Thermochemistry of heteroatomic compounds

18.* The enthalpies of vaporization, solvation, and formation of isomeric 2,5-dimethyl-1-phenyl-1-thioxophosphorinan-4-ones

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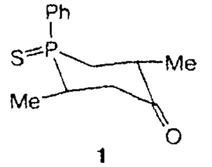
The enthalpies of solvation of four geometric isomers of 2,5-dimethyl-1-phenyl-1-thioxophosphorinan-4-one in chloroform, nitrobenzene, and methanol were calculated using the enthalpies of vaporization of the isomers determined by the modified Solomonov—Konovalov method from the enthalpies of solution of the compounds in CCl_4 and *p*-xylene and molar refractions. The enthalpies of formation ($\Delta H_f°$) of the isomers in the condensed and gas phase were assessed in the framework of Benson's group additivity scheme by summing the $\Delta H_f°$ values for phosphacycloketone fragments obtained from molecular mechanics calculations with the contributions of the phenyl group and S atom attached to the P atom.

Key words: cyclophosphine sulfides, enthalpy of vaporization, enthalpy of solvation, enthalpy of formation, molar refraction, molecular mechanics.

Cyclic organic compounds containing phosphorus and sulfur atoms are used in medicine and agriculture.[2] Thermochemistry of such compounds has been little studied and published data on their enthalpies of vaporization, solvation, and formation in different states of aggregation are scarce.[3]

In this work, calorimetric studies of thermochemistry of four isomers of 2,5-dimethyl-1-phenyl-1-thioxophosphorinan-4-one (**1**—**4**) were carried out.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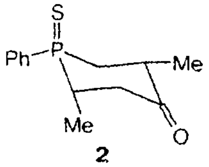
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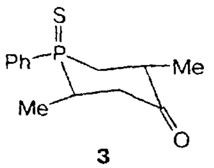
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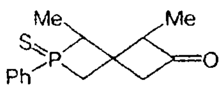
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Previously,[4,5] it was found that the synthesis of 2,5-dimethyl-1-phenyl-1-thioxophosphorinan-4-one results in four crystalline stereoisomers **1**—**4**, which were separated by TLC. The structures of the isomers have been established by X-ray analysis and confirmed by NMR spectroscopy and by the results of measurements of the dipole moments and Kerr constants.[6—8]

Experimental

The enthalpies of solution (ΔH_s) of compounds **1**—**4** * in CCl_4, *p*-xylene, $CHCl_3$, nitrobenzene, and methanol were measured using a differential calorimeter at 298 K. Reliability of the results obtained in this work was checked by calculating the enthalpy of solvation of KCl in water. The value found, ΔH_s = 17.4±0.8 kJ mol^{-1}, appeared to be consistent with the reported data (17.22±0.05 kJ mol^{-1})[9]; electrical calibrations differed by at most 1.5 to 2%; the procedure for determining the ΔH_s value for KCl has been reported earlier.[3] Table 1 lists the numerical values of the enthalpies of solution of compounds **1**—**4** averaged over two to four measurements carried out with an error of at most ±0.4—1.2 kJ mol^{-1}.

The solvents were dried following the known procedure.[10]

Results and Discussion

Previously,[11,12] a method for determination of the enthalpy of vaporization (ΔH_{vap}) was proposed. The method uses the following relationship[11,12]:

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* For Part 17, see Ref. 1

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Table 1. Enthalpies of solution (ΔH_s/kJ mol^{-1}) and vaporization (ΔH_{vap}/kJ mol^{-1}) of isomers **1—4** in different solvents (MR_D = 78.8 cm^3 mol^{-1})

Compound	ΔH_s					ΔH_{vap}		
	CCl_4	*p*-Xylene	$CHCl_3$	MeOH	$PhNO_2$	CCl_4	*p*-Xylene	Average*
1	20.3	20.1	9.6	24.4	13.6	112.5	115.6	114.1±2.7
2	24.8	28.1	14.8	35.6	18.3	116.9	123.6	120.3±4.0
3	17.2	12.1	10.1	25.1	14.9	109.3	107.6	108.5±2.3
4	24.1	13.8	13.3	26.5	23.5	116.2	109.3	112.8±3.8

* Here, the errors include those of determination of the enthalpies of solution in CCl_4 and *p*-xylene and the standard deviations from the above-mentioned linear dependences (2) and (3): $\Delta H_{nsp}(CCl_4) = -13.01 - 1.02MR_D$, $S_0 = 2.40$; and $\Delta H_{nsp}(1,4\text{-}Me_2C_6H_4) = -11.7 - 11.08MR_D$, $S_0 = 1.83$ (ΔH_{nsp} is the non-specific enthalpy of solution).[3]

$$\Delta H_{vap} = \Delta H_s(c\text{-}C_6H_{12}) + 4.39 + 1.05MR_D, \quad (1)$$

where ΔH_s/kJ mol^{-1} is the enthalpy of solution of an inorganic nonelectrolyte in infinitely dilute cyclohexane solution and MR_D/cm^3 mol^{-1} is the molar refraction.

More recently, this method was developed and modified[3,13,14] to be applied to organophosphorus compounds, which are scantily soluble in alkanes. In this case, either CCl_4 or *p*-xylene can serve as an inert solvent and Eq. (1) is transformed into the following relationships:

$$\Delta H_{vap} = \Delta H_s(CCl_4) + 13.0 + 1.02(MR_D - \alpha), \quad (2)$$

$$\Delta H_{vap} = \Delta H_s(1,4\text{-}Me_2C_6H_4) + 11.7 + 1.08(MR_D - \alpha), \quad (3)$$

where α is the hydrocarbon skeleton branching correction for the solute molecule (for >CH, α = 1.6 cm^3 mol^{-1}). The ΔH_{vap} values for high-melting, cyclohexane-insoluble compounds **1—4** were calculated using Eqs. (2) and (3).

Analysis of the data listed in Table 1 shows that the average ΔH_{vap} value for isomer **2** is much higher than those for the other compounds. Passage from axial to equatorial arrangement of the P=S bond has no pronounced effect on the ΔH_{vap} value, though the relative error of determination of ΔH_{vap} values was ±2.3—4.0 kJ mol^{-1} (see note to Table 1).

The enthalpies of solvation (ΔH_{solv}) of compounds **1—4** in $CHCl_3$, nitrobenzene, and methanol (Table 2) were calculated using the equation

$$\Delta H_{solv} = \Delta H_s(\text{Solv}) - \Delta H_{vap}(CCl_4), \quad (4)$$

where Solv is the corresponding solvent.

Table 2. Enthalpies of solvation (ΔH_{solv}/kJ mol^{-1}) and transfer (ΔH_{tr}/kJ mol^{-1}) of compounds **1—4** from CCl_4 into chloroform, nitrobenzene, and methanol

Compound	CCl_4.	$CHCl_3$		$PhNO_2$		MeOH	
	$-\Delta H_{solv}$*	ΔH_{solv}	$-\Delta H_{tr}$	ΔH_{solv}	$-\Delta H_{tr}$	$-\Delta H_{solv}$	ΔH_{tr}
1	93.8	104.5	10.7	100.5	6.7	89.7	4.1
2	95.5	105.5	10.0	102.0	6.5	84.7	10.8
3	91.3	98.4	7.1	93.6	2.3	83.4	7.9
4	88.7	99.5	10.8	89.3	0.6	86.3	2.4

* Enthalpies of solvation were calculated using the average enthalpies of vaporization.

Since CCl_4 is an inert solvent, the differences between the enthalpies of solvation of compounds **1—4** in CCl_4 and in $CHCl_3$, nitrobenzene, and MeOH can be used for assessing the enthalpies of transfer (ΔH_{tr}), which are due to the formation of hydrogen bonds and/or to dipole-dipole interactions:

$$\Delta H_{tr} = \Delta H_{solv}(\text{Solv}) - \Delta H_{solv}(CCl_4). \quad (5)$$

Previously,[3,14] an analogous approach was used for determination of the enthalpy of formation of the hydrogen bond ($\Delta H_{h.b}$) between the P=O group in the phosphonic acid derivatives and $CHCl_3$ molecules. From the data listed in Table 2 it can be seen that the major contribution to the enthalpy of transfer into $CHCl_3$ solution comes from the interaction of the carbonyl group with the proton of the solvent. This is in good agreement with the reported data for cyclic ketones.[15]

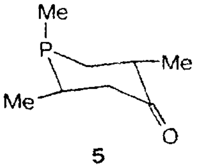
The dipole moments (μ) of compounds **1—3** are 4.21, 3.86, and 3.74 D, respectively,[6,7] whereas that of isomer **4** is unknown. We correlated the μ values with the enthalpies of transfer from CCl_4 into a polar solvent (nitrobenzene) and revealed a tendency for a decrease in the enthalpies. However, the dipole moments have almost no effect on the enthalpy of solvation of all the isomers **1—4** (the ΔH_{tr} values are comparable in magnitude with the errors of determination of the ΔH_{vap} values).

Unexpectedly, we found that (i) the absolute values of the enthalpies of solvation for methanol are smaller than those for nitrobenzene and chloroform and (ii) the ΔH_{tr} values for methanol are opposite in sign (positive) to those of nitrobenzene and chloroform. This is likely due to the cleavage of the hydrogen bonds in the methanol associates and the formation of new hydrogen bonds between the methanol molecules and carbonyl (and, possibly, thiophosphoryl) groups of compounds **1—4**. The endothermic dissociation process was found to dominate an exothermic reaction of the formation of OH...O=C and OH...S=P hydrogen bonds.

We also attempted to assess the enthalpies of formation ($\Delta H°_f$) of compounds **1—4** in the gas phase, since calculations of the binding energies in the molecules require knowledge of this fundamental quantity. Using the known approach,[16] we considered a hypothetical gas-phase dissociation of isomeric molecules **1**—**4** by cleavage of the P=S bond, resulting in an S atom and a tertiary phosphacycloketone. This process is described by the following equation:

$$\Delta H^\circ_f\,(R_3P{=}S)_g = \Delta H^\circ_f(R_3P)_g + \Delta H^\circ_f(S)_g - E(P{=}S)_g. \quad (6)$$

The $\Delta H^\circ_f(S)_g$ value equal to 279.1 kJ mol^{-1} and the P=S binding energy, $E(P{=}S)_g$ = 383.5 kJ mol^{-1} (the subscript "g" indicates that the corresponding value was calculated for the gas phase), were taken from Refs. 16 and 17. Since thermochemical data are unavailable not only for isomeric 2,5-dimethyl-1-phenylphosphorinan-4-ones, but also for simple cyclophosphines with the P^{III} atom, the enthalpies of formation were obtained from the molecular mechanics (MMX2) calculations using gaseous methylated cyclophophaketones (analogs of compounds **1**—**4**) as model compounds. Here, too, because of the lack of the P—C(sp^2) binding energy necessary for determination of the enthalpy of vaporization, we first calculated the enthalpies of formation, $\Delta H^\circ_f(R_3P)_g$, of compounds **5**—**8** with the methyl substituent attached to the P atom.



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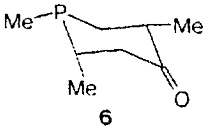

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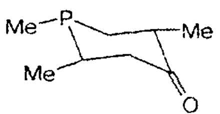

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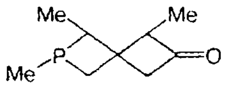

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It was found that $\Delta H^\circ_f(R_3P)_g$ = −279.8 (**5**), −284.7 (**6**), −277.6 (**7**), and −264.8 kJ mol^{-1} (**8**).

Then, following Benson's group additivity scheme,[18] by subtracting the Me group contribution and adding that of the phenyl group attached to the P atom (ΔH°_f(Me) = −42.2 kJ mol^{-1}; ΔH°_f(Ph) = 5[C(β)—H] + 6[C(β)—C(β)] = 193.5 kJ mol^{-1}), we calculated the enthalpies of formation of compounds **9**—**12** in the gas phase using the equation

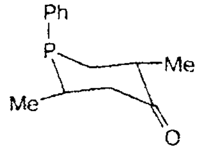
$$\Delta H^\circ_f(\mathbf{9}\text{—}\mathbf{12}) = \Delta H^\circ_f(\mathbf{5}\text{—}\mathbf{8}) - \Delta H^\circ_f(\mathrm{Me}) + \Delta H^\circ_f(\mathrm{Ph}). \quad (7)$$

It was found that $\Delta H^\circ_f(R_3P)_g$ = −44.1 (**9**), −49.0 (**10**), −41.9 (**11**), and −29.1 kJ mol^{-1} (**12**).

Table 3. Enthalpies of formation (ΔH°_f/kJ mol^{-1}) of compounds **1**—**4** in the condensed and gas phase* (MR_D = 78.8 cm^3 mol^{-1})

Compound	ΔH_{vap}	$-\Delta H^\circ_f$	
		Condensed phase	Gas phase
1	114.1	38.6	152.7
2	120.3	37.3	157.6
3	108.5	42.0	150.5
4	112.8	24.9	137.7

* The accuracy of determination is ±5.5—15.0 and ±1.5—2.8%, respectively



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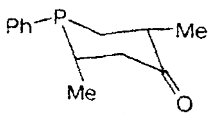

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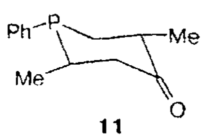

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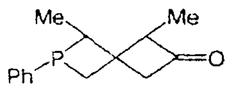

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The enthalpies of formation of isomers **1**—**4** in the gas phase were calculated using Eq. (6). The ΔH°_f values for the condensed (solid) phase ($\Delta H^\circ_f(R_3P)_{cond}$) for these compounds were calculated using the following relationship

$$\Delta H^\circ_f(R_3P)_{cond} = \Delta H^\circ_f(R_3P)_g + \Delta H_{vap}. \quad (8)$$

Taking into account the errors of determination of ΔH_{vap} values, the enthalpies of formation of isomers **1**—**4** in the condensed and gas phase can be assessed with an accuracy of ±5.5—15.0% and ±1.5—2.8%, respectively (Table 3).

The results of calculations of the $\Delta H^\circ_f(R_3P)_g$ values suggest that isomer **4**, with the cyclic skeleton in a *twist*-conformation, is the most unstable among the compounds under study.

* * *

Thus, we first obtained estimates of the enthalpies of vaporization and solvation of four isomers of 2,5-dimethyl-1-phenyl-1-thioxophosphorinan-4-one in weak proton-donor (chloroform and methanol) and polar (nitrobenzene) solvents and the enthalpies of formation of the isomers in the condensed and gas phase. The results obtained can be useful for assessment of thermochemical parameters of related cyclic compounds.

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