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The standard vaporization and formation enthalpies of tetracoordinated phosphorus derivatives
The phosphonic and phosphoric acids derivatives

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Abstract

The standard vaporization enthalpies of more than 50 phosphonic and phosphoric acids derivatives have been collected or determined according to their solution enthalpies in hexane or carbon tetrachloride. The formation enthalpies of compounds of the same series have been determined according to their reaction heat effects. Using the thermochemical data obtained, some group contributions of vaporization enthalpy and formation enthalpy in gas phase of tetracoordinated phosphorus compounds have been estimated and suggested for theoretical calculation of the enthalpies.

Keywords: Enthalpy; Vaporization; Formation; Tetracoordinated phosphorus compounds; Group contributions

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1. Introduction

The derivatives of a tetracoordinated phosphorus atom are known to posses many useful properties [1,2]. The acquisition of quantitative characteristics connected with the reactivity of these compounds would be very useful. The thermochemical parameters associated with vaporization and formation, are the essential properties for the determination of the strength of the chemical bonds associated with phosphorus. However, the acquisition of experimental thermochemical data in the field of organophosphorus chemistry is difficult, and in most cases it is practically impossible. That is why it is very important to provide the methods of calculation of the thermochemical characteristics of organic and organoelement compounds [3–10].

Only few works have been published in the area of calculation of thermochemical characteristics of organophosphorus compounds [3,6,11,12]. In the present article, we have undertaken an attempt to gather practically all previously published and currently obtained data on thermochemistry of alkylphosphonic acids, their esters and halides, and also on dialkylphosphoric acids. As it was reliably established [13], the last ones also have a form with tetracoordinated phosphorus atom both in the solutions and in the gas phase.

2. Experimental

The solution enthalpies of compounds were measured at 298 K using a differential calorimeter constructed according to the Arnett–Rodgers scheme [14,15]. Methods of measurement have been previously described [16]. The ranges of concentration were 10^{-3}–10^{-2} mol l^{-1} for liquid substances and (1–3) × 10^{-3} mol l^{-1} for solids. The measured values have a magnitude with an accuracy of 0.3–0.5 kJ mol^{-1} for liquids and 0.5–0.7 kJ mol^{-1} for solid products. This is taken as a result of the mean value of 3–6 experiments.

The reactions heats were measured using the differential microcalorimeter Calvet type DAC-1-1 in p-xylene or carbon tetrachloride at 298 or 343 K (±0.05 K). The reaction heat is the mean value of 3–5 experiments. The working volume of the glass vessels was 5 cm^3. The heat capacities of the compounds were determinated using a DSC-111 "Setaram" in aluminic cells with constant increase of temperature from 310 to 370 K and with the rate of 3 K/min. The accuracy of heat capacity measurement was 1.3%.

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Table 1
Experimental and calculated enthalpies of vaporization and formation in the condensed and gas phases of tetracoordinated phosphorus derivatives, kJ mol^{-1}

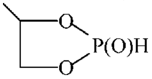
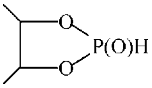
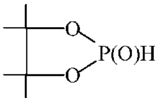
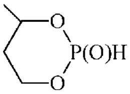
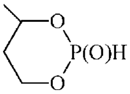
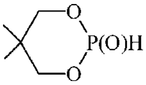
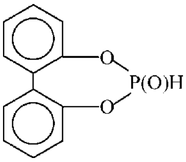
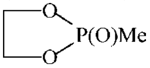
No.	Formula	ΔH_v°		ΔH_f°			
				Gas phase		Condensed phase	
		Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
	2	3	4	5	6	7	8
Phosphoric acids							
1	$(MeO)_2P(O)H$	39.5[a] *	39.5	–	−811.9	–	−851.4
2	$(EtO)_2P(O)H$	49.3[b] 49.5[a]*	45.7	−877.4[b]	−883.0 −877.4[c]	−926.7[b]	−928.7
3	$(PrO)_2P(O)H$	57.0[a]*	55.2	–	−924.4	–	−979.6
4	$(i\text{-}PrO)_2P(O)H$	51.3[a]*	50.0	–	−954.8	–	−1004.8
5	$(PhO)_2P(O)H$	82.1[a]	86.7	–	−604.5	–	−691.2
6	$(ClCH_2CH_2O)_2P(O)H$	65.7[a]	67.9	–	−929.2	–	−997.1
7		39.8[a]*	41.6	−806.0 ± 33.0*	−809.4	−845.8	−851.0
8		43.1[a]*	43.8	−866.0 ± 28.0*	−845.3	−909.1	−889.1
9		67.3[a]	49.5	–	−926.3	–	−975.8
10		32.1[a]	44.2	−845.0 ± 35.0	−815.2	−877.1	−859.4
11		60.7	46.4	−844.0 ± 31.0*	−851.1	−904.7	−897.5
12		60.3[a]	49.8	−867.0 ± 45.0*	−876.7	−927.3	−926.5
13		95.9[a]	106.1	–	−590.6	–	−696.7
Phosphonic acids and phosphonates							
14	$(HO)_2P(O)Me$	48.1[d] *	46.9	−1006.3 ± 26.4[d]	−1002.4 −1002.5[c]	−1054.4 ± 25.9[d]	−1049.3
15	$(HO)_2P(O)Et$	50.6[d] *	51.7	−1007.9 ± 14.6[d]	−1016.6 −1016.7[c]	−1058.5 ± 14.2[d]	−1068.3
16	$(HO)_2P(O)C_{10}H_{21}\text{-}n$	–	89.9	–	−1182.3	−1235.9 ± 14.2[e]	−1272.2
17	$(HO)_2P(O)Ph$	–	71.4	–	−826.8	−889.5 ± 10.9[f]	−898.2
18	$(HO)(i\text{-}PrO)P(O)Me$	60.7[g]	51.7	–	−1014.4 −1014.2[c]	–	−1066.1
19	$(MeO)_2P(O)Me$	42.4[a]	45.9	–	−883.4	–	−929.3
20	$(EtO)_2P(O)Me$	56.5[d] 52.2[a]*	52.1	−969.8 ± 27.6[d]	−954.5 −954.4[c]	−1026.3 ± 27.2[d]	−1006.6
21	$(EtO)_2P(O)Et$	56.0[a] *	56.8	–	−968.8	–	−1025.6
22	$(PrO)_2P(O)Me$	61.6[a] *	61.6	–	−996.0	–	−1057.6
23	$(i\text{-}PrO)_2P(O)Et$	60.7[d]	61.2	−1056.0 ± 17.1[d]	−1040.6 −1040.5[c]	−1116.7 ± 16.3[d]	−1101.8
24	$(PhO)_2P(O)Me$	84.2[a]	93.1	–	−676.1	–	−769.2
25	$(ClCH_2CH_2O)_2P(O)Me$	67.4[a]	74.2	–	−1000.7	–	−1074.9
26		46.0 *	45.8	−874.0 ± 32.0[h]	−845.1	−920.0[h]	−890.9

Table 1 (*Continued*)

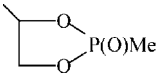
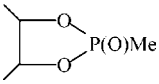
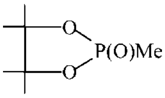
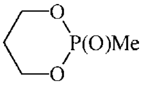
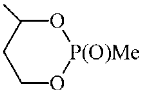
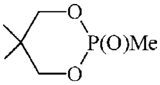
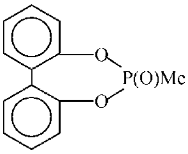
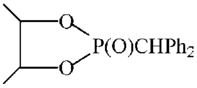
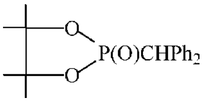
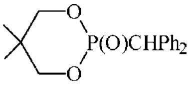
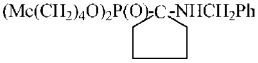
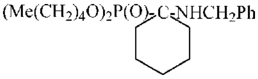
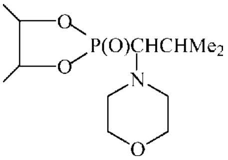
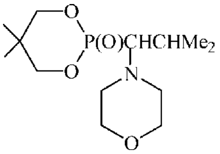
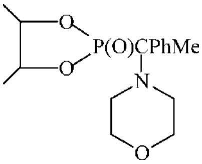
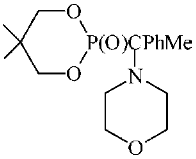
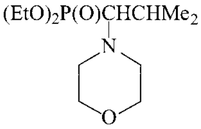
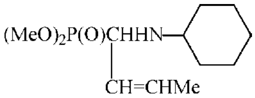
No.	Formula	ΔH_v°		ΔH_f°			
				Gas phase		Condensed phase	
	2	Experimental 3	Calculated 4	Experimental 5	Calculated 6	Experimental 7	Calculated 8
27		50.6[a] *	48.0	−911.0 ± 29.0[h] −916.0 ± 34.0[i]	−881.0	−961.6[h] −966.6[i]	−929.0
28		49.8[a] *	50.1	−962.0 ± 29.0[h] −972.0 ± 33.0[i]	−916.9	−1011.8[h] −1021.8[i]	−967.0
29		53.9[a] *	55.8	−1006.0 ± 25.0[h] −1027.0 ± 36.0[i]	−997.9	−1059.9[h] −1080.9[i]	−1053.7
30		40.6[a]	50.5	−901.0 ± 30.0[i]	−886.7	−941.6[i]	−937.2
31		39.9	52.7	−926.0 ± 31.0[i]	−922.6	−965.9[i]	−975.3
32		72.0[a]	56.2	−960.0 ± 32.0[i]	−948.3	−1032.0[i]	−1004.5
33		94.9[a]	112.5	–	−662.2	–	−774.7
34	$(PhO)_2P(O)CH(Ph)_2$	–	149.5	−471.9*	−457.7	–	−607.2
35		–	106.6	−746.4*	−698.5	–	−805.1
36		–	112.3	−811.5*	−779.5	–	−891.8
37		–	112.6	−720.9*	−729.9	–	−842.5
Chloranhydrides of phosphonic acids							
38	$(i\text{-}PrO)ClP(O)Me$	58.6[g] *	58.6	−797.1[c] *	−797.2 −797.1[c]	−855.7	−855.8
39	$Cl_2P(O)Me$	62.3[d] *	62.3	−556.9 ± 26.4[d] *	−556.8 −556.9[c]	−619.2 ± 25.9[d]	−619.1
40	$Cl_2P(O)Et$	42.7[d]	67.1	−570.7 ± 14.6[d] *	−571.0 −571.1[c]	−613.4 ± 13.8[d]	−638.1
α-Aminophosphonates							
41	$(EtO)_2P(O)CHPhNHMe$	89.4	93.2	–	−819.8	–	−913.0
42	$(PrO)_2P(O)CHPhNHMe$	99.3*	102.7	–	−861.2	–	−963.9
43	$(i\text{-}PrO)_2P(O)CHPhNHMe$	94.2*	97.5	–	−891.6	–	−989.1
44	 $(Me(CH_2)_4O)_2P(O)\text{-}C\text{-}NHCH_2Ph$	138.7	138.1	–	−978.9	–	−1117.0
45	 $(Me(CH_2)_4O)_2P(O)\text{-}C\text{-}NHCH_2Ph$	143.4	142.9	–	−1020.5	–	−1163.4
46	$(EtO)_2P(O)CMe_2NHCH_2Ph$	103.2	102.7	–	−881.2	–	−983.9
47	$(EtO)_2P(O)CMe_2NHPr\text{-}i$	80.0*	80.5	–	−1051.8	–	−1132.3

Table 1 (*Continued*)

No.	Formula	ΔH_v°		ΔH_f°			
				Gas phase		Condensed phase	
	2	Experimental 3	Calculated 4	Experimental 5	Calculated 6	Experimental 7	Calculated 8
48		99.2[a]	87.6	−1070.1[j]	−1105.1	−1169.3[j]	−1192.7
49		99.0[a]	93.6	−1030.7[k]	−1136.5	−1129.7[k]	−1230.1
50		96.3[l]	104.9	−952.3*	−954.5	−1048.6	−1059.4
51		107.0[l]	111.0	−930.6*	−985.9	−1037.6	−1096.9
52		88.4[a] *	89.5	−1037.0[k]	−1142.7	−1125.4[k]	−1232.2
53		89.8[m]	94.9	−903.9*	−890.0	−993.7	−984.9
α-Hydroxyphosphonates							
54	$(EtO)_2P(O)CH_2OH$	48.3*	48.7	–	−1106.4	–	−1155.1
55	$(PrO)_2P(O)CH_2OH$	58.2*	58.2	–	−1147.8	–	−1206.0
56	$(i\text{-}PrO)_2P(O)CH_2OH$	52.8*	53.0	–	−1178.2	–	−1231.2
57	$(EtO)_2P(O)CHMeOH$	50.8*	50.8	–	−1142.3	–	−1193.1
58	$(EtO)_2P(O)CHEtOH$	55.8*	55.6	–	−1163.0	–	−1218.6
59	$(EtO)_2P(O)CHPhOH$	75.1*	75.3	–	−1008.1	–	−1083.4

The compounds values marked by asterisk (*) was used for the evaluation of group contributions of phosphorus containing and some other molecular fragments in vaporization and formation enthalpies.

[a] Data from Ref. [22].

[b] Data from Ref. [23].

[c] Data from Ref. [3].

[d] Data from Ref. [20].

[e] Data from Ref. [24].

[f] Data from Ref. [25].

[g] Data from Ref. [26].

[h] Data were obtained using Scheme 3.

[i] Data were obtained using Scheme 4.

[j] ΔH_f at 323 K.

[k] ΔH_f at 358 K.

[l] Data from Ref. [27].

[m] Data from Ref. [28].

The reaction completion was measured by gas–liquid chromatography methods on Chrom-5D apparatus (adsorbent Chromaton N Super 0.160–0.200 mm, saturated with the phase of 3% OV-17, the column length is 1.5 m, gas-support is helium with the pressure of 0.4 atm) and by ^{31}P nuclear magnetic resonance on Varian Unity-300 apparatus with the frequency on phosphorus of 121 MHz.

All compounds were synthesized and purified by previously reported methods [17,18] and had physical constants in accordance with the literature values. The purity of the compounds studied is 99.9% (confirmed via chromatography). The experiments with water sensitive compounds were performed in dry argon atmosphere. The solvents were dried and purified by standard methods [19].

3. Results and discussion

3.1. The vaporization enthalpies

The vaporization enthalpies of organophosphorus derivatives known at present have been determined according to the vapor pressure of the compounds [20] or by the Solomonov method [21]. The vaporization enthalpies data of the alkylphosphoric acids, alkylphosphonic acids and their derivatives (all in all 59 compounds) are listed in Table 1. The standard vaporization enthalpies of compounds (11), (26), (31), (41–47), (54–59) were obtained by Eqs. (1) and (2) [21] according to the molar refraction data and solution enthalpies in hexane or carbon tetrachloride.

$$\Delta H^{\circ}_{\mathrm{vap}}(\mathrm{kJ\,mol^{-1}}) = \Delta H_{\mathrm{soln}}(\mathrm{C_6H_{14}}) + 4.39 + 1.05\,\mathrm{MR_D} \quad (1)$$

$$\Delta H^{\circ}_{\mathrm{vap}}(\mathrm{kJ\,mol^{-1}}) = \Delta H_{\mathrm{soln}}(\mathrm{CCl_4}) + 13.0 + 1.02\,\mathrm{MR_D} \quad (2)$$

For the calculation of the enthalpies of organophosphorus compounds, we have used the broadly parametrized additive method of group contributions over atoms taking into the account their close atomic environment.

$$Y = m_1X_1 + m_2X_2 + \ldots + m_iX_i \quad (3)$$

where m_i is the number of fragments of the ith type in the molecule and X_i is the increment describing the group contribution of the ith fragment.

Compared with the other additive schemes, the method of group contribution we have used is more universal and better takes into account the special chemical features of compounds, which allows it to be successfully used for calculating various thermochemical characteristics of organic and organoelement compounds [3,4,10].

Listed database (marked by * in Table 1) was used for the evaluation of previously unknown group contributions of phosphorus containing and some other molecular fragments in vaporization enthalpy (Table 2). This approach was earlier reported by Lebedev and Miroshnichenko [10] and was used for the calculation of group contributions (kJ mol^{-1}) in vaporization enthalpy of organic compounds. Contribution designations were introduced by Benson and co-workers [3,4]. The vaporization enthalpies of various classes of organic compounds have been calculated previously [10]. However, except the works [11,12], such calculations were not carried out for organophosphorus compounds.

Table 2
Some group contributions X_i for the calculation of vaporization enthalpy values in kJ mol^{-1}, the number of experimental points and standard deviation

No.	Type of group	X_i	n	S
1	$C-(C)(H)_3$	6.4[a]	–	0.05
2	$C-(C)_2(H)_2$	4.8[a]	–	0.01
3	$C-(C)_3(H)$	1.2[a]	–	0.10
4	$C-(C)(Cl)(H)_2$	17.4	5	0.01
5	$C-(C_B)_3$	15.0	4	0.08
6	$PO-(O)_2(H)$	−24.2	–	–
7	$PO-(C)(O)_2$	−24.2	2	0.27
8	$PO-(C)(O)(Cl)$	15.1	1	–
9	$PO-(C)(Cl)_2$	55.9	1	–
10	$C-(PO)(H)_3$	6.4[b]	–	–
11	$C-(C)(PO)(H)_2$	4.8[b]	–	–
12	$C-(PO)(O)(H)_2$	3.1[b]	–	–
13	$C-(C)(N)(PO)(H)$	−1.0[b]	–	–
14	$C-(C)(PO)(O)(H)$	−1.1[b]	–	–
15	$C-(C_B)_2(PO)(H)$	1.2[b]	–	–
16	$C-(C)_2(N)(PO)$	−6.9[b]	–	–
17	$C_B-(C_B)_2(PO)$	4.3[b]	–	–
18	$O-(C)(PO)$	25.5	2	0.13
19	$O-(PO)(H)$	32.4[b]	–	–
20	$2(O-(C)(PO)) + PO-(O)_2(H)$	26.8[c]	6	0.43
21	$2(O-(C)(PO)) + PO-(C)(O)_2$	26.8[d]	11	0.30
22	$2(O-(C)(PO)) + PO-(C)(O)_2$	−5.7[e]	6	0.05
23	$2(O-(C)(PO)) + PO-(C)(O)_2 + C-(C)(PO)(H)_2$	31.5	–	–
24	Δ_5	6.4[f,a]	–	0.16
25	Δ_6	6.4[f,a]	–	0.16

[a] Data from the Ref. [10].
[b] Group contributions [10]: carbon is replaced by P═O group.
[c] Calculated for phosphoric acids.
[d] Calculated for phosphonates and α-aminophosphonates.
[e] Calculated for α-hydroxyphosphonates.
[f] Correction for cyclic molecules [10].

Group contribution no. 21 (Table 2) was calculated on the basis of 11 compounds vaporization enthalpies (20–22, 26–29, 42, 43, 47, 52). Contribution no. 20 (Table 2) was obtained on the basis of $\Delta H^{\circ}_{\mathrm{vap}}$ of phosphoric acids (1–4, 7, 8) and no. 22 – of α-hydroxyphosphonates (54–59).

The analysis of the data shown in Table 2 indicates that the values of group contributions nos. 20 and 21 (Table 2) of phosphorus-containing fragments are the same for acids, esters and α-aminophosphonates. Consequently, all these compounds can be considered within the framework of the single series. At the same time, the analogous contribution no. 22 (Table 2) for α-hydroxyphosphonates has another value. Probably, this difference is due to the known tendency of hydroxy-derivatives to create strong the H-complexes with the help of phosphoryl and hydroxy-groups [17,29].

On the basis of this work (Table 2) and literature data [10], theoretical calculations of vaporization enthalpy of all compounds shown in Table 1 were carried out. Good correlations between experimental and calculated characteristics were established for both the vaporization enthalpies used for group contribution calculations, and also for other organophosphorus derivatives (5, 6, 23, 41, 44–46, 53). Poorer correlation between the compounds characteristics under consideration (9), (18), (24), (40) could be probably due to the errors in their vaporization enthalpy, since the close analogs of each of these four compounds (29), (14), (5), (39) have demonstrated a satisfactory agreement between experimental and calculated $\Delta H^{\circ}_{\mathrm{vap}}$ values.

Vaporization enthalpies of the six-member cyclic derivatives should be considered very cautiously, especially in cases when they were obtained with the use of solution enthalpies. It has been previously shown, that during the transition of such compounds from the condensed phase into the solution, conformational transformations with energies up to 10–15 kJ mol^{-1} [30] are possible. This contribution leads to changes in vaporization enthalpy. Therefore, calculated values of vaporization enthalpy for compounds (10–12), (30–32) (Table 1) are considered more reliable. The same is probably true for α-aminophosphonates (48, 50) with an optically active carbon α-atom, which can exist as a mixture of d- and l-isomers [31].

3.2. The formation enthalpies

The formation enthalpy is another important thermochemical characteristic. Along with vaporization enthalpy, ΔH_{f} is very useful for the description and prediction of a compounds reactivity and stability. The formation enthalpies of phosphorus derivatives known at present were determined by two methods: by combusting in a bomb calorimeter or by using reaction heats [20]. Hess's law (Eq. (4)) forms the basis of both methods. The formation enthalpy of any reaction participant (initial substance or product) could be calculated from Eq. (4) provided that the formation enthalpies of all other reaction participants are known and the enthalpy of the reaction itself was measured. In addition, the solution enthalpies ΔH_{soln} of compounds contribute to the reaction enthalpy taking place in solution $\Delta H_{s.\mathrm{reac}}$. This contribution is to be considered according to Eq. (5). The formation enthalpies of compounds in gas phase are calculated on the basis of formation enthalpies of compounds in a condensed phase (liquid or solid) according to Eq. (6) [20].

$$\Delta H_{\mathrm{reac}} = \Sigma\Delta H^{\circ}_{\mathrm{f}}(\text{products}) - \Sigma\Delta H^{\circ}_{\mathrm{f}}(\text{reagents}) \qquad (4)$$

$$\Delta H_{\mathrm{reac}} = \Delta H_{s.\mathrm{reac}} - \Sigma\Delta H_{\mathrm{soln}}(\text{products}) + \Sigma\Delta H_{\mathrm{soln}}(\text{reagents}) \qquad (5)$$

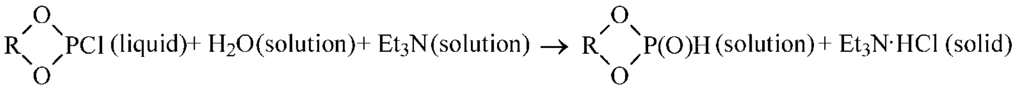
$$\Delta H^{\circ}_{\mathrm{f}}(\text{gas phase}) = \Delta H^{\circ}_{\mathrm{f}}(\text{condensed phase}) + \Delta H^{\circ}_{\mathrm{vap}} \qquad (6)$$

The few data (2, 14–17, 20, 23, 38–40) on formation enthalpies in a condensed and gas phases of phosphonic and phosphoric acids derivatives that were obtained from the literature at the beginning of our research have been collected into Table 1. Because of such a small quantity, we had to make an effort to increase the available database. With this aim in view, thermochemistry of organophosphorus compounds reactions, previously described synthetically in details, was studied. All these processes can be characterized by large reaction rates and large equilibrium constants and significant degree of completion. On the basis of experimental data on reaction heats and with the use of Eqs. (4)–(6), the formation enthalpies of compounds (7, 8, 10–12) and (26–32) were determined.

Formation enthalpies of cyclic phosphoric acids (7, 8, 10–12) were determined on the basis of a known [2] reaction of incomplete hydrolysis of the corresponding chloride derivatives at 298 K. Reagents were taken in a condensed phase (liquid or solid) or in a dioxan solution. As the acceptor of the hydrogen chloride generated, triethylamine was added. The reaction proceeds according to Scheme 1:

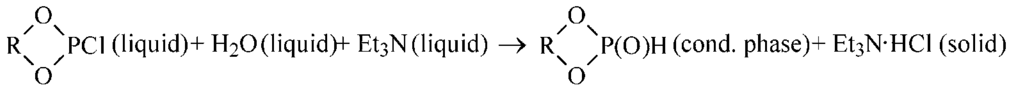
Experimentally obtained heat effects $\Delta H_{s.\mathrm{reac}}$ are shown in Table 3. Using the solution enthalpies in dioxane of all compounds that were soluble at the moment of reaction: products (7, 8, 10–12), water (65) and triethylamine (66) (Table 4) – the heat effect, ΔH_{reac}, of the hypothetical process occurring in the absence of solvent according to Scheme 2, was calculated by Eq. (5).

Then by Eq. (4), taking into account the formation enthalpies of reactants (60–64) and triethylammonium chloride (67)

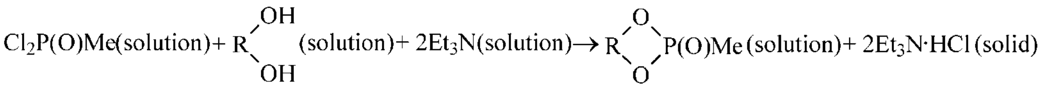


60–64 65 66 7, 8, 10–12 67

Scheme 1.



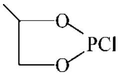
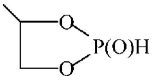
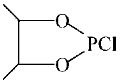
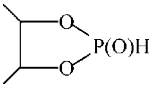
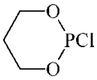
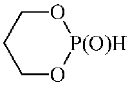
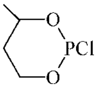
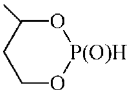
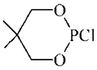
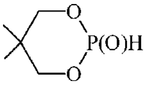
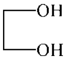
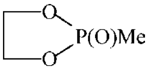
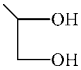
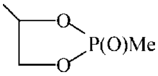
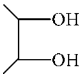
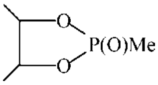
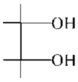
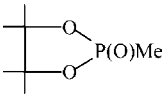
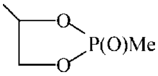
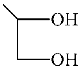
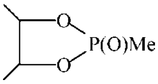
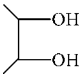
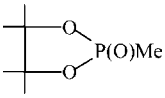
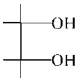
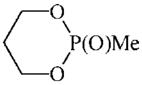
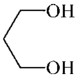
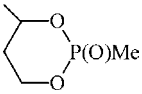
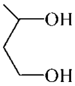
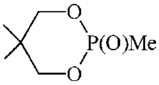
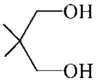
Scheme 2.



39 68–71 66 26–29 67

Scheme 3.

Table 3
Enthalpies of Scheme 1, 3 and 4, kJ mol^{-1}

Reagent		Product		$\Delta H_{s.reac}$	ΔH_{reac} (condensed phase)
No.	Formula	No.	Formula		
Scheme 1					
60		7		−183.0 ± 13.0	−179.7
61		8		−192.4 ± 8.1	−185.3
62		10		−189.4 ± 8.1	−181.0
63		11		−191.8 ± 7.1	−196.1
64		12		−193.0 ± 13.0	−197.4
Scheme 3					
68		26		−366.0 ± 22.0	−337.1
69		27		−375.0 ± 20.0	−348.2
70		28		−368.8 ± 3.5	−340.1
71		29		−363.0 ± 21.0	−313.9
Scheme 4					
27		69		−7.1 ± 2.1	4.7
28		70		−13.2 ± 0.3	3.6
29		71		−19.8 ± 1.8	−11.6
30		72		8.7 ± 0.4	9.1
31		73		−5.0 ± 0.8	−5.5
32		74		17.5 ± 1.7	−2.5

(Table 5), the formation enthalpies of phosphoric acid cyclic esters (7, 8, 10–12) in a condensed phase were determined. Using the vaporization enthalpies of these compounds, the formation enthalpies of compounds (7, 8, 10–12) in the gas phase were calculated (Table 1) according to Eq. (6).

Using the same approach and under the same conditions, the interaction of methyldichlorophosphonite (39) with the polyfunctional alcohols (68–71) according to Scheme 3 was studied and corresponding enthalpies, $\Delta H_{s.reac}$, were determined (Table 3).

The degree of completion of analogous reactions with aliphatic alcohols is known [26] to be rather high (97.8–98.6%). The chromatographic measurements we have carried out show that the formation of five-member cyclic phosphonates from

Table 4
Solution enthalpies of compounds, kJ mol^{-1}

No.	ΔH_{soln} (dioxane)	No.	ΔH_{soln} (dioxane)	No.	ΔH_{soln} (water)
7	3.2 ± 0.7	29	2.6 ± 0.7	69	-10.5^{a}
8	1.6 ± 0.4	65	6.2^{b}	70	−15.5 ± 0.4
10	2.0 ± 0.8	66	4.2^{c}	71	−6.9 ± 0.5
11	14.7 ± 0.6	39	16.3 ± 2.1	72	-3.0 ± 0.7^{d}
12	12.3 ± 1.0	68	7.7 ± 2.6	73	-3.9 ± 0.8^{d}
26	3.3 ± 0.3	69	5.3 ± 2.8	74	2.9 ± 1.3^{d}
27	3.5 ± 1.4	70	6.3 ± 2.8	14	−1.3 ± 1.0
28	2.3 ± 0.6	71	26.6 ± 2.5	14	6.7 ± 1.7^{d}

[a] Data from the Ref. [32].
[b] Data from Ref. [33].
[c] Data from Ref. [26].
[d] 343 K.

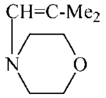
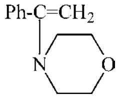
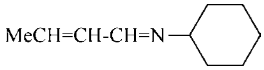
polyfunctional alcohols also proceeds practically quantitatively (97% or more). Corrections to the reaction enthalpy due to incompleteness of reaction were not introduced. Solution enthalpies in dioxane and formation enthalpies of compounds (39, 66–71) necessary for calculating formation enthalpies of methylphosphonic acid esters (26–29) by Eqs. (4) and (5) are shown in Tables 4 and 5.

The formation enthalpies of six-member ring esters of methylphosphonic acid were obtained on the basis of other reaction series – with the use of phosphonates (30–32) hydrolysis was carried out at 343 K. The hydrolysis of phosphonates (27–29) was conducted at 298 K. The direction of the calorimetric reaction is shown by Scheme 4:

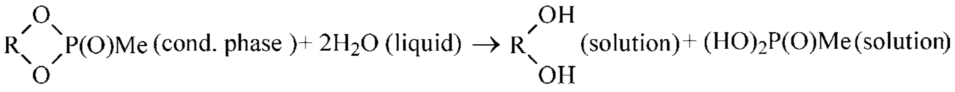
The thermochemical study of this process required some preliminary work. The reliable data on the direction and the completion degree of cyclic phosphonates reactions are not available in the literature. The hydrolysis of cyclic phosphorus esters [33,36–40] can occur with hydrolysis of either one ore both endocyclic bonds. For the analogous acyclic compounds, only basic hydrolysis with the formation of monoesters has been described [41]. It was established, that the cyclic phosphonates (27–32) can be easily hydrolyzed in the excess of water; hydrolysis of the five-member cycles occurs even at room temperature; hydrolysis of the six-member ring esters requires heating. The reaction time for completion is 5–10 min. It was impossible to detect the traces of the initial reagents after completion as monitored by ^{31}P NMR. Methylphosphonic acid was found in all cases as the only phosphorus-containing product. It was isolated from the reaction mixture in a pure state. The degree of completion under conditions of the calorimetric experiments was 99% or better.

The determination of the heat effects of the hydrolysis reaction was carried out by dissolving cyclic phosphonates in a considerable excess of water (Table 3). The reaction products – polyfunctional alcohols (69–74) and methylphosphonic acid (14) were obtained in the form of an aqueous solution. Therefore, enthalpies of solving products (69–74, 14) in water (Table 4) were used for the calculation of the hypothetical reac-

Table 5
Formation enthalpies of compounds, kJ mol^{-1}

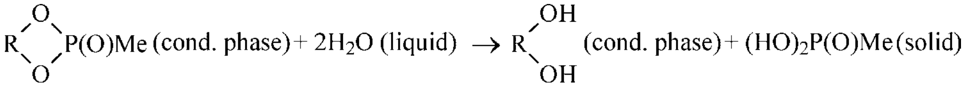
No.	ΔH_f° (condensed phase)	No.	ΔH_f° (condensed phase)	No.	Formula	ΔH_f° (condensed phase)
60	-630.2^{a}	68	-455.3^{b}	75		$-124.7^{c,d}$
61	-684.9^{a}	69	-485.7^{b}			
62	-655.6^{a}	70	-541.4^{b}	76		$1.7^{c,d}$
63	-693.7^{a}	71	-616.0^{c}			
64	-713.4^{a}	72	-464.8^{b}	77		$34.1^{c,d}$
65	-285.8^{b}	73	-500.8^{b}			
66	-127.7^{e}	74	-551.0^{b}	78	Ph_2CN_2	$230.8^{c,d}$
67	-397.6^{e}					

[a] Data from Ref. [34].
[b] Data from Ref. [35].
[c] Were calculated using Benson and co-workers [3,4] and Lebedev and Miroshnichenko [10] contributions.
[d] Enthalpy of formation in the gas phase.
[e] Data from Ref. [20].

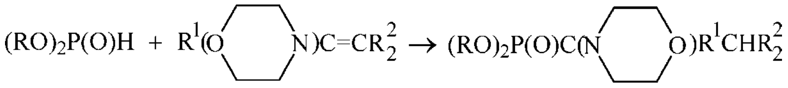


27–32 65 69–74 14

Scheme 4.

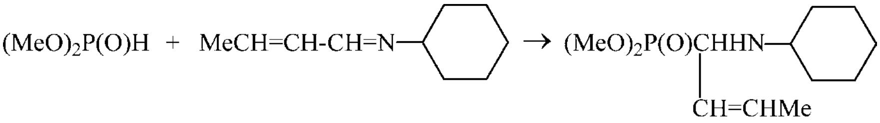


Scheme 5.



2, 8, 12 75, 76 48–52

Scheme 6.



1 77 53

Scheme 7.

tion enthalpy (Eq. (4), Scheme 5), which corresponds to the condensed phase reaction of all participants.

The formation enthalpies of the compounds (27–29) were calculated by the methods described above. Auxiliary enthalpic characteristics of the system are shown in Tables 4 and 5, the results of the calculation – in Table 1. It is necessary to note, that the formation enthalpies of five-member phosphonates (27–29) obtained when investigating various reaction series agree with each other within the uncertainties of the measurements. This testifies to the reliability of both the method used and the data obtained.

Recall that the reaction enthalpies of the cyclic phosphonates (30–32) were obtained at 343 K. Adjustment of the heat effects to 298 K was made by Eq. (7) according to Kirchhoff’s law.

$$\Delta H_{s.\mathrm{reac}}(T_2) = \Delta H_{s.\mathrm{reac}}(T_1) + \int_{T_1}^{T_2} \Delta C_p \,\mathrm{dT} \qquad (7)$$

ΔC_p is the reaction heat capacity that was determined according to the difference between the sum of the heat capacities of the products and the sum of the heat capacities of the reactants. In the temperature interval studied for compounds (31, 32, 72–74, 14), a linear dependence, $C_\mathrm{p} = a + bT$, was found. The parameters of this dependence and heat capacities of compounds extrapolated to 298 K are shown in Table 6. According to Table 6, the temperature corrections to the heat effects of cyclic phosphonate (30–32) hydrolysis reactions were calculated: −4.1, −2.3, 10.2 kJ mol^{-1}.

The formation enthalpies of compounds (34–37) and (48–53) (Table 1) were determined using another method – on the basis of the previously published results of the thermochemical study of reactions of esters of phosphoric acids and some nitrogen-containing compounds: substituted morpholinoethenes (75, 76), 1-cyclohexyliminobutene-2 (77) and diphenyldiazomethane (78) [43,44]. Reactions were going on according to Schemes 6–8.

Table 6
Compounds heat capacities 298 K, J mol^{-1} K^{-1}, temperature dependences and standard values

No.	a	b	r	S	C_p
31	138.00	0.34	0.987	1.17	239.4
32	−55.00	0.88	0.999	0.98	207.4[a]
72	115.00	0.18	0.804	3.19	168.7
73	−146.00	1.18	0.983	5.22	205.8
74	178.36	–	–	–	178.36[b]
14	35.00	0.25	0.996	0.47	109.5

[a] Heat capacities of phosphonates (32) and (30) accepted to be equal.

[b] At 312 K, polyfunctional alcohol has a phase-transition “solid–solid” with the enthalpy of 12.38 kJ mol^{-1} [42].

The enthalpies of Schemes 6–8 in the gas phase were determined by the Eq. (8) [45].

$$\Delta H_{\mathrm{reac}}(\text{gas phase}) = \Delta H_{\mathrm{reac}}\,\text{solution} - \Sigma H_{\mathrm{solv}}\,\text{products} + \Sigma H_{\mathrm{solv}}\text{reagents} \qquad (8)$$

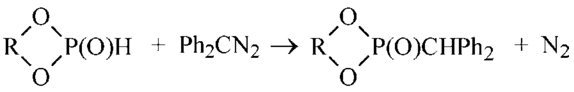
Solvation enthalpies of compounds in p-xylene and carbon tetrachloride necessary for the calculations were obtained by Eq. (9)–(11) [22].

$$\Delta H_{\mathrm{solv}} = \Delta H_{\mathrm{soln}} - \Delta H_{\mathrm{vap}} \qquad (9)$$

$$-\Delta H_{\mathrm{solv}}(p\text{-xylene}) = 11.7 + 1.08\,\mathrm{MR_D} \qquad (10)$$

$$-\Delta H_{\mathrm{solv}}(\mathrm{CCl_4}) = 13.0 + 1.02\,\mathrm{MR_D} \qquad (11)$$

The values of Schemes 6–8 enthalpies in solution and in the gas phase are shown in Table 7. The formation enthalpy



5, 8, 9, 12 78 34–37

Scheme 8.

Table 7
Enthalpies of Schemes 6–8, kJ mol^{-1}

Compound no.			ΔH_{reac}	
Reagents		Product	*p*-Xylene	Gas phase
Scheme 6				
2	75	52	$-25.2^{a,b}$	-34.9 ± 9.1
8	75	48	$-67.0^{a,c}$	-79.0 ± 12.0
12	75	49	$-26.4^{a,b}$	-39.0 ± 8.0
8	76	50	-72.3^{a}	-88.0 ± 15.0
12	76	51	-48.5^{a}	-65.0 ± 12.0
Scheme 7				
1	77	53	$-124.5^{a,d}$	-126.0 ± 16.0
Scheme 8				
5		34	-82.8^{e}	−98.2
8	78	35	-97.9^{e}	−111.1
9		36	-101.3^{e}	−116.0
12		37	-70.3^{e}	−84.7

[a] Data from the Ref. [43].
[b] At 358 K.
[c] At 323.
[d] Carbon tetrachloride.
[e] Data from the Ref. [44].

Table 8
Some group contributions X_i for the calculation of formation enthalpy values in the gas phase (kJ mol^{-1}), the number of experimental points and standard deviation

No.	Type of group	X_i	*n*	*S*
1	$C{-}(C)(H)_3$	-42.2^{a}	–	–
2	$C{-}(C)_2(H)_2$	-20.7^{a}	–	–
3	$C{-}(C)_3(H)$	-7.9^{a}	–	–
4	$C{-}(C)(Cl)(H)_2$	-65.3^{a}	–	–
5	$C{-}(C_B)_3$	20.8^{a}	–	–
6	$PO{-}(O)_2(H)$	−387.0	–	–
7	$PO{-}(C)(O)_2$	-416.3^{a}	–	–
8	$PO{-}(C)(O)(Cl)$	-471.1^{b}	1	–
9	$PO{-}(C)(Cl)_2$	-514.6^{c}	2	0.08
10	$C{-}(PO)(H)_3$	-42.2^{d}	–	–
11	$C{-}(C)(PO)(H)_2$	-14.2^{d}	–	–
12	$C{-}(PO)(O)(H)_2$	-35.6^{d}	–	–
13	$C{-}(C)(N)(PO)(H)$	-21.8^{d}	–	–
14	$C{-}(C)(PO)(O)(H)$	-29.3^{d}	–	–
15	$C{-}(C_B)_2(PO)(H)$	-7.9^{d}	–	–
16	$C{-}(C)_2(N)(PO)$	-13.4^{d}	–	–
17	$C_B{-}(C_B)_2(PO)$	40.6^{d}	–	–
18	$O{-}(C)(PO)$	-170.3^{a}	–	–
19	$O{-}(PO)(H)$	-272.0^{a}	–	–
20	$2(O{-}(C)(PO)) + PO{-}(O)_2(H)$	−727.6	4	2.47
21	$2(O{-}(C)(PO)) + PO{-}(C)(O)_2$	−756.9	–	–
22	$2(O{-}(C)(PO)) + PO{-}(C)(O)_2$ $+ C{-}(C)(PO)(H)_2$	-771.1^{e}	7	4.39
23	Δ_5	$25.1^{f,a}$	–	–
24	Δ_6	$4.2^{f,g}$	–	–

[a] Data from the Ref. [3,4].
[b] 471.1 kJ mol^{-1} [3].
[c] 514.6 kJ mol^{-1} [3].
[d] Group contributions [3]: carbon is replaced by P=O group.
[e] 771.1 kJ mol^{-1} [3].
[f] Correction for cyclic molecules.
[g] Data from the Ref. [46].

of compounds (75–78) in the gas phase was calculated by group additivity [3,4] (Table 5).

Using the enthalpies of reactions in the gas phase and the known formation enthalpies of the reactant and products in the gas phase (Tables 1 and 5), we have calculated the formation enthalpies of compounds (34–37, 48–53) in the gas phase by Eq. (12), and formation enthalpies in the condensed phase by Eq. (6) (Table 1).

$$\Delta H_{\text{reac}}(\text{gas phase}) = \Sigma \Delta H_f^{\circ}(\text{gas phase})\text{products} - \Sigma \Delta H_f^{\circ}(\text{gas phase})\text{reagents} \qquad (12)$$

It's necessary to note, that the formation enthalpies of compounds (48, 49, 52) in the condensed and gas phases were calculated at higher temperatures and were not adjusted to 298 K (Table 1).

Previously [3,4], on the basis of an additivity scheme, the group contributions in formation enthalpy in the gas phase of some phosphorus-containing and other fragments of organic molecules were estimated. Using the literature values [3,4] and those obtained our work (Table 1) we have evaluated the group contributions in ΔH_f° of a phosphoryl group and of heteroatoms connected to (Table 8). Group contribution no. 22 (Table 8) was calculated from formation enthalpies in the gas phase of seven compounds (34–37, 50, 51, 53) and no. 20 – ΔH_f° (gas phase) of phosphoric acids (7, 8, 11, 12). The values of contributions nos. 8 and 9 (Table 8) were calculated from the data of formation enthalpies of phosphonic acid chloranhydrides (38–40) (Table 1).

As Table 8 reveals, group contributions nos. 8, 9 and 22 agree with previously calculated contributions [3] with high accuracy. The value of contribution no. 20 was obtained for the first time. As it follows from Table 1, there is a good correlation between the experimental data on formation enthalpies and the calculated values, obtained by the additive scheme, and for compounds (2, 10, 14, 15, 20, 23, 26–32, 48) as well. The formation enthalpies in the gas phase of the latter were not used for group contributions determination.

4. Conclusion

The set of group contributions for calculating the vaporization enthalpy and formation enthalpy in the gas phase of organophosphorus compounds studied within the present research allows estimation of a wide range of phosphoric acid derivatives and dialkylphosphonates. The estimation is accurate and does not require thermochemical experiments. The contributions obtained make it possible to calculate thermochemical characteristics for new, still un-synthesized compounds.

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