

# 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. © 2008 Elsevier B.V. All rights reserved.

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## 1. Introduction

The derivatives of a tetracoordinated phosphorus atom are known to possess 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 all 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<sup>-1</sup> for liquid substances and  $(1-3) \times 10^{-3}$  mol l<sup>-1</sup> for solids. The measured values have a magnitude with an accuracy of 0.3–0.5 kJ mol<sup>-1</sup> for liquids and 0.5–0.7 kJ mol<sup>-1</sup> for solid products. This is taken as a result of the mean value of 3–6 experiments.

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

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