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N.S. Zefirov on His 70th Anniversary

Calculation of Fundamental Thermochemical Parameters of Phosphoranes by the Additivity Scheme

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Abstract—Using the additivity scheme, experimental enthalpies of vaporization and formation of phosphoranes were analyzed, group contributions to the enthalpies of vaporization and formation were determined, and thermochemical parameters of five-coordinate phosphorus derivatives were calculated.

Acyclic alkoxyphosphoranes (derivatives of five-coordinate phosphorus) have been studied relatively poorly due to their instability under normal conditions. By contrast, cyclic and especially spirocyclic five-coordinate phosphorus compounds are quite stable. Up to now, the preparative chemistry of phosphoranes in which the phosphorus atom belongs to one, two, or three five- or six-membered heterocyclic fragments have been well documented, and data on their reactivity and mechanisms of some reactions have been reported [1, 2]. On the other hand, thermochemical properties of these compounds, in particular their enthalpies of formation and vaporization, remain almost unknown; only a few publications on this topic are available [3, 4].


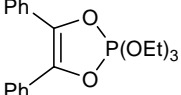
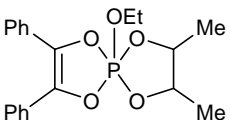
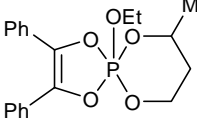
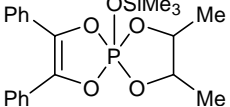
In continuation of our studies [4–7] on thermochemistry of organophosphorus compounds, in the present work we analyzed the available experimental enthalpies of vaporization and formation of alkoxyphosphoranes on the basis of the additivity scheme using group contributions and made an attempt to develop an approach to calculation of fundamental thermochemical parameters of these compounds. All experimental thermochemical data that we succeeded in finding in the literature for five-coordinate phosphorus derivatives are collected in Table 1. The enthalpies of vaporization of alkoxyphosphoranes **II–V** were determined by an indirect method, using the Solomonov equation [8, 9], from the data on dissolution of these compounds in inert organic solvents [4]. The

experimental enthalpies of vaporization and formation of five-coordinate phosphorus compounds, used for the calculation of contributions to $\Delta H_{\text{vap}}^{\circ}$ and ΔH_f° of phosphorus-containing groups by the additivity scheme are marked with an asterisk. The group contributions were calculated with the aid of ENTHALPY program [5].

Table 2 contains the obtained group contributions (or increments) to enthalpy of vaporization for a phosphorus atom linked to other heteroelements. The increments are denoted according to the Benson–Buss symbols [10] modified in the present work. For example, P–(O)₅ means a phosphorus atom linked to five oxygen atoms in alkoxyphosphoranes; O–(C)(P) corresponds to an oxygen atom linked to carbon and phosphorus, etc.

We have found considerable scattering of the group contributions $\{3[\text{O}-(\text{C})(\text{P})] + 2[\text{O}-(\text{C}_d)(\text{P})] + \text{P}-(\text{O})_5\}$ to the enthalpies of vaporization within the series of alkoxyphosphoranes **II–IV**. The corresponding values for compounds **II**, **III**, and **IV** are 51.3, 14.2, and 11.9 kJ/mol, respectively. As we showed previously [5, 7], analysis of group contributions to fundamental thermochemical parameters could favor refinement and more correct interpretation of the experimental data. Analysis of the group increments $\{3[\text{O}-(\text{C})(\text{P})] + 2[\text{O}-(\text{C}_d)(\text{P})] + \text{P}-(\text{O})_5\}$ to the enthalpies of vaporization of alkoxyphosphoranes **II–IV** suggests that the $\Delta H_{\text{vap}}^{\circ}$ values of compounds **III** and **IV** given in [4] are conditionally underestimated due to effect of some additional factors which were not taken into account

Table 1. Experimental and calculated enthalpies of vaporization and formation of alkoxyphosphoranes I–V (298 K)

Comp. no.	Structure	$\Delta H_{\text{vap}}^{\circ}$, kJ/mol		ΔH_f° , kJ/mol			
		experiment	calculation	gas phase		condensed state	
				experiment	calculation	experiment	calculation
I		–	98.6	–	–1349.8	–1484.7 ± 5.5 ^a	–1448.4
II		154.1* ^b	154.1	–911.8* ^c	–909.2	–1065.9 ^c	–1063.3
III		115.0 ^b	152.2	–852.2 ^c	–871.5	–967.2 ^c	–1023.7
IV		115.3 ^b	154.8	–874.6* ^c	–877.3	–989.9 ^c	–1032.1
V		142.5* ^b	142.5	–	–	–	–

^a Data of [3].^b Data of [4].^c This work.

previously. As applied to alkoxyphosphoranes **III** and **IV**, each possessing two five- (or six)- membered rings, the most probable reason is their conformational behavior. According to [11], the conformational transformations in going from the crystalline state to solution in an inert solvent is characterized by an energy of no less than 10–15 kJ/mol. In the case of six-membered cyclic phosphoranes, these transformations involve *chair* conformers with axial and equatorial orientations of the exocyclic P–O bond [12, 13]. Five-membered cyclic phosphoranes undergo flexible modifications of *half-chair* conformers [14]. This factor leads to underestimated experimental enthalpies of vaporization of crystalline compounds **III** and **IV**.

Analogous transformations are not typical of liquid alkoxyphosphorane **II**. Therefore, the group contribution $\{3[\text{O}-(\text{C})(\text{P})] + 2[\text{O}-(\text{C}_d)(\text{P})] + \text{P}-(\text{O})_5\}$ to $\Delta H_{\text{vap}}^{\circ}$, calculated from the enthalpy of vaporization of compound **II**, may be regarded as the most appropriate within the examined series of experimental data (Table 2). That is why we used just the $\{3[\text{O}-(\text{C})(\text{P})] + 2[\text{O}-(\text{C}_d)(\text{P})] + \text{P}-(\text{O})_5\}$ increment calculated from the experimental enthalpy of vaporization of compound **II** in both further refinement of the enthalpies of vapor-

ization of phosphoranes **III** and **IV** (Table 1) and calculation of the enthalpies of vaporization of alkoxyphosphoranes (Table 3) for which the corresponding experimental data are unavailable. The $\Delta H_{\text{vap}}^{\circ}$ values were calculated by ENTHALPY program [5] using the known increments of carbon-containing groups [15].

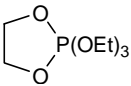
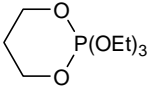
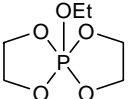
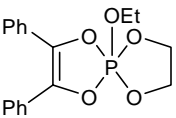
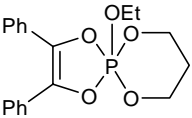
In order to create a database of calculated enthalpies of formation of five-coordinate phosphorus derivatives, we determined ΔH_f° of three alkoxyphosphoranes **II–IV** (Table 1) from the previously reported results of thermochemical study on the reaction of

Table 2. Group contributions X_i for the calculation of enthalpies of vaporization, kJ/mol

Group contribution	X_i
$5[\text{O}-(\text{C})(\text{P})] + \text{P}-(\text{O})_5$	51.3
$3[\text{O}-(\text{C})(\text{P})] + 2[\text{O}-(\text{C}_d)(\text{P})] + \text{P}-(\text{O})_5$	51.3
$2[\text{O}-(\text{C})(\text{P})] + 2[\text{O}-(\text{C}_d)(\text{P})] + \text{O}-(\text{Si})(\text{P}) + \text{P}-(\text{O})_5$	36.7
$\text{Si}-(\text{C})_3(\text{O})$	–4.6 ^a
$\Delta_5 = \Delta_6$	6.4 ^b

^a Data of [7]; Δ_5 and Δ_6 are the corrections for cyclic structure.^b Data of [15].

Table 3. Calculated enthalpies of vaporization and formation of alkoxyphosphoranes **VI–X** (298 K)

Compound no.	Structure	$\Delta H_{\text{vap}}^{\circ}$, kJ/mol	ΔH_f° , kJ/mol	
			gas phase	condensed state
VI		92.3	-1240.4	-1332.7
VII		97.1	-1282.0	-1379.1
VIII		86.1	-1130.9	-1217.0
IX		147.8	-799.7	-947.5
X		152.6	-841.4	-994.0

P(III) derivatives with α -dicarbonyl compounds (Kuchtin–Ramirez reaction or [1+4]-cycloaddition) [4]. Table 4 contains the calculated group contributions to enthalpies of formation of five-coordinate phosphorus compounds. The lack of experimental enthalpy of formation of compound **V** did not allow us to calculate the group contribution $\{2[\text{O}-(\text{C})(\text{P})] + 2[\text{O}-(\text{C}_d)(\text{P})] + \text{O}-(\text{Si})(\text{P}) + \text{P}-(\text{O})_5\}$ to ΔH_f° ; therefore, calculation of the $\text{Si}-(\text{C})_3(\text{O})$ increment seems to be unreasonable. The enthalpies of formation of compounds **I–IV**, calculated by ENTHALPY program [5] with the use of group contributions estimated in the present work and previously [16, 17], are given in Table 1. There is a good agreement between the experimental and calculated enthalpies of formation of

all the examined five-coordinate phosphorus compounds. It should also be noted that the calculated enthalpy of formation of pentaethoxyphosphorane (**I**) in condensed state (Table 1) almost coincides with the experimental value given in [3], which was not used in the calculation of group contributions to ΔH_f° . Therefore, the calculated $\{3[\text{O}-(\text{C})(\text{P})] + 2[\text{O}-(\text{C}_d)(\text{P})] + \text{P}-(\text{O})_5\}$ increment was used in the subsequent determination of the enthalpies of formation of compounds **VI–X**, for which the corresponding experimental data are absent (Table 3).

The proposed approach may be extended to estimation of fundamental thermochemical parameters of a fairly wide series of oxygen-containing five-coordinate phosphorus compounds.

Table 4. Group contributions X_i for the calculation of gas-phase enthalpies of formation, kJ/mol

Group contribution	X_i
$5[\text{O}-(\text{C})(\text{P})] + \text{P}-(\text{O})_5$	-961.1
$3[\text{O}-(\text{C})(\text{P})] + 2[\text{O}-(\text{C}_d)(\text{P})] + \text{P}-(\text{O})_5$	-961.1 ^a
Δ_5	25.1 ^b
Δ_6	4.2 ^c

^a Number of experimental points $n = 2$, standard deviation $s = 0.90$; Δ_5 and Δ_6 are the corrections for cyclic structure.

^b Data of [16].

^c Data of [5].

REFERENCES

1. Polezhaeva, N.A. and Cherkasov, R.A., *Usp. Khim.*, 1985, vol. 64, p. 1899.
2. Cherkasov, R.A. and Polezhaeva, N.A., *Usp. Khim.*, 1987, vol. 66, p. 287.
3. Guthrie, J.P., *J. Am. Chem. Soc.*, 1977, vol. 99, p. 3991.
4. Ovchinnikov, V.V., Safina, Yu.G., and Cherkasov, R.A., *Zh. Obshch. Khim.*, 1990, vol. 60, p. 997.
5. Sagadeev, E.V. and Safina, Yu.G., *Zh. Fiz. Khim.*, 2002, vol. 76, p. 1565.
6. Sagadeev, E.V., Safina, Yu.G., and Cherkasov, R.A., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 940.

7. Sagadeev, E.V. and Safina, Yu.G., *Zh. Fiz. Khim.*, 2004, vol. 78, p. 2147.
8. Solomonov, B.N. and Konovalov, A.I., *Usp. Khim.*, 1991, vol. 60, p. 45.
9. Fuchs, R., Chambers, E., and Stephenson, W.K., *Can. J. Chem.*, 1987, vol. 65, p. 2624.
10. Benson, S.W. and Buss, J.H., *J. Chem. Phys.*, 1958, vol. 29, p. 546.
11. Klochkov, V.V., Aganov, A.V., Samitov, Yu.Yu., and Arbuzov, B.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, p. 316.
12. Lopusinski, A., Michalski, J., and Potrzebowski, M., *Phosphorus, Sulfur, Silicon*, 1986, vol. 28, p. 299.
13. Borisenko, A.A., Sorokina, S.F., Zavalishina, A.I., Sergeev, N.M., and Nifant'ev, E.I., *Zh. Obshch. Khim.*, 1978, vol. 48, p. 1251.
14. Samitov, Yu.Yu., *Khim. Geterotsikl. Soedin.*, 1980, p. 1443.
15. Lebedev, Yu.A. and Miroshnichenko, E.A., *Termokhimiya paroobrazovaniya organicheskikh veshchestv* (Thermochemistry of Vaporization of Organic Substances), Moscow: Nauka, 1981.
16. Cohen, N. and Benson, S.W., *Chem. Rev.*, 1993, vol. 93, p. 2419.
17. Cohen, N., *J. Phys. Chem., Ref. Data*, 1996, vol. 25, p. 1411.