Thermochemistry of heteroatomic compounds
17.* Theoretical calculations of vaporization enthalpies for alkylphosphines and alkyl(aryl)phosphines

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The vaporization enthalpies (ΔH_{vap}) of 97 primary, secondary, and tertiary alkylphosphines and alkyl(aryl)phosphines with different spatial structures were calculated using the Trouton and Wadso equations and the first-order topological solvation index $^1\chi^s$. The contributions of the H_2P and HP groups and the phosphorus atom to the vaporization enthalpies of primary, secondary, and tertiary phosphines, respectively, were calculated. The results obtained can be used in calculations of ΔH_{vap} for related phosphorus compounds.

Key words: phosphines, vaporization enthalpy, molar refraction, topological solvation index.

The capability of three-coordinated phosphorus compounds, especially tertiary phosphines, of forming complexes with transition metals of different valence has been studied theoretically in detail and is widely used in synthetic practice.[2,3]

Particular interest has been given to compounds of the $P(C_6H_4SO_3Na)_3$ type, possessing some properties analogous to those of ion-exchange resins and synthetic surfactants, which makes it possible to use them for the synthesis of organic compounds in two-phase aqueous-organic media.[4]

Recently, it has been reported that heavy-metal (*e.g.*, ^{99}Tc) complexes with phosphines can be effectively used as transportation media in living organisms[5,6] and in chemotherapy of certain forms of cancer (Au and Pt complexes).[7,8] It is believed[9] that phosphine-containing peptides can be useful in studies of the secondary structure of proteins, for diagnostics of diseases of internal organs, and in medical studies by instrumental methods.

Despite considerable demands for organic phosphines, almost no reliable data of thermochemical experiments (heats of vaporization, formation, and solvation) are available even for simple representatives of this class of compounds, namely, RPH_2, R_2PH, and R_3P, which is mainly due to their easy oxidizability and inflammability in air under conditions of calorimetric experiments. Therefore the aim of this work was to carry out a detailed study of the thermochemistry of the above-mentioned compounds and first of all to determine their vaporization enthalpies.

Calculation procedure

The vaporization enthalpies (ΔH_{vap}/kJ mol^{-1}) of primary, secondary, and tertiary phosphines were assessed using two independent calculation procedures:

1) by the Trouton (1) and Wadso (2) equations derived for weakly associated and low-boiling liquids[10]:

$$\Delta H_{vap} = (0.00736 T_b + 1.056) \cdot 22, \tag{1}$$

where 22 is the Trouton constant characteristic of many compounds of three-coordinated phosphorus,[11] and

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

2) using the model for description of dispersion interactions suggested previously[12,13] and based on the topological solvation index $^m\chi^s$ (Eq. (3)), which in essence is the Randič connectivity index augmented with the factors dependent on the period number. This makes it possible to take into account not only peculiarities of the molecular structure (different-unit structure, the presence of cycles, *etc.*), but also the size of the atoms constituting the molecule in question:

$$^m\chi^s = (1/2)^{m+1} \sum_1^n Z_i Z_j ... Z_k/(\delta_i \delta_j ... \delta_k)^{1/2}, \tag{3}$$

where m is the order of the index; n is the number of subgraphs of the order m; δ_i, δ_j, ..., δ_k are the connectivities of the vertices of the given subgraph n; Z_i, Z_j, ..., Z_k are coefficients characterizing the size of the atom and numerically equal to the number of the period of the periodic system to which the corresponding element belongs. The first-order topological solvation index $^1\chi^s$ is calculated by Eq. (4)[13]:

$$^1\chi^s = 0.25 \sum_1^n Z_i Z_j/(\delta_i \delta_j)^{1/2}. \tag{4}$$

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* For Part 16, see Ref. 1.

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A correlation (Eq. (5)) for calculating the ΔH_{vap}/kJ mol^{-1} values has been suggested in the framework of this model[13]:

$$\Delta H_{vap} = 4.26 + 9.37\,{}^1\chi^s + 0.87\mu^2, \tag{5}$$
$$n = 527,\ r = 0.990,\ S_0 = 1.9,$$

where μ is the dipole moment of the compound under study. This dependence makes it possible to calculate the vaporization enthalpies of both nonpolar organic substances and those of low polarity (more than 500 compounds), incapable of forming self-associates due to hydrogen bonding or donor-acceptor interactions, using the first-order topological solvation index ${}^1\chi^s$ and the dipole moment with an accuracy of ±2 kJ mol^{-1}.

Results and Discussion

To be certain that these equations can be used for calculating the vaporization enthalpies of three-coordinated phosphorus compounds, we calculated the ΔH_{vap} values for several phosphines (Table 1, compounds **1—3**, **25—27**, **56**, **58**, and **61**) using Eqs. (1), (2), and (5) and found a reasonable agreement between the calculated and experimental data.

Let us illustrate the sequence of the calculation procedure taking calculations of ΔH_{vap} for primary phosphines as an example. First, we calculated the vaporization enthalpies for the first (low-boiling) representatives of the homologous series of this class of compounds (see Table 1, compounds **3—11**) using Eqs. (1) and (2). Then, the first-order topological solvation indices ${}^1\chi^s$ and ΔH_{vap} values were calculated for the same compounds using Eq. (3) and Eq. (5), respectively. For several compounds, the experimental values of the dipole moments (μ_{exp}) measured in inert solvents (hexane, CCl_4, benzene) were taken from the literature[18]; otherwise they were obtained from gas-phase calculations by the molecular mechanics (MMX2) method (see note "*c*" to Table 1). In some instances, the experimental (μ_{exp}) and calculated (μ_{calc}) values are somewhat different, *e.g.*, 1.28 and 1.12 D for Me(Et)PH, 1.19 and 1.22 D for Me_3P, and 1.84 and 1.15 D for Et_3P, respectively. According to calculations,[12] the ΔH_{vap} values for the compounds with $\mu < 1$ D can be estimated neglecting the effect of the dipole moment. Moreover, an error of ±0.2 D obtained when assessing the μ values for substances of high polarity ($\mu > 4$ D) results in a ΔH_{vap} calculation error of no greater than ±1.0 kJ mol^{-1}. Therefore, small differences between the experimental and calculated dipole moments lead to small errors that were neglected in our calculations.

The ΔH_{vap} values for the RPH_2 compounds **3—11** calculated using Eqs. (1), (2), and (5), the average ΔH_{vap} values, and their standard deviations are listed in Table 1.

Then, we calculated the contributions of the PH_2 group to the vaporization enthalpies of primary alkylphosphines using the ΔH_{vap} values obtained and the group additivity scheme (Eq. (6)):

$$\Delta H_{vap} = \sum_{i=1}^{\nu} N_i X_i\,, \tag{6}$$

where ν is the number of different groups (fragments) in the molecule, N_i is the number of fragments of the *i*th type in the molecule, and X_i is the contribution (increment) of the *i*th fragment.

The corresponding group contributions of the alkyl substituents at the phosphorus atom were taken from the literature[24] (6.4±0.2, 4.77±0.04, 1.2±0.4, 5.3±0.1, and 4.3±0.4 kJ mol^{-1} for $C-(C)(H)_3$, $C-(C)_2(H)_2$, $C-(C)_3(H)$, $C_\beta-(C_\beta)_2(H)$, and $C_\beta-(C_\beta)_2(H)$, respectively; for notations of the C_β aromatic groups at the phosphorus and carbon atoms, see Refs. 10 and 24). Statistical processing of the results obtained showed that the contribution of the PH_2 group is 13.6±1.2 kJ mol^{-1} with probability (reliability) $\alpha = 0.999$. This value was used in the ΔH_{vap} calculations for compounds **12—24** using Eq. (6). For these compounds the ΔH_{vap} values were also calculated using the topological solvation index ${}^1\chi^s$ (see Table 1).

The contributions of the PH group and phosphorus atom at R_3P to the vaporization enthalpies of secondary and tertiary alkylphosphines were calculated analogously and proved to be 12.8±0.4 kJ mol^{-1} for R_2PH (compounds **25—34** and **48—52**, at $\alpha = 0.999$) and 8.8±0.7 kJ mol^{-1} for R_3P (compounds **56**, **58**, **59**, **61—63**, and **80—84**, at $\alpha = 0.95$). These values were used in calculations of ΔH_{vap} for compounds **35—47**, **53—55**, **64—79**, and **85—90** (see Table 1).

From the data presented it can be seen that the ΔH_{vap} values calculated using the two above-mentioned procedures are in good agreement, thus indicating a reliability of both the ΔH_{vap} values obtained and the contributions of the PH_2 and PH groups and the P atom with respect to substituted phosphines.

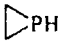
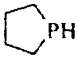
To assess the ΔH_{vap} values of mixed alkyl(aryl)phosphines from the experimental ΔH_{vap} values of triphenylphosphine (118.3 [25] and 113.2 [26] kJ mol^{-1}), we calculated the contribution of the $(C_\beta)_3-P$ group, which proved to be 23.2 kJ mol^{-1}. Then, the ΔH_{vap} values for alkyl(aryl)phosphines **91—97** were calculated using Eq. (6) and the contribution of the phosphorus atom in R_3P (8.8 kJ mol^{-1}) and the found contribution of the $(C_\beta)_3-P$ group. For instance, for Me_2PhP we obtained $\Delta H_{vap} = 2\ C(C)(H)_3 + 5\ C_\beta(C_\beta)_2(H) + C_\beta(C_\beta)_2(C) + 2/3\ P(R)_3 + 1/3\ P(C_\beta)_3 = 57.2$ kJ mol^{-1}.

An important fact is that the ΔH_{vap} values calculated for alkylphosphines (86 points, compounds **3—56**, **58**, **59**, and **61—90**) and alkyl(aryl)phosphines (7 points, compounds **91—97**) correlate well with their molar refractions (MR_D) (Table 2 and Eqs. (7a) and (7b), respectively). Previously,[17] a similar dependence was observed for simple alkanes. The general correlation equation has the form

$$\Delta H_{vap}(\text{phosphines}) = a + bMR_D(\text{phosphines}). \tag{7}$$

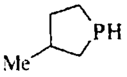
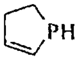
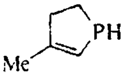
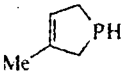
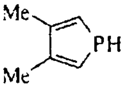
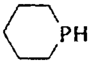
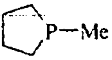
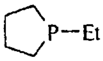
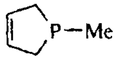
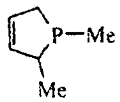
The average ΔH_{vap} values for phosphines also correlate with the experimental vaporization and sublimation enthalpies of isostructural compounds, *i.e.*, primary

Table 1. Thermochemical characteristics of alkyl- and alkyl(aryl) phosphines

Compound	T_{melt} ^{a} /°C	MR_D ^{b} /cm^3 mol^{-1}	μ ^{c} /D	$^1\chi^s$	ΔH_{vap}/kJ mol^{-1} experiment	calculations using equation (1)	(2)	(5)	(6)	average
Primary phosphines										
$CHF_2CF_2PH_2$ (**1**)	20—22		1.61	1.768	26.7^d	26.9	24.7	23.1		
$Me_2CF_3PH_2$ (**2**)	46.8		1.74	2.598	29.1^d	30.9	28.9	31.2		
$MePH_2$ (**3**)	−17.1	17.7	1.10	1.500	22.2^e	20.5	18.0	19.4		20.0±1.8
$EtPH_2$ (**4**)	25.0	22.3	1.22	1.768		27.3	25.2	22.1		24.9±2.6
Pr^nPH_2 (**5**)	53.5	27.0	1.17	2.268		31.9	30.1	26.7		29.6±2.6
Pr^iPH_2 (**6**)	41.0	25.4	1.23	2.021		29.9	28.0	24.5		27.4±2.7
Bu^nPH_2 (**7**)	87.8	31.3	1.36	2.768		37.5	36.0	31.8		35.0±2.9
Bu^iPH_2 (**8**)	79.6	28.7	0.98	2.624		36.2	34.6	29.7		33.5±3.3
Bu^sPH_2 (**9**)	67	28.7	0.98	2.559		34.1	32.4	29.1		31.9±2.5
Bu^tPH_2 (**10**)	54	25.5	0.96	2.250		32.0	30.2	26.2		29.5±3.0
$C_5H_{11}PH_2$ (**11**)	104	35.4	0.99	3.268		40.1	38.8	35.8		38.2±2.2
i-$C_5H_{11}PH_2$ (**12**)	106—107	34.6	0.98	3.124				34.4	37.0	35.7±1.8
$HexPH_2$ (**13**)	128	40.3	1.34	3.768				41.1	43.8	42.5±1.9
$C_7H_{15}PH_2$ (**14**)	149.5	44.5	0.99	4.268				45.1	48.6	46.9±2.5
$C_8H_{17}PH_2$ (**15**)	169.0	49.0	0.99	4.768				49.8	53.3	51.6±2.5
$C_9H_{19}PH_2$ (**16**)	187	53.7	0.99	5.268				54.5	58.1	56.3±2.5
$C_{10}H_{21}PH_2$ (**17**)	203	58.3	0.99	5.768				59.2	62.9	61.1±2.6
cyclo-$C_5H_9PH_2$ (**18**)	121	33.4	0.98	3.183				34.9	40.3	37.6±3.8
cyclo-$HexPH_2$ (**19**)	146	38.1	0.98	3.683				39.6	44.9	42.3±3.7
H_2PPH_2 (**20**)	56	24.0	—	2.250				25.6	27.2	26.4±1.1
$H_2PCH_2PH_2$ (**21**)	83.4	28.6	1.83	2.121				32.2	32.0	32.1±0.1
$H_2P(CH_2)_2PH_2$ (**22**)	113	33.2	1.96	2.621	38.1^d			32.2	36.7	35.7±3.1
$H_2P(CH_2)_3PH_2$ (**23**)	143	37.8	1.36	3.121	40.3^d			35.1	41.5	39.0±3.4
$H_2P(CH_2)_4PH_2$ (**24**)	172.3	42.5	1.96	3.621	36.1^d			46.4	41.3	43.9±3.6
Secondary phosphines										
Me_2PH (**25**)	21.1	21.5	1.23	2.121	26.2^f	26.7	24.5	25.5		25.7±0.9
$Me(Et)PH$ (**26**)	54.5	26.2	1.28	2.518	31.0^d	32.1	30.3	29.3		30.7±1.2
$Me(Pr^n)PH$ (**27**)	78.2	30.8	1.12	3.018	35.2^d	36.0	34.3	33.6		34.8±1.0
$Me(CH_2{=}CHCH_2)PH$ (**28**)	81	28.6	1.16	3.018	34.2^d	36.4	34.8	33.7		34.8±1.0
$Me(Bu^n)PH$ (**29**)	112.7	35.4	1.12	3.518	34.3^d	41.5	40.3	38.3		40.0±1.6
$Me(Pr^i)PH$ (**30**)	78—80	29.2	1.08	2.828		36.2	34.6	31.8		34.2±2.2
Et_2PH (**31**)	85	30.6	1.40	2.914		37.1	35.5	33.3		35.3±1.9
$Pr^n{}_2PH$ (**32**)	136	40.0	1.19	3.914		45.3	44.2	42.2		43.6±1.3
$Pr^i{}_2PH$ (**33**)	118	36.8	1.30	3.534		42.4	41.2	38.8		40.8±1.8
$Pr^i(Bu^i)PH$ (**34**)	139	41.4	1.08	4.080		45.8	44.8	43.5		44.7±1.2
$Bu^n{}_2PH$ (**35**)	178	49.1	1.37	4.914				51.9	54.1	53.0±1.6
$Bu^i{}_2PH$ (**36**)	169.0—171.8	45.9	1.11	4.626				51.4	50.1	50.8±0.9
$Bu^s{}_2PH$ (**37**)		45.9	1.11	4.610				48.5	50.1	49.3±1.1
$Bu^t{}_2PH$ (**38**)		39.5	1.06	4.061				46.3	43.3	44.8±2.1
$(C_5H_{11})_2PH$ (**39**)		58.5	1.08	5.914				60.7	63.7	62.2±2.1
(*i*-$C_5H_{11})_2PH$ (**40**)	210—215	56.9	1.12	5.626				58.1	59.7	58.9±1.1
$Pr^n(Hex)PH$ (**41**)	194	53.9	1.12	5.414				56.1	58.9	57.5±2.0
Hex_2PH (**42**)		67.7	1.09	6.914				71.2	73.2	72.2±1.4
$(C_7H_{15})_2PH$ (**43**)		77.0	1.09	7.914				79.4	82.8	81.1±2.4
$(C_8H_{17})_2PH$ (**44**)		85.9	1.11	8.014				89.0	92.3	90.1±2.3
$(C_9H_{19})_2PH$ (**45**)		95.4	1.09	9.914				98.2	101.8	100.0±2.5
$(C_{10}H_{21})_2PH$ (**46**)		104.7	1.09	10.914				107.6	111.4	109.5±2.7
(*cyclo*-$Hex)_2PH$ (**47**)	281—282	60.1	1.10	6.858				69.6	69.3	69.5±0.2
 (**48**)	36.5	19.3	1.12	2.000	28.9^d 29.2^g	29.2	27.2	24.1		27.7±2.2
 (**49**)	105.4	28.6	1.22	3.000	37.8^d	40.4	39.0	33.7		37.7±2.8

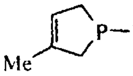
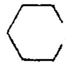
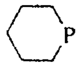
(*to be continued*)

Table 1 (*continued*)

Compound	T_{melt} [a] /°C	MR_D [b] /cm^3 mol^{-1}	μ [c] /D	$^1\chi^s$	ΔH_{vap}/kJ mol^{-1}					
					experiment	calculations using equation				average
						(1)	(2)	(5)	(6)	
 (**50**)	119	33.1	1.20	3.394		42.6	41.3	37.3		40.4±2.8
 (**51**)	75	26.4	1.54	3.000		35.4	33.8	34.4		34.5±0.8
 (**52**)	80	31.3	1.63	3.394		36.2	34.6	38.4		36.4±1.9
 (**53**)		32.1	1.07	3.394			37.1	42.7		39.9±4.0
 (**54**)	146—148	33.4	2.00	3.805			42.4	47.1		45.3±2.6
 (**55**)	110	33.2	1.12	3.500				38.1	43.1	40.6±3.5
			Tertiary phosphines							
Me_3P (**56**)	38.4	26.3	1.19	2.598	29.0^f 27.6±2.1^h 29.1^d	29.5	27.5	28.0		28.5±0.9
$Me_2(CH_2{=}CH)P$ (**57**)	67.9		1.52	3.052	32.4^d	34.3	32.6	34.9		33.6±1.2
Me_2EtP (**58**)	71.2	28.7	1.31	3.052	32.8^d	34.8	33.1	34.4		33.8±1.0
Et_2MeP (**59**)	110—112	35.5	1.58	3.505		41.3	40.0	39.6		40.3±0.9
$(CH_2{=}CH)_3P$ (**60**)	116.6		1.87	3.958	37.2^d	42.2	40.9	44.4		41.2±3.0
Et_3P (**61**)	127.5	40.1	1.84	3.958	39.7±2.1^i 39.5^d	43.9	42.8	39.8		41.1±2.1
Et_2Pr^nP (**62**)	146—149	44.8	1.14	4.458		47.1	46.1	47.2		46.8±0.6
Pr^n_3P (**63**)	187.5	54.1	1.14	5.458	46.7^j	53.7	53.1	55.8		54.2±1.4
Pr^i_3P (**64**)		49.2	1.32	4.954				52.3	50.5	51.4±1.3
cyclo-Pr_3P (**65**)		47.4	—	5.449				55.7	61.4	58.6±4.0
Bu^n_3P (**66**)	240—242	68.2	1.49	6.958	53.6^k			71.4	69.8	70.6±1.1
Bu^i_3P (**67**)	215	63.1	1.10	6.526	49.5^d			66.5	64.8	65.7±1.2
Bu^s_3P (**68**)		63.1	1.05	6.578				66.8	64.8	65.8±1.4
Bu^t_3P (**69**)		53.5	0.86	5.799				59.2	59.0	59.1±0.1
$Et_2(CH_2{=}CHCH_2CH_2)P$ (**70**)	170—172	47.2	1.12	4.958				51.8	50.9	51.3±0.6
$Et_2(i\text{-}C_5H_{11})P$ (**71**)	185—187	52.4	1.14	5.314				55.2	54.5	54.9±0.5
$Et_2(PhCH_2)P$ (**72**)	250—255	59.6	—	6.476				65.4	66.7	66.1±1.0
Bu^t_2MeP (**73**)	170—172	44.4	1.11	4.732				49.7	48.6	49.1±0.8
$(C_5H_{11})_3P$ (**74**)		80.9	1.48	8.458				85.4	85.1	85.3±0.2
Hex_3P (**75**)		95.6	1.48	9.958				99.5	99.4	99.5±0.1
$(C_7H_{15})_3P$ (**76**)		109.4	1.14	11.458				112.8	113.7	113.3±0.6
$(C_8H_{17})_3P$ (**77**)		123.3	1.15	12.958				126.8	128.0	127.4±0.8
$(C_9H_{19})_3P$ (**78**)		137.1	1.14	14.458				140.9	142.4	141.7±1.1
$(C_{10}H_{21})_3P$ (**79**)		151.0	1.15	15.958				154.9	156.7	155.8±1.3
 (**80**)	123	33.3	0.00	3.591		43.2	42.0	41.3		42.2±1.0
 (**81**)	145—147	37.9	0.00	4.044		46.9	46.0	42.2		45.0±2.5
 (**82**)	114—115	31.1	0.23	3.591		41.9	40.6	38.0		40.2±2.0
 (**83**)	135—136	35.9	0.23	3.964		45.2	44.1	41.4		43.6±2.0

(*to be continued*)

Table 1 (*continued*)

Compound	T_{melt} [a] /°C	MR_D [b] /cm^3 mol^{-1}	μ [c] /D	$^1\chi$ [s]	ΔH_{vap}/kJ mol^{-1}					
					experiment	calculations using equation (1)	(2)	(5)	(6)	average
 P—Me (**84**)	135—138	35.9	0.16	3.985		45.4	44.3	41.6		43.7±1.9
 P—Me (**85**)		37.9	1.23	4.091				43.9	45.5	44.7±1.1
 P—Et (**86**)	170	42.5	1.22	4.544				48.1	50.2	49.2±1.5
 P—Pr^i (**87**)		45.6	1.14	4.879				51.1	53.0	52.1±1.3
 P—Bu^t (**88**)		47.0	1.14	5.158				53.7	55.8	54.8±1.5
$Me_2P(CH_2)_2PMe_2$ (**89**)	188.1	50.4		5.189				52.9	53.3	53.1±0.3
$Et_2P(CH_2)_2PEt_2$ (**90**)	220—230	68.9		7.003				70.4	72.0	71.2±1.1
			Tertiary alkyl(aryl)phosphines							
Me_2PhP (**91**)	192	45.8	1.31	5.049	43.4[d]			53.1	57.2	55.2±2.9
Et_2PhP (**92**)	221.9	55.0	1.40	5.955	52.1[d]			66.7	61.6	64.2±3.6
$Et_2(4\text{-}ClC_6H_4)P$ (**93**)	255—257	58.8	1.90	6.638	54.9[d]			69.6	75.8[k]	72.7±4.4
$Et_2(4\text{-}BrC_6H_4)P$ (**94**)	265	61.7	1.97	6.927	59.3[d]			72.5	79.3[k]	75.9±4.8
$Et_2(4\text{-}MeC_6H_4)P$ (**95**)	240	58.5		6.349	53.3[d]			64.2	72.0	68.1±5.5
Ph_2MeP (**96**)	284	65.3	1.39	7.499				76.2	86.4	81.3±7.2
Ph_2EtP (**97**)	293	69.9	1.35	7.952				80.4	91.2	85.8±7.6

[a] Data taken from Refs. 14—16.

[b] Experimental MR_D values are listed for compounds **7—9**, **13—19**, **31**, **35—37**, **44**, **50**, **53**, **61**, and **66**; for other compounds the MR_D values were calculated using the group additivity scheme; corrections to the MR_D values were introduced for branched R.[17]

[c] Experimental μ values are listed for compounds **3—7**, **13**, **25—26**, **31—33**, **35**, **48**, **49**, **56**, **58**, **59**, **61**, **63**, **64**, **66**, **74**, **75**, **91—95**, and **97**[16,18]; otherwise the dipole moments were calculated by the molecular mechanics (MMX2) method.

[d] The ΔH_{vap} values for these compounds were calculated from the temperature dependence of vapor pressure.[16]

[e] Data taken from Ref. 19.

[f] Data taken from Ref. 11.

[g] Data taken from Ref. 14.

[h] Data taken from Ref. 20.

[i] Data taken from Ref. 21.

[j] Data taken from Ref. 22.

[k] The contribution of the C_β—Cl group with respect to compound **93** (14.4 kJ mol^{-1}) and that of the C_β—Br group with respect to compound **94** (17.9 kJ mol^{-1}) were calculated from the experimental ΔH_{vap} values for C_6H_5Cl and C_6H_5Br, respectively, taken from Ref. 23.

(RNH_2), secondary (R_2NH), and tertiary (R_3N) amines (see Table 2 and Eqs. (8a), (8b), and (8c), respectively), and the corresponding alkanes RCH_3, R_2CH_2, and R_3CH (see Table 2 and Eqs. (8d), (8e), and (8f), respectively) [23,24,27] The general correlation equation has the form

$$\Delta H_{vap}(\text{phosphines}) = a + \Delta H_{vap}(\text{amines, alkanes}). \quad (8)$$

The high correlation coefficients r and small standard deviations S_0 of the correlations obtained suggest that the calculated vaporization enthalpies of alkyl- and alkyl(aryl)phosphines with different spatial structures are reliable.

Nevertheless, the available experimental data on ΔH_{vap} for a number of high-boiling (and, hence, low-volatility) phosphines are strongly different from the values we calculated (in kJ mol^{-1}):

Table 2. Parameters of correlation equations (7) and (8)

Equation	a	b	S_0	r	Number of points
(7a)	4.9±0.5	0.99±0.01	2.37	0.996	86
(7b)	−7.2±5.9	1.33±0.10	1.89	0.986	7
(8a)	−4.7±1.2	1.11±0.04	0.62	0.996	9
(8b)	3.3±1.8	1.00±0.03	2.66	0.996	13
(8c)	8.3±3.1	0.99±0.03	3.94	0.997	8
(8d)	8.6±1.1	0.93±0.03	1.37	0.991	15
(8e)	8.8±1.0	0.96±0.02	1.98	0.996	19
(8f)	11.4±1.6	0.99±0.05	1.25	0.986	12

Compound	**24**	**29**	**32**	**65**	**67**	**91**	**92**	**93**	**94**	**95**
$\Delta(\Delta H_{vap})$	7.9	5.7	7.5	20.0	16.3	9.5	9.8	15.6	14.4	12.6

Likely, the previously used method of vaporization enthalpy determination from the temperature dependence of the vapor pressure of the substance under study is unsuitable for high-molecular-weight compounds and results in large errors of the ΔH_{vap} values.

Thus, we first determined the ΔH_{vap} values for alkyl- and alkyl(aryl)phosphines of different structure using the Trouton and Wadso equations and the first-order topological solvation index and showed the correspondence between the calculated and experimental ΔH_{vap} values. The PH_2 and PH group contributions (13.6 ± 1.2 kJ mol^{-1} for primary and 12.8 ± 0.4 kJ mol^{-1} for secondary phosphines, respectively) and the contribution of the phosphorus atom in R_3P (8.8 ± 0.7 kJ mol^{-1}) for tertiary phosphines obtained in this work can be used for calculating the ΔH_{vap} values for analogous phosphorus compounds. Additionally, we found that the ΔH_{vap} values of phosphines depend on their molar refractions and change in parallel to the vaporization enthalpies of isosteric amines and alkanes.

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