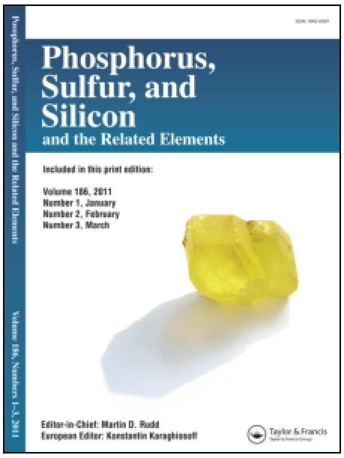

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THE EXPERIMENTAL AND THEORETICAL THERMOCHEMISTRY OF P-H-CONTAINING ORGANOPHOSPHORUS COMPOUNDS

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THE EXPERIMENTAL AND THEORETICAL THERMOCHEMISTRY OF P-H-CONTAINING ORGANOPHOSPHORUS COMPOUNDS

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The thermochemistry of primary, secondary phosphines, RPH_2, R_2PH, and hydrophosphorylic compounds, $(RO)_2P(O)H$, of the different spatial structure is presented in this review. The values of the vaporization, solvation, and formation enthalpies (for nearly 100 compounds) belonging to the above mentioned classes of compounds are determined. For these aims of the Trouton, Wadso equations, and the molar topological solvation index approaches, and half-empirical Solomonov-Konovalov equation ($\Delta H_{vap}/kJ\,mol^{-1} = \Delta H_{soln}(alkane) + 4.39 + 1.05\,MR_D$), have been used. The questions of solvation, tautomeric transformations, complex formation or the hydrogen bonding formation have been used also. The heats of the addition reactions of hydrophosphorylic compounds are presented as well. The group contributions into the vaporization and formation enthalpies for primary and secondary phosphines, [$-PH_2$, $>PH$], are calculated and discussed.

Keywords: Formation enthalpies; heat capacity; heat of reaction; hydrophosphorylic compounds; molar refraction; phosphines; solvation; topological solvation index; vaporization

The reactivity of organic and heteroatomic compounds is connected, as a rule, with the cleavage of the weak bonds and the formation of the new, more stronger, bonds. At the same time, the hydrogen bridges or donor-acceptor complexes, which are often formed during the various chemical or biochemical processes can serve as specific models of the transition states or intermediates.[1–4]

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The interplay between the chemical or biochemical activity of the substances with phosphorus-hydrogen bonds and their thermochemical parameters consists of the one of important problems. Nevertheless, the some groups of mentioned above phosphorus compounds (especially phosphines) have often an explosive and burning on the air properties, which consist the technical difficulties for the determination of their thermochemical values.

The thermochemistry of compounds with phosphorus-hydrogen bonds have a special interest. That's way, we summed up in present review all known data on the thermochemical parameters of the such type of compounds: the heats of reactions, the enthalpies of vaporization, solvation, and their formation in the different aggregate states.

The main characteristics of P—H bonds (bond lengths, IR frequencies (ν_{PH}) and coupling constants ($^1J_{PH}$) in NMR spectra) for all types of the above mentioned compounds with various phosphorus coordination are presented in Table I.

The dipole moment of the P—H bond, derived[5] from the simple PH_3 phosphine, is small (0.36 D) and does not vary appreciably for compounds of the different spatial structure and different phosphorus coordination.[6–10] However, the polarization anisotropy of this bond (γ A^{o3} -1.1) appreciably differs from similar values for bonds C—H, O—H, and Si—H (0.0, 0.46, 0.50 γ A^{o3} correspondingly).[11]

The most sensitive parameter of the P—H bond is the coupling constant ($^1J_{PH}$). It varies in a wide interval, which can be explained by the regibridization of atomic orbitals,[12,13] i.e., by change of the *s*-share in the hybrid orbital. The known equation (1) allows to assume that the P—H bonds in simple phosphines have predominantly *p*-character with a small *s*-contribution (6–7%).

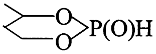
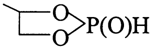
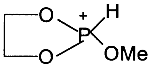
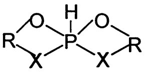
$$^1J_{PH} = 29.3 \cdot S_{PH} \tag{1}$$

where S_{PH} is the share of *s*-character of the P—H bond.[12,24,25]

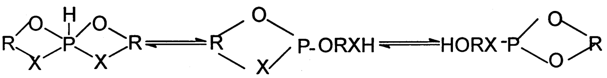
However, the transition from phosphines to cyclic hydrophosphorylic compounds (>P(O)H, HPC) is accompanied by an essential increase of the *s*-character contribution (15–20%). The largest *s*-contribution is observed for five-membered cyclic phosphites and phosphoranes 24–26% and 30% correspondingly.

The energy of the P—H bond in various compounds of phosphorus is practically unexplored, however it is known,[3] that this value consists about 322 kJ mol^{-1} in PH_3. It is reasonable to expect that the length (l) changes of the P—H bond in the some akin compounds make this magnitude essentially differ. It has been shown[26] that the estimated magnitude of the P—H-bond energy in bicyclic 1,4,6,9-2,3,7,8-tetramethyl-5-hydrophosphaspiro[4,4]-nonane[27,28] is more than five times smaller

TABLE I The Some Properties of the Phosphorus Derivatives Having P–H Bonds

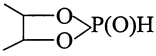
Compound	Lengths (l) of P—H, A^o	γ_{PH}, cm^{-1}	$^1J_{PH,Hz}$
	Phosphines		
PH_3	1.437^{14}	2306^{16}	$180, 182^{1}$
$H_2P\text{-}PH_2$	1.451^{14}	2297^{16}	186^{1}
$MePH_2$	1.423^{14}	2311^{16}	$1186, 210^{1}$
$PhPH_2$	1.412^{15}	2280^{16}	$196, 207^{1}$
	Hydrophosphorylic compounds		
$R_2P(O)H$	—	$2300\text{–}2307^{16}$	$460\text{–}470^{18\text{–}21}$
$R(RO)P(O)H$	—	$2320\text{–}2356^{16}$	$518\text{–}550^{18\text{–}21}$
	1.39^{22}	—	$666\text{–}713^{7}$
	1.39^{22}	$2435\text{–}2440^{17}$	$700\text{–}724^{17}$
	Charged compounds and phosphoranes		
$(MeO)_3\overset{+}{P}\text{–}H$	—	—	827^{23}
	—	—	$850\text{–}870^{23}$
	$1.32\text{–}1.35^{14}$	$2350\text{–}2400^{16}$	$820\text{–}918^{19,20}$
$F_4P\text{—}H$	1.36^{14}	2485^{16}	$1075\text{–}1092^{20}$

(~58.5 kJmol^{-1}). Probably that the such difference in this thermochemical parameter stipulates to connect of the hydrogen atom mobility with the acidity properties of the simple phosphites and cyclohydrophosphoranes more known as tautomeric equlibrium.[29]



The experimental ionization constants (pK_a) indicate the large distinction of the different types of P—H-containing compounds (Table II). The consecutive replacement of the donor alkyl or aryl groups by the acceptor alkoxy- and dioxyalkylene groups at phosphorus monotonously increases the ability for ionization of the P—H acids. The high acidity of HPC in non-aqueous solvents is connected with the tautomeric equlibrium of hydrophosphorylic compounds between >P(O)H (form **A**) and >P—OH (form **B**).[32]

TABLE II The Ionization Constants of the Different Compounds with P–H Bond

Type of Compound	pK_a	Type of Compound	pK_a
	Phosphines		
Et_2PH	$34^{4,30}$	PH_3[1]	29^4
Ph_2PH	$22–23^{4,30}$		
	Hydrophosphorylic compounds		
$Alk_2P(O)H$	$27–28^{31}$	$Ar_2P(O)H$	$18.8–21.8^{31}$
$(RO)_2P(O)H$	$20.8–22.0^{31,32}$		$14.6–17.4^{32–34}$

PRIMARY AND SECONDARY PHOSPHINES

The research in the field of the thermochemistry of phosphorus compounds is characterized by an extremely small number of works concerning the vaporization enthalpy. Among the characterized compounds there are some primary and secondary phosphines. The ability of the three-coordinated phosphorus compounds, in particular phosphines, to form complexes with transition metals has been theoretically studied and widely used in synthetic practice.[3,4] Particular interest has been given to the compounds of the $P(C_6H_4SO_3Na)_3$ type, possessing some properties analogues 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 solvents.[35,36] 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 [37,38] and in chemotherapy of certain forms of cancer (Au and Pt complexes).[39,40] It is believed[41] that phosphine-containing peptides can be used in the 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 realiable data of thermochemical experiments (heats of vaporization, formation, and solvation) are available even for simple representatives of this class of compounds, namely, RPH_2 and R_2PH, mainly because they are easily oxidized and flare up in the air under conditions of calorimetric experiments. Therefore the aim of this review was to show of the special features of the study of the thermochemistry of the above-mentioned compounds.

Calculations of the Vaporization Enthalpies of Phosphines

The enthalpies of evaporation and sublimation are important parameters in organic and heteroatomic chemistry for practical calculations of the heats of reactions at different temperatures and phases. The calculations of the vaporization enthalpies (ΔH_{vap}/kJ mol^{-1}) of primary and secondary phosphines were performed using two independent calculation procedures.

First, this problem could serve the Trouton (2) and Wadso (3) equations, derived for weakly associated and low-boiling liquids.[42–44] These equations were chosen as more suitable ones to estimate the required thermochemical term in laboratory:

$$\Delta H_{\text{vap}} = (0.00736\text{T}_\text{b} + 1.056) \cdot 22, \qquad (2)$$

where T_b is the boiling point, and 22 is the Trouton-constant characteristic for many of three-coordinated phosphorus compounds,[1] and

$$\Delta H_{\text{vap}} = 0.172\text{T}_\text{b} + 20.9. \qquad (3)$$

Second, using the model description of the dispersion interactions, suggested previously[45,46] and which based on the topological solvation index ${}^m\chi^s$ (Eq. 4) which is essential in the Randic 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 (the presence of cycles, functional groups etc.), but also the size of the atoms constituting the molecule:

$${}^m\chi^s = (1/2)^{\text{m}+1} \sum_1^n Z_i Z_j \ldots Z_k/(\delta_i \delta_j \ldots \delta_k)^{1/2}, \qquad (4)$$

where m is the order of the index; n is the number of subgraphs of the order m; $\delta_i \delta_j \delta_k$ 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 the Eq. 5:[46]

$${}^1\chi^s = 0.25 \sum_1^n Z_i Z_j/(\delta_i \delta_j)^{1/2} \qquad (5)$$

A correlation (Eq. 6) for calculating the ΔH_{vap} values (in kJ mol^{-1}) was suggested in the framework of this model:[46]

$$\Delta H_{\text{vap}} = 4.26 + 9.37\,{}^1\chi^s + 0.87\mu^2, \qquad (6)$$

where μ is the dipole moment of the compound under study.

This dependence makes it possible to calculate the vaporization enthalpies of the non-polar or low-polar organic and heteroatomic substances, using the first-order topological solvation index ${}^1\chi^s$ and the dipole moment with an accuracy of ±2–4 kJ mol^{-1}.

To be certain that these equations (2, 3, 6) possible to use for calculating the vaporization enthalpies of three-coordinated phosphorus compounds, the authors of the work[52] calculated the ΔH_{vap} values for several phosphines (compounds **1–11, 25–27** in Table III) and found a resonable agreement between the calculated and experimental. The experimental values of the dipole moments for several compounds (μ_{exp}) have been measured in inert solvents (hexane, CCl_4, benzene); some of them have been also calculated by molecular mechanics (MMX) method (see note c in Table III). 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 the previously suggested calculations,[45] the ΔH_{vap} values for compounds with $\mu \leq$ 1–3 D can be estimated neglecting the effect (see higher) of the dipole moment. Therefore, the to the small differences between the experimental and calculated dipole moments lead to the small errors in vaporization enthalpies (±2.0–4.0 kJ mol^{-1}).

Then, the contribution of the group-PH_2 has been used for the calculations of the vaporization enthalpies of some primary alkylphosphines according to the additive scheme (Eq. 7):

$$\Delta H_{\text{vap}} = \sum_{i-1}^{n} n_i X_i, \tag{7}$$

where n 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[53] (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)$_2$, and C—(C)$_3$(H) respectively). 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 $\alpha = 0.999$. This value was used in the ΔH_{vap} calculations for compounds (**12–24**, Table III) using the Eq. 7. For these compounds the ΔH_{vap} values were also calculated using the topological solvation index ${}^1\chi^s$. The contributions of the >PH group atom into vaporization enthalpies of secondary dialkylphosphines were calculated in a similar way and proved to be 12.8 ± 0.4 kJ mol^{-1} for R_2PH compounds (**25–34** and **48–52**, Table III; $\alpha = 0.999$). These

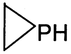
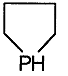
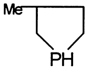
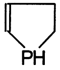
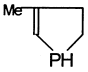
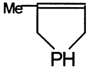
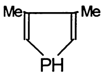
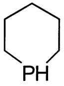
TABLE III Thermochemical Characteristcs of Phosphines (kJ mol⁻1)

							ΔH_{vap}/kJ mol^{-1}				
							Calculations using Equation				
(No.)	Compound	T_b^a/°C	MR_D^b/ cm^3 mol^{-1}	μ^c/D	$^1\chi^s$	Exp.	(2)	(3)	(6)	(7)	Average
					Primery Phosphines						
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
(1)	$CHF_2CF_2PH_2$	20–22		1.61	1.768	26.7^d	26.9	24.7	23.1		25.4 ± 2.3
(2)	$Me_2CF_3PH_2$	46.8		1.74	2.598	28.9^d	30.9	28.9	31.2		30.5 ± 1.4
(3)	$MePH_2$	−17.1	17.7	1.10	1.500	22.2^e	20.5	18.0	19.4		20.0 ± 1.8
(4)	$EtPH_2$	25.0	22.3	1.22	1.768		27.3	25.2	22.1		24.9 ± 2.6
(5)	Pr^nPH_2	53.5	27.0	1.17	2.268		31.9	30.1	26.7		29.6 ± 2.6
(6)	Pr^iPH_2	41.0	25.4	1.23	2.021		29.9	28.0	24.5		27.4 ± 2.7
(7)	Bu^nPH_2	87.8	31.3	1.36	2.768		37.5	36.0	31.8		35.0 ± 2.9
(8)	Bu^iPH_2	79.6	28.7	0.98	2.624		36.2	34.6	29.7		33.5 ± 3.3
(9)	Bu^sPH_2	67	28.7	0.98	2.559		34.1	32.4	29.1		31.9 ± 2.5
(10)	Bu^tPH_2	54	25.5	0.96	2.250		32.0	30.2	26.2		29.5 ± 3.0
(11)	Am^nPH_2	104	35.4	0.99	3.268		40.1	38.8	35.8		38.2 ± 2.2
(12)	Am^iPH_2	106–107	34.6	0.98	3.124				34.4	37.0	35.7 ± 1.8
(13)	$HexPH_2$	128	40.3	1.34	3.768				41.1	43.8	42.5 ± .9
(14)	$HeptPH_2$	149.5	44.5	0.99	4.268				45.1	48.6	46.9 ± 2.5
(15)	$OktPH_2$	169.0	49.0	0.99	4.768				49.8	53.3	51.6 ± 2.5
(16)	$NonPH_2$	187	53.7	0.99	5.268				54.5	58.1	56.3 ± 2.5
(17)	$DezPH_2$	203	58.3	0.99	5.768				59.2	62.9	61.1 ± 2.6
(18)	cyclo-$AmPH_2$	121	33.4	0.98	3.183				34.9	40.3	37.6 ± 3.8
(19)	cyclo-$HexPH_2$	146	38.1	0.98	3.683				39.6	44.9	42.3 ± 3.7
(20)	H_2PPH_2	56	24.0	—	2.250				25.6	27.2	26.4 ± 1.1
(21)	$H_2PCH_2PH_2$	83.4	28.6	1.83	2.121				32.2	32.0	32.1 ± 0.1

(*Continued on next page*)

TABLE III Thermochemical Characteristcs of Phosphines (kJ mol^{-1}) (*Continued*)

							ΔH_{vap}/kJ mol^{-1}				
							Calculations using equation				
(No.)	Compound	T_b^a/°C	MR_D^b/ cm^3 mol^{-1}	μ^c/D	$^1\chi^s$	Exp.	(2)	(3)	(6)	(7)	Average
					Primery Phosphines						
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
(22)	$H_2P(CH)_2PH_2$	113	33.2	1.96	2.621	38.1^d			32.2	36.7	35.7 ± 3.1
(23)	$H_2P(CH)_3PH_2$	143	37.8	1.36	3.121	40.3^d			35.1	41.5	39.0 ± 3.4
(24)	$H_2P(CH)_4PH_2$	172.3	42.5	1.96	3.621	36.1^d			46.4	41.3	43.9 ± 3.6
					Secondary Phosphines						
(25)	Me_2PH	21.1	21.5	1.23	2.121	26.2^f	26.7	24.5	25.5		25.7 ± 0.9
(26)	Me(Et)PH	54.5	26.2	1.28	2.518	31.0^d	32.1	30.3	29.3		30.7 ± 1.2
(27)	Me(Pr^n)PH	78.2	30.8	1.12	3.018	35.2^d	36.0	34.3	33.6		34.8 ± 1.0
(28)	Me(CH=CHCH2)PH	81									
(29)	Me(Bu^n)PH	112.7	35.4	1.12	3.518	34.3^d	41.5	40.3	38.3		40.0 ± 1.6
(30)	Me(Pr^i)PH	78–80	29.2	1.08	2.828		36.2	34.6	31.8		34.2 ± 2.2
(31)	Et_2PH	85	30.6	1.40	2.914		37.1	35.5	33.3		35.3 ± 1.9
(32)	Pr^n_2PH	136	40.0	1.19	3.914		45.3	44.2	42.2		43.6 ± 1.3
(33)	Pr^i_2PH	118	36.8	1.30	3.534		42.4	41.2	38.8		40.8 ± 1.8
(34)	Pr^iBu^iPH	139	41.4	1.08	4.080		45.8	44.8	43.5		44.7 ± 1.2
(35)	Bu^n_2PH	178	49.1	1.37	4.914				51.9	54.1	53.0 ± 1.6
(36)	Bu^i_2PH	169.0–171.8	45.9	1.11	4.626				51.4	50.1	50.8 ± 0.9
(37)	Bu^s_2PH		45.9	1.11	4.610				48.5	50.1	49.3 ± 1.1
(38)	Bu^t_2PH		39.5	1.06	4.061				46.3	43.3	44.8 ± 2.1
(39)	Am_2PH		58.5	1.08	5.914				60.7	63.7	62.2 ± 2.1
(40)	Am^i_2PH	210–215	56.9	1.12	5.626				58.1	59.7	58.9 ± 1.1
(41)	Pr^n(Hex)PH	194	53.9	1.12	5.414				56.1	58.9	57.5 ± 2.0
(42)	Hex_2PH		67.7	1.09	6.914				71.2	73.2	72.2 ± 1.4
(43)	$(Hept)_2PH$		77.0	1.09	7.914				79.4	82.8	81.1 ± 2.4
(44)	$(Okt)_2PH$		85.9	1.11	8.014				89.0	92.3	90.1 ± 2.3

(45)	(Non)$_2$PH		95.4	1.09	9.914				98.2	101.8	100.0 ± 2.7
(46)	(Dez)$_2$PH		104.7	1.09	10.914				107.6	111.4	109 ± 2.7
(47)	(*cyclo*-Hex)$_2$PH		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	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
(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

[a] Data taken from Refs. 2, 46, 47.

[b] Experimental MR$_D$ values are listed for compounds **(7–9, 13–19, 31, 35–37, 44, 50, 53)**; for other compounds the MR$_D$ values were calculated using the group additive scheme; corrections to the MR$_D$ values were introduced for branched R.[48]

[c] Experimental μ values are listed for compounds **(3–7, 13, 25, 26, 31–33, 48, 49)**;[48,50] otherwise the dipole moments were calculated by the molecular mechanics (MMX) method.

[d] The ΔH_{vap} values for these compounds were calculated from the temperature dependence of vapor pressure.[48]

[e] Data taken from Ref. 51.

[f] Data taken from Ref. 1.

TABLE IV Parameters of Correlation Equations 8–10

Equation	a	b	S_o	r	Number of points
8	4.9 ± 0.5	0.99 ± 0.01	2.37	0.996	86
9a	-4.7 ± 1.2	1.11 ± 0.04	0.62	0.996	9
9b	3.3 ± 1.8	1.00 ± 0.03	2.66	0.996	13
10a	8.6 ± 1.1	0.93 ± 0.03	1.37	0.991	15
10b	8.8 ± 1.0	0.96 ± 0.02	1.98	0.996	19

values were used in calculations of ΔH_{vap} for compounds (**35–47, 53–55**; Table III).

From the presented data it is clear that the ΔH_{vap} values calculated using the two procedures mentioned above are in a good agreement, thus indicating the reliability of both ΔH_{vap} values obtained and the contributions of $-PH_2$ and $>PH$ groups for substituted phosphines.

An important fact is that the ΔH_{vap} values calculated for alkylphosphines correlate well with their molar refraction (MR_D) (Table IV). It is necessary to note that this correlation is observed also for tertiary phosphines which are not discussed in this review;[52] 86 points). Previously, a similar dependence was observed for simple alkanes.[49] The general correlation equation has the form (Eq. 8):

$$\Delta H_{\text{vap}}\,(\text{phosphines}) = a + b\text{MR}_{\text{D}}(\text{phosphines}). \tag{8}$$

The average values for phosphines also correlate with the experimental vaporization and sublimation enthalpies of isostructural compounds, i.e., primary (RNH_2), secondary (R_2NH) amines[54] (Table IV, Eqs. 9a and 9b) and the corresponding alkanes RCH_3, R_2CH_2 (Eqs. 10a and 10b):

$$\Delta H_{\text{vap}}\,(\text{phosphines}) = a + b\Delta H_{\text{vap}}\,(\text{amines, alkanes}). \qquad (9, 10)$$

The high correlation coefficients r and small standard deviation S_0 of the correlation obtained suggest that the calculated vaporization enthalpies of alkylphosphines with different spatial structures are reliable.

Thus, the ΔH_{vap} values first determined for alkylphosphines of different structure using the Trouton and Wadso equations and the first-order topological solvation index showed the good correspondence between the calculated and experimental ΔH_{vap} values. The $-PH_2$ and $>PH$ group contributions for primary and secondary phosphines can be used for calculating the ΔH_{vap} values for analogous phosphorus compounds. Additionally, it has been found that the ΔH_{vap} values of phosphines depend on their molar refraction and change in parallel to vaporization enthalpies of isosteric amines and alkanes.

Solvation and Complex Formation of Primary Phosphines

It is known that the influence of the solvent on the course of chemical processes with the P^{III}-compounds represent the large theoretical and practical interest. One of the important components of this problem is the study of the solvating factors of phosphorus compounds in various media. It should be noted, that in the literature there is lack of quantitative data on enthalpies or free energies of solvation of phosphorus compounds with the phosphorus atom possessing various coordination.[3,44,49,55,56] Under "solvation" one should understand the sum of the energy changes, occurring during the transition of the gaseous molecules, ions, radicals or atoms into the liquid phase with formation of the solution of the certain structure, except those changes, which are accompanied by the cleavage of chemical bonds. It is necessary to distinguish such terms as "solvation (ΔH_{solv})" and "solution (ΔH_{soln})", as far as they have an identical physical sense only in those cases, when they characterize the solution processes of gases.

Thus, the above mentioned cycle (Figure 1) represents energy transition of the particles of substance A_i from the gas phase (outside of environment) into a solution.

This transition represents the common effect of various intermolecular forces, which can be realized in a solution, and just its value gives us an energy level of the substance in a given solvent, which, in its turn, determines the essence of the solvation effect. The development of the studies on the analysis of enthalpy of organophosphorus compounds

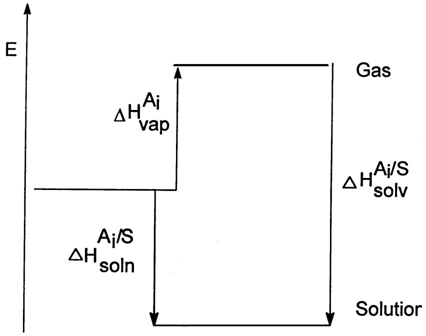


FIGURE 1 The thermodynamic cycle, connected the ΔH_{vap}, ΔH_{solv}, and ΔH_{soln} for compound A_i.

(OPC) was until recently constrained, basically, due to two reasons: the absence of the uniform methods of the study of solvation of organic and heteroatomic compounds in nonaqueous solvents and difficulties of the experimental determination of the heats of vaporization of OPC, required for these purposes.

In the work of B. N. Solomonov and A. I. Konovalov[49] a new way of the analysis of the solvation enthalpy of non-electrolytes in organic media has been given. A universal linear dependences of the solvation enthalpy of organic compounds in alkanes on their molar refractions were found. The essence of the offered approach is the Eq. 11, connecting the non-specific solvation and $\mathrm{MR_D}$ of the solute $\mathrm{A_i}$ in the solvent S:

$$\Delta H_{\mathrm{solv}}{}^{\mathrm{Ai/S}}(\mathrm{alkane})/\mathrm{kJ\,mol^{-1}} = 4.39 + 1.05\mathrm{MR_D^{Ai}}. \tag{11}$$

The observed enthalpy of solvation of any substance ($\mathrm{A_i}$) is the sum of the contributions of non-specific solvation and solute-solvent (S) specific interactions (Eq. 12):

$$\Delta H_{\mathrm{solv}}^{\mathrm{Ai/S}}(\mathrm{obs.}) = \Delta H^{\mathrm{Ai/S}}(\text{non-spec.}) + \Delta H^{\mathrm{Ai/S}}(\text{spec. int.}). \tag{12}$$

According to the approach, which has been suggested in the work,[49] the contribution of non-specific solvation enthalpy in different media can be estimated by Eq. 13:

$$\Delta H_{\mathrm{solv}}^{\mathrm{Ai/S}}(\text{non-spec.}) = a_s + b_s\mathrm{MR_D^{Ai}}. \tag{13}$$

In previous work,[56,57] it has been shown that compounds with three-coordinated phosphorus atom do not participate in any detectable specific interactions with carbon tetrachloride, benzene, *p*-xylene. These results allow us to use the earlier deduced equations with corresponding coefficients (Table V; similar a_s and b_s solvation parameters for P(III) and P(IV)-compounds are also given for comparison) for estimation of nonspecific solvation.

The calculated solvation enthalpy values of alkylphospines (**3–17)** and alkylenediphosphines (**20–24)** have been represented in Table VI for the solvents mentioned above, since the determination of ΔH_{solv} for such compounds by other methods is practically impossible. The estimation of non-specific solvation enthalpy has been made, these data are often required for the interpretation of the reactivity of phosphines in various solvents.[61]

Nevertheless, we do not discuss here any possibilities of hydrogen bonding between the lone pair of phosphines and the HO-group of methanol, as soon as the H-atoms of phosphines and lone pair of pyridine form a very weak hydrogen bonds. At the same time, the cyclic

TABLE V The a_s and b_s-Solvation Parameters (kJ mol^{-1}, Eq. 13) for the Solvation P(III) and P(IV) Compounds[55–57,67]

Solvents	P(III) a_s	P(III) b_s	P(IV) a_s	P(IV) b_s
CCl_4	−9.1 ± 0.6	−1.08 ± 0.01	−13.0 ± 1.9	−1.02 ± 0.04
Benzene	−7.8 ± 2.8	−1.11 ± 0.05	—	—
p-Xylene	−6.1 ± 1.7	−1.13 ± 0.03	−11.7 ± 1.9	−1.08 ± 0.04
Methanol	−6.4 ± 1.7	−1.04 ± 0.03	—	—
Acetone	—	—	−21.2 ± 3.1	−0.95 ± 0.07
Nitrobenzene	—	—	−18.6 ± 3.1	−0.93 ± 0.19
Dioxane	—	—	−22.9 ± 1.4	−0.81 ± 0.03
Pyridine	−12.6 ± 5.1	−0.97 ± 0.12	−17.0 ± 3.5	−1.01 ± 0.07

secondary phosphines able to form the molar complexes with such strong acceptor as $B(Me)_3$. These results obviously show the acceptor and steric influence of cyclic substituents (**49,55**) in comparison to methyl groups (**25**) at phosphorus on the stability of complexes (Table VII).

TABLE VI Calculated Values of Non Specific Solvation Enthalpies for Phosphines **(3–17, 20–24)** in Some Solvent (kJ mol^{-1})[61]

	$-\Delta H_{\text{solv}}$ (calc.)				
Compound	CCl_4	Benzene	*p*-Xylene	Methanol	Pyridine
(3)	23.3	22.3	20.9	20.0	25.3
(4)	28.2	27.5	26.1	24.8	30.0
(5)	33.1	32.6	31.3	30.0	34.2
(6)	38.3	37.8	36.6	34.5	38.8
(7)	35.6	36.0	34.8	32.8	37.2
(8)	43.0	42.5	41.5	39.0	43.0
(9)	40.1	40.0	38.5	36.3	40.4
(10)	40.1	40.0	38.5	36.3	40.4
(11)	36.6	36.1	35.0	32.9	37.3
(13)	47.3	47.1	46.1	43.2	46.9
(14)	52.6	52.5	51.6	48.3	51.7
(15)	57.2	57.2	56.4	52.7	55.8
(16)	62.0	62.2	61.5	57.4	60.1
(17)	67.1	67.4	66.8	62.3	64.7
(20)	35.0	34.4	33.2	31.4	35.9
(21)	40.0	39.5	38.4	36.1	40.3
(22)	45.0	44.7	43.6	40.9	44.8
(23)	50.0	49.8	48.8	45.7	49.3
(24)	55.0	55.0	54.1	50.6	53.8

TABLE VII The Thermodynamic Parameters of Compleses $R_2PH{\bullet}B(Me)_3$ Obtained via the Gaseous Dissociation[58]

Phosphine (No.)	$-\Delta H^{o}_{\text{compl}}$, kJ mol^{-1}	$-\Delta S^{o}_{\text{compl}}$, J mol^{-1} K^{-1}	$-\Delta G^{o}_{\text{compl}}$, kJ mol^{-1}
(25)	47.6	146.9	3.9
(49)	36.4	128.0	−1.7
(55)	13.0	51.5	−2.5

Enthalpies of Formation in the Gaseous Phase and Condensed State

The standard formation enthalpy of compounds (ΔH_f^o) is the thermal effect of reaction from the simple substances under standard conditions: temperature 298.15 K and pressure 101325 P. In practice it is possible to execute such reactions and to determine the formation enthalpy only for most simple substances: H_2O, HCl, CO_2, etc. For organophosphorus compounds, in particular primary or secondary alkylphosphines, this method has been used very seldom due to technical reasons: taking into account their easy oxidation and burning in the air. Nevertheless, some results in the experimental and calculating forms on the determination of ΔH_f^o have been obtained (Table VIII).

The formation enthalpies of these simple substances are precisely determined and this allows to use them for the calculations of unknown values of the formation enthalpies of compounds, using the Hess-law.[44]

The quick progress in the field of computer facilities resulted in wide application of quantum chemistry and molecular mechanics for the determination of the formation enthalpy. Two ways of the calculation of the formation enthalpy of organic and heteroatomic compounds will be briefly considered below (Table VIII): a method of molecular mechanics

TABLE VIII Some Literary and Self-Calculated Formation Enthalpies of Phosphines in kJ mol^{-1}

	$-\Delta H_f^o$			
Phospine (No.)	Experimetal[60]	MNDO/3[62]	MNDO (PM3)[a]	MMX[a]
$MePH_2$ **(3)**	29.2	34.7	39.7	32.2
$EtPH_2$ **(4)**	50.2	49.0	47.5	52.2
Me_2PH **(25)**	62.8	69.5	81.8	50.8
Et_2PH **(31)**	104.6	100.0	99.6	112.1

[a] Calculated by the authors.

(program MMX in the environment PC MODEL) and quantum chemistry methods.[59]

The relative simplicity and availability of the methods of a computer chemistry, reliability of the obtained estimated values, have resulted in a reasonably wide usage of the computer calculations of the thermochemical parameters of organic compounds. The calculations of the molecules of heteroatomic compounds can cause difficulties, connected with a large number of parameters in the programs and with the small number of precisely determined thermochemical data.

From the data listed in Table VIII one can see a reasonably good correspodence between the experimental and calculated by different methods formation enthalpies, nevertheless, the data for RPH_2 much better correspond to each other. Taking into account this circumstance, the ΔH_f^o values have been calculated for some primary phosphines (**5–11**, **13–17**, and **21–24**) using the MMX method (Table IX).[52,63] With the use of the formation enthalpy values for compounds (**5–9** and **20–24**) and the contributions in ΔH_f^o for CH_3—, —CH_2— and >CH obtained by Benson and coauthors,[43] the contribution of the H_2P-fragment values into the gaseous formation enthalpy (9.6 ± 0.8 kJ mol^{-1}) has been estimated.

The reliability of the formation enthalpies of alkylphosphines and diphosphines in the gaseous phase calculated by various methods can be confirmed by good correlation (14–16) between ΔH_f^o of mentioned above phosphines and the experimental formation enthalpies for the primary amines RNH_2 (R corresponds to compounds **5–11** and **13–15**) and alkanes RCH_3 (R corresponds to compounds **5–17, 21–24**).[54]

$$\Delta H_f^o(RPH_2, gas) = (-11.2 \pm 2.5) + (0.88 \pm 0.03)\Delta H_f^o(RNH_2, gas) \quad (14)$$

$$r = 0.996, So = 2.68, n = 10,$$

$$\Delta H_f^o(RPH_2, gas) = (51.4 \pm 0.9) + (1.00 \pm 0.01)\Delta H_f^o(RCH_3, gas) \quad (15)$$

$$r = 0.999, So = 1.12, n = 16,$$

$$\Delta H_f^o[H_2P(CH_2)_mPH_2] = (94.7 \pm 11.1) + (0.94 \pm 0.08)\Delta H_f^o[CH_3(CH_2)_mCH_3] \quad (16)$$

$$r = 0.993, So = 3.76, n = 4.$$

The values of the formation enthalpies for alkylphosphines in the condensed phase are calculated via the Eq. 17 (Table IX):

$$\Delta H_f^o(RPH_2, cond. phase) = \Delta H_f^o(RPH_2, gas) - \Delta H_{vap}. \quad (17)$$

TABLE IX The Formation Enthalpies (kJ mol^{-1}) in the Gaseous and Condensed Phases of Primary Phosphines RPH_2[52,63]

	$-\Delta H_f^o$	
Phosphine	Gas	Cond. phase[a]
1	**2**	**3**
(5)	73.9	103.5
(6)	83.5	110.9
(7)	94.1	129.1
(8)	102.5	136.0
(9)	103.5	135.4
(10)	114.5	144.0
(11)	115.0	153.2
(13)	135.7	178.2
(14)	156.4	203.3
(15)	177.1	228.7
(16)	197.8	254.1
(17)	218.5	279.6
(20)	20.9	47.3
(21)	6.7	38.8
(22)	19.3	55.0
(23)	43.6	82.6
(24)	64.1	108.0

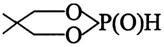
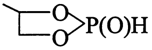
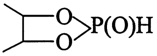
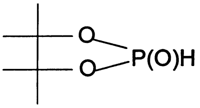
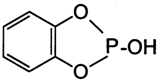
[a] The magnitudes can be easy calculated this the use of Figure 1; error of ΔH_f^o in condensed phase has been taken as equal to the error of ΔH_{vap} (see Table 3).

Hydrophosphorylic Compounds

The chemistry of hydrophosphorylic compounds (HPC) is the most comprehensively developed area of phosphorus chemistry from the point of view of thermochemistry. However, despite of the significant progress, achieved in the understanding of reactivity HPC, interest to this class of phosphorus compounds still do not decrease because these compounds are important key reagents in the synthesis of practically useful chemicals. The reactivity of hydrophosphorylic compounds ($>P(O)H$) has been previously predicted and studied by J. R. Van Wazer, A. E. Arbusov, A. N. Pudovik, and other scientists.

The presence in HPC, as well as in alkylphosphines, of a mobile hydrogen atom permits to introduce phosphorus-containing fragments into various classes of compounds, such as peptides, polymers, medical preparations, pesticides, and others.[64] It is necessary to add, that for a

TABLE X NMR ^{31}P-Spectral Characterisric and Experimental Dipole Moments of Cyclic Hydrophosphorylic Compounds

Compound		NMR		μ, D	
		δ_P, ppm	$^1J_{PH}$, Hz	CCl_4	Dioxane
(56)	$(EtO)_2P(O)H$	8	690	3.08	3.31
(57)		9	660–670	5.76	6.16
(58)		24	720	—	5.45
(59)		21	710	4.80	5.55
(60)		20	720	—	5.45
(61)		129	—	1.62 (benzene)	—

long time the interests of researchers have been displayed in the study of cyclic derivatives of this class of compounds.[64,65] The certain success in the development of this specific area has been reached thanks to structural studies and studies of some dynamic aspects of the behavior of these acids in different solvents.[24,25]

The reactivity of cyclic phosphoric acids, especially with five-membered cyclic fragments, has been shown in the comprehensive research of their structure in a condensed phase and solvents of various nature. It has been known for a long time, that acyclic phosphoric acids $(RO)_2P(O)H$ exist in the form (A) with the four-coordinated phosphorus atom.[64] According to the data of dipole moments (μ) the same form is characteristic for HPC with six and five-membered cycles (**57–60**) (Table X).[6–9] The only exception from this row is the acid **(61)**, containing the o-phenylenic fragment in a five-membered cycle.

Such structural features require the detailed study of the ability of HPC to form hydrogen bonds with the solvent. It is necessary to note, that the thermochemistry of vaporization, solvation, especially of the tautomerism and formation enthalpies of hydrophosphorylic compounds in any aggregate states have been practically not investigated.

The Vaporization Enthalpy

The vaporization enthalpy is one of the important thermochemical parameters of organophosphorus compounds. It is well known that the solution enthalpy of different organic substances can be easily and accurately measured practically in any type of calorimetric system. In contrast, the vaporization enthalpy can not be so easily obtained, especially in the case of organophosphorus compounds, which are able to hydrolyze in the air or have very high boiling points and hence low vapor pressure. As a consequence the application of the Trouton's or Clausius-Clapeyron's approaches as well as other direct experimental methods often lead to the essential errors in the values of vaporization enthalpies of heteroatomic, including phosphorus compounds.[44,53]

However B. N. Solomonov, A. I. Konovalov, and coworkers suggested the Eq. 18 for the determination of this energy term.[49]

$$\Delta H_{\mathrm{vap}}/\mathrm{kJ\,mol^{-1}} = \Delta H^{\mathrm{Ai}}_{\mathrm{soln}}\,(\mathrm{alkane}) + 4.39 + 1.05\left(\mathrm{MR}^{\mathrm{Ai}}_{\mathrm{D}} - \alpha\right), \quad (18)$$

where α is a correction into the molar refraction,[55] for branched alkyl groups; $\mathrm{MR}^{\mathrm{Ai}}_{\mathrm{D}}$ is in $\mathrm{cm^3\ mol^{-1}}$.

This equation was successfully used for the determination of the vaporization enthalpies for compounds, having $\mathrm{P^{IV}}$ atoms.[55–57,66–68] It is necessary to note that the error in determination of ΔH_{vap} using Eq. 18 was about ±2.5–4.5 kJ $\mathrm{mol^{-1}}$ depending on the aggregate state of the dissolved product. This is in the most cases comparable to the uncertainties of other experimental methods. However, it can be noted, that the determination of ΔH_{vap} for example for six-membered cyclic compounds, as well as for some other structurally mobile compounds, is obviously accompanied by a larger error, because for this type of compounds conformational equilibrium is observed.

Nevertheless as it has been shown[55,66] that the Eqs. 19 and 20 could be also successfully used for the determination of vaporization enthalpy because they account for the solution enthalpy values in carbon tetrachloride or *p*-xylene; which is connected with a very small solubility of some organophosphorus compounds in hexane:

$$\Delta H_{\mathrm{vap}}/\mathrm{kJ\,mol^{-1}} = \Delta H^{\mathrm{Ai}}_{\mathrm{soln}}(\mathrm{CCl_4}) + 13.0 + 1.02\,\mathrm{MR}^{\mathrm{Ai}}_{\mathrm{D}}, \quad (19)$$

$$\Delta H_{\mathrm{vap}}/\mathrm{kJ\,mol^{-1}} = \Delta H^{\mathrm{Ai}}_{\mathrm{soln}}(p\text{-xylene}) + 11.7 + 1.08\,\mathrm{MR}^{\mathrm{Ai}}_{\mathrm{D}}. \quad (20)$$

In Table XI are listed the ΔH_{vap} values of hydrophosphorylic compounds obtained via Eqs. 18 and 19. Using all values of vaporization enthalpies listed in Table XI and the values of ΔH_{vap} for the derivatives of methylphosphonic acids $\mathrm{(RO)_2P(O)Me}$ published,[55] we

TABLE XI Solution, Solvation, and Vaporization Enthalpies in kJ mol^{-1} for Some Phosphoric Acids $RO_2P(O)H$[55]

		ΔH_{soln}				$-\Delta H_{solv}$[a]		
Compound	R	C_6H_{14}	CCl_4	MR_D	ΔH_{vap}	C_6H_{14}	CCl_4 Obs.	Calc.
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
		Acyclic Phosphoric Acids						
(56)	Et_2	11.9	−0.2	31.6	49.5[b]	37.6	49.7	
(62)	Me_2	11.5	4.4	22.5	39.5	28.0	35.1	
(63)	Pr_2	9.6		41.0	57.0	47.4		54.8
(64)	*i*-Pr_2	7.3	−1.5	40.9	51.3	44.0	52.8	
(65)	Ph_2	—	5.7	62.2	82.1	69.7		76.4
(66)	$(ClCH_2-CH_2)_2$	—	10.7	41.2	65.7	47.6		55.0
		5-Membered Cyclic Phosphoric Acids						
(59)	MeCH—CHMe	10.5	5.9	30.1	43.1	32.6	37.2	
(60)	Me_2C-CMe_2	32.4	24.6	38.6	67.3	34.9	42.7	
(58)	$MeCH-CH_2$	—	3.2	24.7	39.8	28.6		36.6
		6- and 7-Membered Cyclic Phosphoric Acids						
(57)	$-CH_2C=Me_2CH_2-$		17.5	34.0	60.3	35.0		42.8
(67)	$(CH_2)_3$	—	−6.1	24.7	32.1	30.3		38.2
(68)	—Ph—Ph—	—	22.6	59.1	95.9	66.0		73.3

[a] Calculated for hexane using Eq. 11; calculated for CCl_4 using Eq. 19.

[b] $\Delta H_{vap} = 49.3$ kJ mol^{-1} [69].

calculated the contribution into the vaporization enthalpy for groups **$H-P(O)(O)_2 \equiv C-P(O)(O)_2$** to be equal 26.8 ± 3.4 kJ mol^{-1}.[67]

Hydrogen Bonding and Acidic Properties

As it has been mentioned earlier in the article, the experimentally determined enthalpy of solvation, according to the Figure 1, presented itself the sum of the enthalpy of non-specific solvation and of the specific interaction of the solute with the solvent (Eq. 12). The problem of the determination of ΔH_{solv} (nonspecific) for organophosphorus compounds (A_i) in many solvents (S) has been already solved; see Eq. 13 and Table V with the a_s and b_s solvation-coefficients.

Derivatives of phosphorus, possessing mobile hydrogen atoms, are able of specific interactions (hydrogen bonding) with the solvents, having lone electron pairs or π-systems. The differences between the values of solvation enthalpies experimentally found (obs.) and calculated using Eq. 13 (calc.) constitute the enthalpies of specific interaction (or hydrogen bonding). This approach has been applied to the system HPC-pyridine; the results are presented in Table XII.

TABLE XII Enthalpies in kJ mol^{-1} of Solution, Solvation, and Specific Interaction of Some HPC in Pyridine

Compound	ΔH_{soln} in pyridine	$-\Delta H_{\text{solv}}$ obs.	$-\Delta H_{\text{solv}}$ calc.	$-\Delta$H of specific interaction
(57)	−1.0	50.5	48.9	1.6
(62)	0.1	39.4	39.7	−0.3
(57)	10.4	49.2	46.5	2.7
(59)	−41.2	84.3	44.2	40.1

As it can be seen from the data in Table XII the acyclic and six-membered cyclic hydrophosphorylic compounds practically do not form hydrogen bonds with pyridine. Only five-membered cyclic phosphoric acid (**59**) exhibit the pronounced specific interaction with the mentioned solvent, forming not only the H-bond, but probably the charge transfer complexes: $>$P-O^{-} … HPy^{+}. The similar situation has been shown previously by the interaction of cyclic phosphoric acids with hexamethyldisilasane [(Me)$_3$Si]$_2$NH and triethylamine.[70]

As it was marked earlier, HPC belong to the class of H-donor derivatives of phosphorus, therefore for them the interaction with various *p*- or *n*-electron donor solvents is possible at the expense of hydrogen bonds (hb) with the P-H group. Hydrogen donor properties of the compounds of the elements of the fifth group of the Periodic system are investigated in detail only for the nitrogen derivatives.

So, the studies of the hydrogen exchange have shown, that at transition from amines to phosphines or from ammonium salts to phosphonium, the H-donor ability of the X—H bond decreases (X=N, P).[72] According to the ab initio calculations,[73] the absolute value of the hydrogen bond enthalpy of NH$_3$ with water is equal −17.0 kJ mol^{-1}, and the ΔH of PH$_3$-phosphine is much less −4.4 kJ mol^{-1} with the same solvent.

For the characteristic of the specific interaction enthalpy, especially when this interaction is weak enough, it is reasonable to use not only the method specified by us earlier, but also a sensitive thermochemical E. Arnett's method, so-called "pure base" method.[74] Main thermochemical equation of this approach is the Eq. 21:

$$\Delta H_{\text{hb}} = \left(\Delta H^{\text{A}}_{\text{soln}} - \Delta H^{\text{M}}_{\text{soln}}\right)_{\text{S}} - \left(\Delta H^{\text{A}}_{\text{soln}} - \Delta H^{\text{M}}_{\text{soln}}\right)_{\text{CCl}_4}, \tag{21}$$

where $\Delta H^{\text{A}}_{\text{soln}}$ and $\Delta H^{\text{M}}_{\text{soln}}$ are the solution enthalpies of acid A in the base-solvent S and their model compound M, in which the active hydrogen atom is replaced by methyl group with the assumption being made, that the non-specific solvation of the acid and model compound

TABLE XIII Solution and Hydrogen Bond (hb) Enthalpies in kJ mol^{-1} for Some Phosphoric Acids $RO_2P(O)H$[55,71]; the Numbers of the Model Compounds $RO_2P(O)Me$ of the Same Acids are Marked Using the Letter M

		ΔH_{soln}			$-\Delta H_{hb}$[a]	
Compound	R	CCl_4	Dioxane	Acetone	Dioxane	Acetone
1	**2**	**3**	**4**	**5**	**6**	**7**
		Acyclic Phosphoric Acids				
(62)	Me_2	4.4	—	0.5	—	1.9
M		2.7	—	0.7	—	—
(56)	Et_2	−0.2	—	−0.2	—	−0.8
M		0.9	—	0.1	—	
(63)	Pr_2	4.0	1.9	—	0.6	—
M		3.7	1.2	—		
(65)	Ph_2	5.9	—	−0.9	—	2.4
M		4.0	—	−0.2	—	
(66)	$(ClCH_2{-}CH_2)_2$	10.7	—	−0.4	—	3.9
M		7.6	—	0.4	—	
		5-Membered Cyclic Phosphoric Acids				
(60)	$(Me)_2C{-}C(Me)_2$	24.6	20.3	1.6	1.2	15.3
M		5.9	2.6			—
(61)	$o{-}C_6H_4$	−7.7	−28.1		19.0	
M[b]		0.7	0.7		—	
(59)	MeCH—CHMe	5.9	1.6	−24.0	1.9	23.5
M		4.7	2.3	−1.7		
(58)	$MeCH{-}CH_2$	3.2	—	−22.0	—	16.4
M		9.5	—	0.7	—	
		6- and 7-Membered Cyclic Phosphoric Acids				
(57)	$CH_2C{=}Me_2CH_2$	17.5	12.3	10.9	0.6	4.2
M		24.5	19.9	22.1		
(67)	$(CH_2)_3$	−6.1	2.0	—	0.6	—
M		−2.2	6.5	—		
(68)	$-C_6H_4{-}C_6H_4-$	22.6	—	15.8	—	5.2
M		16.9	—	15.3	—	

[a] Has been determined to be no worse than ±0.3–0.8 kJ mol^{-1}.

[b] For the acid (**61**) 2-methoxy-4,5-benzo-1,3,2-dioxaphospholane has been used as a model compound with P(III) atom.

with the solvent S in such inert medium as CCl_4 remains practically constant.

With the application of the specified approach the values of hydrogen bond enthalpies of hydrophosphorylic compounds with dioxane and acetone were determined. It is necessary to note, that the reaction between acetone and investigated HPC during the solution time ~10–15 sec does not occur; which is proved by a special NMR by experiment.[71] All values are submitted in the Table XIII.

As it has been shown by the calorimetric study, the enthalpy values of the hydrogen bonding of HPC with dioxane do not exceed 2 kJ mol^{-1}, which characterizes them as weak $(RO)_2(O)P$-H acids.[75] The interpretation of such small values, as well as of some magnitudes of ΔH_{hb} with pyridine, is rather difficult owing to a large experimental error. Thus, only the tendency of the absolute ΔH_{hb}-value to increase upon the transition from the acyclic and six-membered cyclic acids to five-membered cyclic acids is possible to establish. So, the highest H-donor ability respective to dioxane is displayed by 4,5-benzo-2-hydroxy-1,3,2-dioxaphospholane (**61**) which adopts the >P—OH form in the condensed phase and solutions according to NMR ^{31}P spectroscopy.[75,76] The formation energy of a complex with dioxane (−19.0 kJ mol^{-1}) is comparable to the energy of appropriate complexes of alcohols and phenols.[74]

The obtained values of the hydrogen bond formation enthalpies of HPC with acetone (Table XIII) essentially differ from each other 0–23 kJ mol^{-1}; the ΔH values for six-membered and seven-membered cyclic acids exceed the magnitudes of ΔH with dioxane. In some cases the small effects of interaction solute-solvent can be connected not only to forces of hydrogen bonding.[74] In conditions of calorimetric experiment the concentration of acids was made 10^{-2}–10^{-3} mol l^{-1}, that allows to exclude the contribution of the association into the enthalpy values of the hydrogen bonding of the solutes.

Other important factors can be conformational transformations especially for six-membered cyclic acids, with large dipole moments (Table X). The compounds (**57** and **57-M**, Table XIII) have been investigated in acetone and carbon tetrachloride in wide temperature range (203–383 K) with the use of NMR ^{1}H method for the determination of the contribution of the enthalpy of the conformational equilibrium into observed ΔH_{hb} values. The evaluation of conformational enthalpies (chair with equatorial and axial P=O positions) was made on the basis of the $^{1}J_{pocH}$ coupling constants of endocyclic methylene protons. ΔH_{conf} values were found to be equal for (**57**) 7.3 ± 0.8 and 5.0 ± 0.8, for (**57-M**) 7.4 ± 0.8 and 4.8 ± 0.4 kJ mol^{-1} in acetone and CCl_4 correspondingly.[71] These data allows to conclude, that the energy of the conformational transformations of acids and model compounds are identical and have no essential influence on the hydrogen bond enthalpy with acetone. It is possible to assume, that the conformational factors will be also identical for other investigated pairs: acid-model compound; for this reason all considered ΔH_{hb} values can be correctly attributed to formation of H-complexes (Table XIII).

The higher H-donor ability in acetone, as well as in dioxane is characteristic of five-membered cyclophosphoric acids, which is connected with the ring strain of 1,3,2-dioxaphospholane hydrophosphoryl system.[57]

The attempts to determine the acidic properties of cyclic and acyclic hydrophosphoryl compounds in water, organic solvent-water and non-aqueous media have been mentioned.[17,33,34] However, the high acidity found for five-membered analogues of phosphoric acids in water-alcohol medium has been explained by the hydrolytic cleavage of dioxyalkylene cycle at phosphorus atom. Nevertheless, the determination of the ionization constant (pK) of acid (**59**) with the use of the hydrogen-metal-substitution method in dry tetrahydrofurane (17.4), cyclohexylamine (16.8), ethelenediamine (16.4), and aniline (14.6) has shown the significant difference from the pK-magnitudes (20.9) of diethylphosphite (**56**) in the same solvents.[32,77] It is possible to describe the structure of ambident anions as $>P^{-}{=}O$ for acyclic and $>P{-}O^{-}$ for cyclic phosphoric acids correspondingly and to make more detailed thermochemical investigation of the tautomerism of hydrophosphoryl compounds with different molecular structure.

Enthalpies of Tautomeric Transformations

The data on enthalpy, free energy, and entropy of formation of both tautomeric forms ($>P(=O)H \Leftrightarrow >P{-}O{-}H$, **A** ⇔ **B**) of phosphoric acids is listed in the literature.[69] On the basis of these calculations the magnitudes pK_a of both forms in water and free energy of the tautomeric transformations (ΔG_{tt}) of hydrophosphorylic compounds have been determined by J. P. Guthrie[69] (Table XIV).

This is in a good agreement with the data of the studies of isotopic exchange of hydrogen by deuterium ($P{-}H \Leftrightarrow P{-}D$)[78,79] in water and with conclusion made on this basis about the extremely small content of the (**B**) form in the equilibrum mixture.

The energy of tautomeric transformation of dialkylphosphites was evaluated also with the use of the ion-cyclotron resonance data,[80] with form (**A**) being more stable in the opinion of the authors. It should be noted that the values of ΔG and ΔH essentially differ from the energy difference of the A and B forms, which is about 44–100 kJ mol^{-1}, obtained from the bond energies, formed by both tautomers.[3]

TABLE XIV The Calculated pK_a Values for Forms A and B and the Free Energies of Tautomeric Transformations in kJ mol^{-1} [69]

Equilibrium	Form (A) pK	Form (B) pK$_1$	pK$_2$	pK$_3$	ΔG_{tt} A ⇔ B
$(EtO)_2P(O)H \Leftrightarrow (EtO)_2P\text{-}OH$	13.0	6.1	—	—	41.0
$HO(EtO)P(O)H \Leftrightarrow EtOP(OH)_2$	—	6.7	11.3	—	49.8
$(HO)_2P(O)H \Leftrightarrow P(OH)_3$	—	7.4	11.9	14.0	59.0

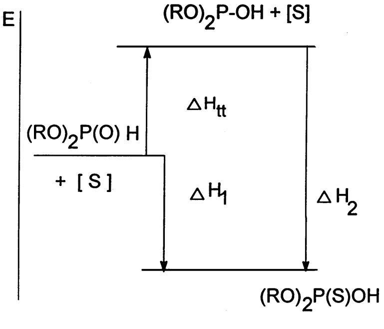


FIGURE 2 Thermochemical cycle of the interaction of the different tautomeric forms (**A** and **B**) of hydrophosphorylic compounds $(RO)_2P(O)H$ towards sulfur.

Taking into account all above mentioned results the experimental determination of the tautomerism enthalpy of HPC of the different structure using the calorimertry of reaction in solutions has been undertaken.[76]

M. Kabachnik and E. Golubeva[85] showed that hydrophosphorylic compounds interact with rhombohedral sulfur in the solution through tautomeric form (B) forming thiophosphorus acids:

$$(RO_2P(O)H \rightarrow RO_2P\text{—}OH) + [S] \text{ ---------}\rightarrow RO_2P(S)OH + \Delta H_1.$$

The cyclic phosphoric acids react with elementary sulfur in the same manner.[81] This situation can be illustrated by a thermochemical cycle in the Figure 2.

the enthalpy of tautomeric transformation is determined as a difference between the reaction enthalpies of hydrophosphorylic compound and sulfur in the forms (**A**) and (**B**) (Eq. 22):

$$\Delta H_{tt} = \Delta H_1 - \Delta H_2 \tag{22}$$

The heat of reaction (ΔH_1) of tautomer (**A**) with sulfur has been calorimetrically measured at 363–373 K; sulfur does not change their rhombohedral modification in such conditions.[82] The interaction enthalpy of tautomer (**B**) with sulfur (ΔH_2) can not be directly determined due to the unstability of enol form in such conditions, therefore this transformation has been modelled by the determination of the reaction heat of the corresponding esters of phosphites with sulfur:

$$RO_2POEt + [S] \rightarrow RO_2P(S)OEt + \Delta H_2.$$

Because there are some calculated values of the tautomeric transformation energy of dialkylphosphites[69,83,84] in solutions, it was reasonable to determine this important thermochemical parameter in the

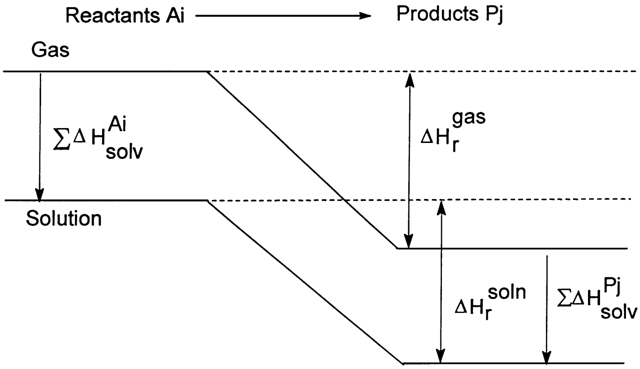


FIGURE 3 The thetmochemical cycle for the reaction Ai → Pj in the solution and the gaseous phase.

absence of the influence of solvent (p-xylene), i.e., in the gaseous phase. It is known that the reaction enthalpy (ΔH_r) in the gaseous phase can be expressed by Eq. 23 or Figure 3.[57]

$$\Delta H_r(\text{gas}) = \Delta H_r(\text{xyl}) - \Sigma\Delta \text{H}_{\text{solv}}(\text{products}) + \Sigma\Delta \text{H}_{\text{solv}}(\text{reagents}) \quad (23)$$

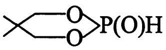
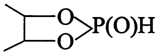
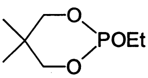
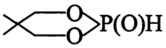
Combining Eqs. 22 and 23, the Eq. 24 can be obtained, according to which the tautomeric transition enthalpy in the gaseous phase is represented as a difference of the heats ΔH_1 and ΔH_2 in p-xylene and algebraic sums of solvation enthalpies of all products and reagents of both reactions:

$$\begin{aligned}\Delta H_{tt}(\text{gas}) = {} & \Delta H_1(\text{xyl}) - \Delta H_2(\text{xyl}) - \Delta H_{\text{solv}}[\text{RO}_2\text{P(S)OH}] \\ & + \Delta H_{\text{solv}}[\text{RO}_2\text{P(O)H}] + \Delta H_{\text{solv}}[\text{RO}_2\text{P(S)OEt}] \\ & - \Delta H_{\text{solv}}[\text{RO}_2\text{POEt}]. \qquad (24)\end{aligned}$$

Because the reaction enthalpies have been measured at 363–373 K it will be more correct to take into consideration the heat capacities (C_p) for all participants of both processes (according to Kirchhoff"s equation[44]). The absence of required C_p data for all investigated compounds in literature can be compensated by taking the values in Eq. 24 and to suppose the calculated values of ΔH_{tt} (gas) in the comparable row of substances to be acceptable for consideration. The reaction and solvation enthalpy values of phosphorus containing derivatives are listed in Tables XV and XVI.

It can be seen from the data in Table XV that ΔH_{tt} values for dioxaphosphorinane and acyclic acids (**56** and **57)** are practically identical within the range of experimental errors. Moreover, the observed

TABLE XV The Reaction Enthalpies (ΔH_1 and ΔH_2) of Phosphoric Acids and Phosphites with Sulfur in kJ mol^{-1} in *p*-xylene and Enthalpies of Tautomeric Transformation in the Gaseous Phase

Compound	Formula	T, K	ΔH_1 and ΔH_2 (*p*-xylene)	ΔH_{tt}[a] (gas)
(57)		368–373	17.6	61.4
(59)		368–373	20.5	37.3
(56)	$(EtO)_2P(O)H$	363	47.7	68.0
(69)		363	62.8	—
(70)		363	27.2	—
(71)	$(EtO)_3P$	363	91.2[b]	—

[a] Thermochemical data for majority of compounds and methods of its determination were previously published.[55,57,76]

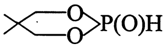
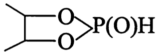
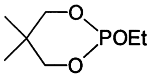
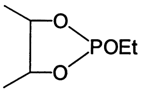
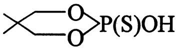
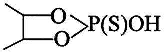
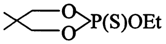
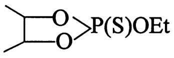
[b] $\Delta H_r = -110.4$ kJ mol^{-1} for solid sulfur and liquid phosphite.[86]

values are rather close to the calculated magnitude of the tautomeric transformation energy (44–100 kJ mol^{-1}) which has been obtained on the basis of approximate bond energies of both tautomeric forms;[3] this corresponds to the existence of this type of compounds in the gaseous phase in a stable form (**A**) with a tetra-coordinated phosphorus atom.

The enthalpy of tautomeric transition for five-membered cyclic analogue (**59**) is almost twice smaller than the values for acids (**56** and **57**). This fact is in a good agreement with the assumption about the weaker P—H bond in phospholane derivatives (reduced pK$_a$ and higher ΔH_{hb} magnitudes) and indicates their easy transformation from keto-structure into enol form.

Thus, as it follows from the experimental data of the tautomeric transition enthalpies of the hydrophosphorylic compounds of different spatial structure, the acyclic and six-membered cyclic phosphoric acids exist in form (**A**). As regards the five-membered cyclic analogue, a ring strain (about 25 kJ mol^{-1}),[57] an acceptor ability of 1,2-dioxyalkylene substituents at phosphorus together with geometric factors of molecule assist their transformation from (**A**) into (**B**). The change of the configuration of phosphorus atom from sp^3 to p^3 is connected with the change of valence angle from 109 to 90°. The inner O—P—O angle in five-membered cycles is essentially decreased (98–100°) respective to this

TABLE XVI The Solution, Vaporization and Solvation (in kJ mol^{-1}) for the Reactants and Products of the Reaction of Acids **(56, 57, 59)** and Phosphites **(69–71)** with the Sulfur[a]

Compound	Formula	$-\Delta H_{soln}$	ΔH_{vap}	$-\Delta H_{solv}$
(57)		14.4	60.3	45.9
(59)		4.3	43.1	38.8
(56)	$(EtO)_2P(O)H$	2.3	49.5	47.3
(69)		0.2	52.8	52.6
(70)		0.0	50.1	50.1
(71)	$(EtO)_3P$	−1.2	53.0	54.2
(72)	**$(EtO)_3P$** 	43.8	121.8	78.0
(73)		42.0	126.6	84.6
(74)	$(EtO)_2P(S)OH$	20.4	104.9	84.5
(75)		19.2	88.4	69.2
(77)	$(EtO)_3P(S)$	−0.5	66.6	67.1
(76)		1.2	66.2	65.0

[a] Thermochemical data for the majority compounds and the method of determination of their were peviously published.[55,57,76]

value in six-membered or acyclic analogues (104–106°).[14] This circumstance makes the mentioned tautomeric transformation more reliable. The similar possibility of such “sterical assistance” has been observed when investigating keton-enol tautomerism of cyclic ketones.[87]

The Formation Enthalpies and the Heats of Reactions

The enthalpies of formation as well as the enthalpies of vaporization of many organophosphorus compounds are very important magnitudes in thermochemistry of heteroatomic compounds and are often used for the calculation of the bond energies. For many substances this energetic term is not yet determined experimentally or due to the technical difficulties can not be determined in general. In this case it is reasonable to use methods of calculation of it based, as a rule, on the Benson's additive scheme, which is based on the use of experimental data obtained earlier.[43] It is necessary to note that the determination of the contributions of various groups for the calculation of the formation enthalpies of the esters of hydrophosphorylic compounds in a gas phase is restricted by a small number of the experimental data being present in literature.[43,44]

As a starting material for the determination of the formation enthalpy of HPC the halides of phosphoric acids of the different spatial structure can serve. It is well known,[2–4] that the halides of phosphoric acid easily undergo exothermic hydrolysis in water at room temperature in accordance with Eq. 25:

$$\mathrm{R_{3-n}(O)PCl_n + H_2O \rightarrow R(OH)_{3-n} + H_3PO_3 + nHCl} + \Delta H_{\mathrm{hydr}}, \qquad (25)$$

where R is alkyl or alkylene and n is equal 1 or 2.

Taking from the literature the formation enthalpy values for water, alcohols, phosphoric acid, and aqueous hydrogen chloride,[93] it is possible to calculate the formation enthalpies for the corresponding halides according to the Hess-law[44] (Eq. 26):

$$\Delta H_{\mathrm{hydr}} = \Sigma \Delta H_{\mathrm{f}}^{\mathrm{o}}\,(\text{products}) - \Sigma \Delta H_{\mathrm{f}}^{\mathrm{o}}\,(\text{reagents}). \qquad (26)$$

These values have been used for the determination of the heats of the hydrolysis reaction and for the calculation of the formation enthalpies of some acyclic and five- and six-membered cyclic halides of phosphoric acid[56,57,88] (Table XVII).

The next stage on the way to experimental determination of the formation enthalpy values of hydrophosphorylic compounds was the partial hydrolysis (p.hydr(exp)) of cyclic halides in dioxane at 298.15 K in the presence of triethylamine as the acceptor of hydrogen chloride[91] (Eq. 27).

$$\begin{aligned}&\mathrm{RO_2PCl(liq) + H_2O(soln) + Et_3N(soln) \rightarrow RO_2P(O)H(soln)}\\&\quad \mathrm{+\,Et_3N \cdot HCl(solid)} + \Delta H_{\mathrm{p.hydr}}. \qquad (27)\end{aligned}$$

Taking into account the solution enthalpies of all reagents and products in dioxane (Table XIII) and their formation enthalpies in condensed state,[92,93] the formation enthalpies of the five- and six-membered HPC in the condensed phase have been calculated; the formation enthalpies of the same phosphoric acids were calculated using the Eq. 17 (Table XVIII).

TABLE XVII The Enthalpies of Hydrolysis, Vaporization and Formation in kJ mol^{-1} of P(III) Halides at the Standard Conditions, T 298.15 K[57,88,89]

				$-\Delta H_f^o$	
No	Compound	ΔH_{vap}	$-\Delta H_{hydr}$ (water)	(liq. or solid)	Gas
		Acyclic Halides			
(78)	$MeOPCl_2$	37.3	218.0	455	418.2 ± 7.1
(79)	$EtOPCl_2$	40.4	—	501.5[a]	461.1 ± 2.1
(80)	$PrOPCl_2$	45.2	208.4	532.7	487.5 ± 7.0
(81)	$BuOPCl_2$	48.9	207.9	556.6	507.7 ± 9.6
(82)	$PhOPCl_2$	57.4	212.5	367.2	309.8 ± 8.3
(83)	$(EtO)_2PCl$	48.5	—	683.2[a]	
		Five and Six-Memebered Cyclic Halides R(O)$_2$PCl			
(84)	CH_2CH_2	40.5	124.4	598.3	557.8 ± 4.2
(85)	CH_2CHMe	41.4	126.6	630.2	588.8 ± 5.4
(86)	MeCHCHMe	44.9	132.6	684.9	640.0 ± 6.7
(87)	$Me_2C\text{-}CMe_2$	48.0	140.6	743.1	695.1 ± 8.4
(88)	o-C_6H_4	52.3[b]	128.9	479.2	431.0 ± 5.0
(89)	$(CH_2)_3$	44.5	78.6	655.6	611.1 ± 7.5
(90)	$(CH2)_2CHMe$	47.1	78.2	693.7	646.6 ± 8.4
(91)	$CH_2C(Me)_2CH_2$	47.0	89.3	713.4	666.4 ± 10.0

[a] Calculated using the thermochemical data of reaction $PCl_3 + (EtO)_2CHMe$.[89]
[b] Data from Ref. 90.

The above mentioned H-donor and acidic properties as well as the formation enthalpies of hydrophosphorylic compounds, especially with the cyclic structure, allow to consider them as electrophilic reagents able to enter reactions with unsaturated ogranic compounds. Thus, the kinetics and thermochemistry of the nitrogen-elimination reaction (NER) of

TABLE XVIII The Partial Hydrolysis and Formation Enthalpies in kJ mol^{-1} of $RO_2P(O)H$, the Numbers of Which Correspond to the Numbers of the Previous Tables[91]

		$-\Delta H_f^o$	
Compound	$-\Delta H_{p.hydr.}$ (exp. in dioxane)	Gas phase exp.[a]	Condenced pase Calc.
(56)	—	877.4 ± 14.2[b]	926.9
(57)	192.7	867.0 ± 18.7	928.0
(58)	182.8	805.7 ± 13.7	845.5
(59)	192.4	866.1 ± 11.7	909.2

[a] The experimental error were calculated using the errors of solution and partial hydrolysis.
[b] Data from Ref. 69.

HPC with diphenyldiazomethane (DDM) have been investigated previously, and high activity of five-membered cyclic acids towards acyclic and six-membered cyclic analogues has been shown (Eq. 28):[94]

$$\mathrm{RO_2P(O)H(soln) + N_2CPh_2(soln) \rightarrow RO_2P(O)CHPh_2(soln) + N_2(gas) + \Delta \mathit{H}_{NER}} \quad (28)$$

$$(\mathbf{57}, \mathbf{59}, \mathbf{60}, \mathbf{65}) \qquad (\mathbf{92}) \qquad (\mathbf{93} - \mathbf{96})$$

$(\mathbf{57}, \mathbf{93})$: $\mathrm{R{=}CH_2C(Me)_2CH_2}$; $(\mathbf{59}, \mathbf{94})$: $\mathrm{R{=}MeCHCHMe}$;

$(\mathbf{60}, \mathbf{95})$: $\mathrm{R{=}(Me)_2CC(Me)_2}$; $(\mathbf{65}, \mathbf{96})$: $\mathrm{R{=}Ph_2}$.

This process has been studied in *p*-xylene at 298.15 K. However, only at the present time it is possible to calculate the processes enthalpy in the gaseous phase (Eq. 23), using the knowledge of the calculated solvation enthalpy in solutions (Table V). The required calculations according the presented procedure have been made and all results are listed in Table XIX.

Hydrophosphorylic compounds also can serve as precursors for the synthesis of such important substances as α-aminophosphonic derivatives, which have useful biological and medical properties like aminoacids.[95] Some ways of the synthesis of α-aminophosphonates (toward P=O group) have been based on the addition reaction of hydrophosphorylic compounds to unsaturated species with C=N bond (CNR)[96] (Eq. 29) and on the non-catalyzed electrophilic ($\mathrm{A_dE}$) Pudovik-reaction (PR), i.e., the interaction of cyclic and acyclic phosphoric

TABLE XIX The Solvation and Reaction Enthalpies in kJ $\mathrm{mol^{-1}}$ of the Interaction of Acids (**57, 59**, **60, 65**) with DDM (**92**); *p*-xylene, 298.15 K[94]

Compound	$\mathrm{MR_D}$, $\mathrm{cm^3\ mol^{-1}}$	$-\Delta H_{\mathrm{solv}}{}^{a}$ (*p*-xylene)	$-\Delta H_{\mathrm{NER}}$ *p*-xylene	$-\Delta H_{\mathrm{NER}}$ gas phase
(57)	34.0	43.2	70.5	85.8 ± 3.1
(59)	30.1	38.8	97.9	111.3 ± 3.9
(60)	38.6	43.3	101.3	117.0 ± 4.1
(65)	62.2	78.9	82.8	98.2 ± 3.4
(92)	57.8	72.4	—	—
(93)	86.8	100.3	—	—
(94)	82.9	97.8	—	—
(95)	91.4	100.0	—	—
(96)	115.0	135.9	—	—

[a] Calculated using the equation $\Delta H_{\mathrm{solv}} = 11.7 + 1.08\ \mathrm{MR_D}$ from Table V.

acids with enamines containing the morpholine fragment (OC_4H_8N) (Eq. 30):[97–100]

$$(MeO)_2P(O)H(soln) + MeCH{=}CH{-}CH{=}NC_6H_{11}\text{-cyclo}(soln) \rightarrow$$

(**62**) (**97**)

$$(MeO)_2P(O)CH(CH{=}CHMe)NHC_6H_{11}\text{-cyclo}(soln) + \Delta H_{CNR} \qquad (29)$$

(**98**)

$$RO_2P(O)H(soln) + R_1(OC_4H_8N)C{=}CR_2^2(soln) \rightarrow$$

(**56**, **57**, **59**) (99, 100)

$$RO_2P(O)CR_2^2(NC_4H_8O)R_1(soln) + \Delta H_{PR} \qquad (30)$$

(**101–105**)

(**99**): $R_1{=}H$, $R_2{=}Me$; (**100**): $R_1{=}Ph$, $R_2{=}H$; (**56,101**): R=2 Et, $R_1{=}H$, $R_2{=}Me$; **(57,102)**: $R{=}CH_2C(Me)_2CH_2$, $R_1{=}H$, $R_2{=}Me$; (**59,103**): R=MeCHCHMe, $R_1{=}H$, $R_2{=}Me$; (**57,104**): $R{=}CH_2C(Me)_2CH_2$, $R_1{=}Ph$, $R_2{=}H$; (**59,105**): R=MeCHCHMe, $R_1{=}Ph$, $R_2{=}H$.

The enthalpies of reaction (30) have been measured in hexane and carbon tetrachloride at 298 K; the ΔH_{soln}, ΔH_{solv}, ΔH_{vap} and ΔH_{CNR} for this interaction were calculated according to Figure 1 and Eqs. 18 and 23 (Table XX).

In previous work,[100] the results of the study of thermochemistry of noncatalyzed Pudovik-reaction are presented. The reaction enthalpies in solution and gaseous phase have been calculated on the basis of the known data of solution, vaporization, and solvation enthalpies of all reagents and products of the reaction (30) in *p*-xylene[55,100] (Table XXI).

From the series of the data (ΔH_{PR} in *p*-xylene and in the gaseous phase) for acids with enamine (**99**) it seems surprising, that the enthalpy of the reaction (**59** + **99**) in *p*-xylene and in the gas phase is almost twice as large (about 40 kJ mol^{-1}) as the value of ΔH_{PR} for

TABLE XX Thermochemical Data in kJ mol^{-1} for the Interaction (29)[96]

	ΔH_{soln}			$-\Delta H_{solv}$		$-\Delta H_{CNR}$	
Compound	Hexane	CCl_4	ΔH_{vap}	Hexane	CCl_4	Solution	Gas
(62)	11.5	4.4	39.5	28.0	35.1	117.2 (hexane)	
(97)	3.2	−2.2	58.3	55.1	60.5	124.5 (CCl_4)	126.2 ± 4.4
(98)	15.7	−4.1	89.8	74.1	93.9	—	—

TABLE XXI The Reaction Enthalpies in kJ mol^{-1} Between Phosphoric Acids (**56, 57, 59**) and Enamines **(99, 100)** (Eq. 30) in *p*-xylene and in the Gaseous Phase

Reaction (No. of Reactants)	$-\Delta H_{\mathrm{PR}}$						
	T, K						
	298	323	343	358	363	373	Gas
(56 + 99)				25.2			34.9 ± 2.5
(57 + 99)				26.4			39.0 ± 2.0
(59 + 99)		67.0					79.3 ± 3.5
(57 + 100)	48.5[a]				32.9	30.5	65.3 ± 3.5
(59 + 100)	72.3[a]	59.3	48.9				87.9 ± 4.5

[a] Recalculated values.

(**56** + **99**) and (**57** + **99**) processes. As it has been shown previously (see Table XIX), the difference in enthalpies of the reactions of acids (**59** and **57**) with DDM in *p*-xylene at 298.15 K was only about 15 kJ mol^{-1}.

As it appeared, the explanation of such differences in the magnitudes of $\Delta\Delta H_{\mathrm{PR}}$ of acids (**59** and **57**) with enamine (**99**) at 323–358 K and $\Delta\Delta$H with DDM at 298.15 K could be done from the point of view of the dependence of the thermal effect of the reaction on the temperature according to Kirchhgoff's equation in the simplest form (Eq. 31).[44]

$$\Delta H_{\mathrm{T}} = \Delta H_{\mathrm{T1}} + \Delta \mathrm{C_p}(\mathrm{T} - \mathrm{T_1}). \tag{31}$$

For this reason the following reaction series between acids (**59** and **57**) and enanime (**100**) has been conducted at different temperatures (Table XXI).

It is necessary to note, that the enthalpies of reactions of both processes, mentioned above, decrease essentially in the absolute magnitude with the increasing of the temperature of the thermochemical experiment. Probably it could be connected with the convertible decomposition of products (**103** and **104**) with the increasing of temperature. However, the products of reaction, allocated at these temperatures, had the same characteristics, which are known in the literature:[99] (**103**): m.p. 169–171°C, δ_{p} 42 ppm, $\nu_{\mathrm{p—o}}$ 1250 cm^{-1}; (**104**): m.p. 106–108°C, δ_{p} 19 ppm, $\nu_{\mathrm{p=o}}$ 1245 cm^{-1}.

These results testified the complete realization of reactions in specified intervals of temperatures (323–348 K for **59** + **100** and 363–373 K for **57** + **100**) and served as a basis for the estimation of the heat capacities (ΔC_{p}) of both reaction systems using Eq. 31. The estimated average values of $\Delta \mathrm{C_p}$ for both processes are equal 520 and 240 J mol^{-1} K^{-1}

correspondingly. The latter values allow to calculate the magnitudes of ΔH_{PR} at 298 K in *p*-xylene and using the dependence (23)—for the gaseous phase. As it is seen from the data in Table XXI the difference between the ΔH_{PR} (**59** + **100**) and (**57** + **100**) is about 24 and 23 kJ mol^{-1} for solution and gaseous phase accordingly, that essentially differs from similar results for a series of reactions of the same acids with enamine (**99**).

CONCLUSIONS

Thus, the thorough consideration of the thermochemical data for organophosphorus compounds containing phosphorus-hydrogen bonding and phosphorus atoms with different coordination allows to make the following important conclusions:

- The applicability of the Truton, Wadso equations as well as of the molar solvation index of the first order for the calculation of the vaporization enthalpy of primary and secondary phosphines of various structures has been shown. On the other hand, the Solomonov-Konovalov equation can be successfully used for the determination of the heats of vaporization of the solute in inert solvents (hexane, carbon tetrachloride, *p*-xylene) of phosphines and hydrophosphorylic compounds having high molecular weights and boiling points.
- The methods of calculation of nonspecific solvation of the considered classes of P(III, IV) compounds are developed. Thus, the dependence of the solvation enthalpy values on the molar refractions of solutes and at the same time the knowledge of nonspecific solvation of solute-solvent opens the opportunity to calculate the contribution of specific solvation (hydrogen bond or donor-acceptor interactions) into the general solvation effect. The large number of the hydrogen bond enthalpy values has been determined using solution calorimetry.
- The solvation enthalpy magnitudes open wide possibilities for more detailed interpretations of heat values, such processes as tautomeric transformations and substitution and addition reactions of hydrophosphorylic compounds in solvents and in the gaseous phase, which are of importance for the technical evaluation of the substances with useful properties. Nevertheless, it is necessary to note that a very small number of the data on the heat capacity for compounds with P(III) and P(IV) atoms.
- All presented in this review, allow not only to significantly enrich the database of the thermochemical data of organophosphorus compounds but also to allow the calculation of the group contributions for

$-PH_2$, $>PH$ fragments into vaporization and formation enthalpies. The latter can be useful for the calculation of thermochemical functions of new practically important compounds such as water soluble phosphines, phosphorylated sugars, proteins, and others.

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