Available online at www.sciencedirect.com

ScienceDirect

Thermochimica Acta 470 (2008) 1–11

thermochimica acta

www.elsevier.com/locate/tca

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

R.A. Cherkasov [a,*], E.V. Sagadeev [b], J.G. Safina [b], V.V. Brus'ko [a]

[a] *Kazan State University, 18 Kremlevskaya Street, Kazan 420008, Russia*
[b] *Kazan State Technological University, 68 K. Marx Street, Kazan 420015, Russia*

Received 13 November 2006; received in revised form 17 December 2007; accepted 7 January 2008

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

---

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.

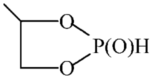
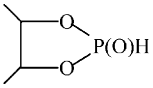
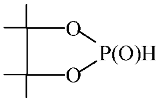
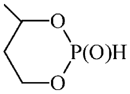
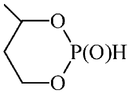
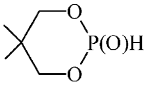
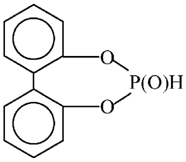
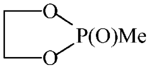
The reactions heats were measured using the differential microcalorimeter Calvet type DAC-1-1 in p-xylene or carbon tetrachloride at 298 or 343 K (±0.05 K). The reaction heat is the mean value of 3–5 experiments. The working volume of the glass vessels was 5 cm^3. The heat capacities of the compounds 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%.

---

[*] Corresponding author. Tel.: +7 843 2315 416; fax: +7 843 2315 416.
E-mail address: Rafael.Cherkasov@ksu.ru (R.A. Cherkasov).

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.01.001

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