.01, and −2.34 ± 0.19 kJ mol^{-1} for $C-(C)(H)_3$, $C-(C)_2(H)_2$, and $C-(C)_4$, respectively).

Statistical processing of the results obtained showed that the contribution of the $-AsH_2$ group is 16.6 ± 0.2 kJ mol^{-1} with a probability of no less than 95% (compounds **1–5** were taken for calculations). The contribution of the $>AsH$ group and arsenic atom (As) in R_3As into the vaporization enthalpies of secondary and tertiary alkylarsines were calculated analogously and proved to be 16.7 ± 0.1 kJ mol^{-1} (compounds **6–10** were taken for calculations) and 13.7 ± 1.0 kJ mol^{-1} (compounds **11–18** were taken from Table I).

It is necessary to note an important fact, that the ΔH_{vap} calculated values for alkylarsines (**1–18**) correlate with their molar refraction (MR_D, Equation (5) and Table I). Previously, a similar dependence was observed for the simple alkanes:[13]

$$\begin{aligned} \Delta H_{vap}\,(\text{arsine}) &= a + b\, MR_D\,(\text{arsine}) \\ r = 0.986, \quad S_o &= 2.62, \quad n = 18\,(\text{points}) \end{aligned} \tag{5}$$

Calculation Procedure of ΔH_{vap} Values of Stibines and Bismuthines

The methods of the calculation of the ΔH_{vap} for the previous, secondary, and tertiary alkylstibines and bismuthines (Table I, compounds **19–26**) cannot be realized by us in the same volume as for the arsines. It is connected with the extremely small data for the experimental values.[3,6,14]

The average ΔH_{vap} values (column 11 in Table I) of the alkyl-Sb- and -Bi-derivatives represent the average between the experimental magnitudes and calculated values via the Trouton and Wadso Equations (1) and (2) only. The topological solvation index ($^1\chi^S$) and μ in Equation (3) is not useful for the appreciation of the same energetic term because the element-alkyl bonds of the mentioned compounds have more metallic character in the fifth group of the Periodic Table. It leads to the substantial differences between the experimental and calculated ΔH_{vap} values, from our point of view.

Nevertheless, taking into account all circumstances, we believe that it would be useful to consider of the $-SbH_2$, $>SbH$, $-BiH_2$, and $>BiH$ groups and three-coordinated atoms $\equiv Sb$ and $\equiv Bi$ contributions into ΔH_{vap} values with the similar contributions in the different degree alkylated of N, P, As atoms (all contributions were calculated on the additive scheme, Equation (4)). Taking into account the results represented in Table II, it can to note the next.

First, there is a general tendency of increasing of the contribution values into vaporization enthalpy at the transform from the top to the bottom of the groups. However, the contribution of RNH_2-fragment[12] presented itself as the sensitive exclusion from this range, probably due to several low atomic radiis or the high electronegativity (EN) of nitrogen atom, which leads to the increasing of the hydrogen bonds in such liquids (Table II).

Second, there is also little difference (in the range of the errors) between the ΔH_{vap} contributions for the previous, secondary, and tertiary amines, phosphines, arsines, stibines, and bithmutines.

TABLE II The Values of the Group Contributions (in kJ mol^{-1}) into Vaporization Enthalpy of Compounds of General Formula R_nE_{3-n} (1 ÷ 3)

E	Atomic radius, r(Å)[a]	EN[a]	The group contributions in ΔH_{vap}		
			$-EH_2$	$>EH$	$E(R)_3$
N	0.92	3.07	17.0 ± 0.5^b	11.3 ± 1.0^b	4.2 ± 1.1^b
P	1.20	2.06	13.7 ± 1.4^c	12.8 ± 0.4^c	8.8 ± 0.7^c
As	1.31	2.00	16.6 ± 0.2	16.7 ± 0.1	13.7 ± 1.0
Sb	1.50	1.82	$22.0 \pm [2.0]^d$	$19.0 \pm [2.0]^d$	12.7 ± 3.5^e
Bi	1.70	1.67	$26.3 \pm [2.2]^d$	$24.3 \pm [2.2]^d$	16.2 ± 3.1^e

[a] Data of Cox and Pilcher.[6]

[b] Data of Lebedev and Mirosshnichenko.[12]

[c] Data of Ovchinnikov et al.[4]

[d] Calculated using only one value.

[e] Calculated using two values.

At last, the above-mentioned contributions into vaporization enthalpy of the tertiary heteroatomic alkylated derivatives are lower and more differentiated than for their hydrides. Probably it can be connected with the "steric repulsion" of the alkylic groups at heteroatoms.

CONCLUSIONS

The ΔH_{vap} values have been for the first time determined for the previous, second, and tertiary alkylarsines, -stibines and -bismuthines, through the application of Trouton and Wadso equations and the first-order topological solvation index. The correlation of the ΔH_{vap} of alkylated arsines between the values of their $\mathrm{MR_D}$ was also established.

REFERENCES

[1] V. V. Ovchinnikov, L. I. Lapteva, and M. G. Kireev, *Russian Chem. Bull.*, in press (2003).

[2] V. S. Gamayurova, *The Arsenic in Ecology and Biology* (Nauka, Moskow, 1993), pp. 208 (in Russian).

[3] M. Dub, Ed., *Organometallic Compounds. Methods of Synthesis, Physical Constants and Chemical Reactions, Vol. III. Compounds of Arsenic, Antimony, and Bismuth* (Spinger-Verlag, Berlin, 1972).

[4] V. V. Ovchinnikov, L. R. Khazieva, L. I. Lapteva, and A. I. Konovalov, *Russian Chem. Bull.*, **9,** 33 (2000).

[5] S. W. Benson, F. R. Cruikshank, D. M. Golden, G. R. Haugen, H. E. O.'Neal, A. S. Rodgers, R. Show, and R. Walsh, *Chem. Rev.*, **69,** 279 (1969).

[6] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic Press, London).

[7] I. S. Antipin, N. A. Arslanov, V. A. Palyutin, A. I. Konovalov, and N. S. Zefirov, *Dokladi Akad. Nayk SSSR*, **316,** 925 (1991). (*Engl. Trans. Dokl. Chem.*, 1991).

[8] I. S. Antipin, N. A., and I. Konovalov, *Zh. Obsch. Khim.*, **66,** 389 (1996). (*Engl. Trans. Russ. J. Gen. Chem.*, 66 (1996).

[9] W. C. Johnson and A. Pechukas, *J. Am. Chem. Soc.*, **59,** 2068 (1937).

[10] E. J. Rosenbaum and C. R. Sandberg, *J. Am. Chem. Soc.*, **62,** 1622 (1940).

[11] A. Gordon and R. Ford, *The Chemist's Companion* (New York, 1972).

[12] Yu. A. Lebedev and E. A. Mirosshnichenko, *Thermokhimiya Paroobrazovaniya Organicheskikh Veshchestv (Vaporization Thermochemistry of Organic Substances)* (Nauka, Moskow, 1981) (in Russian).

[13] B. N. Solomonov and A. I. Konovalov, *Uspechi of Chem.*, **60,** 45 (1991).

[14] V. V. Ovchinnikov, T. B. Makeeva, L. I. Lapteva, V. A. Valiullina, L. M. Pilishkina, and A. I. Konovalov, *J. Thermal Analysis*, **45,** 735 (1995).

[15] L. H. Long and J. F. Sackman, *Trans. Faraday Soc.*, **52,** 1201 (1956).

[16] W. Lantsch, F. Trober, and W. Zimmer, *Z. Chem.*, **3,** 415 (1963).

[17] W. Lantsch, A. Tröber, H. Korner, K. Wagner, R. Kaden, and S. Blase, *Z. Chem.*, **4,** 441 (1964).

[18] A. K. Baev, B. I. Silvanchik, and B. I. Kozirnin, *Zh. Obshch. Khim.*, **66,** 389 (1996). (*Engl. Trans. Russ. J. Gen. Chem.*, 50, 1980).