



ELSEVIER

Thermochemica Acta 288 (1996) 105–111

thermochemica
acta

Thermochemistry of heteroatomic compounds Part 9¹. Enthalpies of tautomeric transformation of hydrophosphorylic compounds

V.V. Ovchinnikov^{a,*}, L.I. Lapteva^a, E.V. Sagadeev^a, A.I. Konovalov^b

^a Kazan State Academy of Construction and Architecture, Zelonaya str.1, Kazan 420043, Tatarstan, Russia

^b Institute of Organic and Physical Chemistry of Russian Academy of Sciences, Arbusov str. 8, Kazan 420083, Tatarstan, Russia

Received 1 December 1995; accepted 1 March 1996

Abstract

The enthalpies of hydrogen bonding (ΔH_{hb}) and tautomeric transformation (ΔH_{tt}) of hydrophosphorylic compounds of different space groups have been determined. It was found that acyclic and six-membered cyclic phosphoric acids, except calicylic derivatives exist in a form with

P(O)H fragment and have ΔH_{tt} values in the gaseous phase of about 70 kJ mol⁻¹; 1,3,2-dioxophospholanic analogues are about 40 kJ mol⁻¹.

Keywords: Thermochemistry; Heteroatomic compounds; Hydrophosphorylic compounds

1. Introduction

Phosphorus compounds having the P(O)H hydrophosphorylic group in their structure have for a long period of time served as a phosphorylating material and have been a subject for theoretical investigations. Since the time of their discovery the question of the existence of different tautomeric forms of such compounds has been discussed. It is found [2–6] that the form with the P=O group is more stable than that with the P–OH structure. Previously we reported that the inclusion of P(OH) fragment into the strained five-membered ring structure leads to the formation of the

* Corresponding author.

¹ For part 8 see Ref. [1].

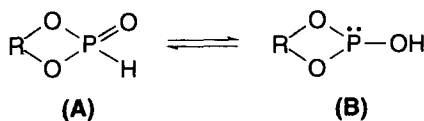
P-OH-form; this has been proved from its reactivity [7], ability to hydrogen bond [8] and increasing acidic properties in non-aqueous media [9]. Taking into account all the above mentioned results we undertook experimental determination of tautomerism enthalpy using the calorimetry of reaction in solutions.

2. Experimental

Enthalpies of reaction between phosphites, phosphoric acids, and rhomboidal sulfur have been measured in *p*-xylene at 363–373 K in the DAC-1-1 differential automatic calorimeter, as described previously [10]. Enthalpies of solution of all compounds were measured at 298 K in a differential calorimeter, all substances and solvents were synthesized, purified, and dried by standard methods [11].

3. Results and discussion

As found by us previously [7] cyclic catechol and salicylic acids (1 and 2) (Table 1) exist in two tautomeric forms (A and B) with three- and four-coordinated phosphorus atoms, i.e.



where R is *o*-C₆H₄ or *o*-C₆H₄(CO).

This situation should be reflected in the strength of hydrogen bonding to basic solvents. We used a calorimetric “pure base” method, suggested by Arnett and co-workers [8,12] for the determination of weak intermolecular interactions (Eq. (1)):

$$\Delta H_{\text{hb}} = (\Delta H_{\text{soln}}^{\text{Ai}} - \Delta H_{\text{soln}}^{\text{Mi}})_S - (\Delta H_{\text{soln}}^{\text{Ai}} - \Delta H_{\text{soln}}^{\text{Mi}})_{\text{CCl}_4} \quad (1)$$

where $\Delta H_{\text{soln}}^{\text{Ai}}$ and $\Delta H_{\text{soln}}^{\text{Mi}}$ are solution enthalpies of acid A_i and their model compound M_i which do not hydrogen bond to the solvent-base S.

2-Methoxy-4,5-benzo-1,3,2-dioxaphospholane (3) was chosen as a model compound for catecholphosphoric acid (1) with three-coordinated phosphorus atoms as compared to acyclic and cyclic derivatives of methylphosphonic acid (5,7,9,11) which served as a model compounds for acids (4,6,8,10). The enthalpy values of solution in dioxane, hydrogen bonding, and tautomeric transition of phosphoric acids are seen in Table 1. The calculated value of ΔH_{hb} for catecholphosphite (1) is 19 kJ mol⁻¹, comparable to that for such hydroxylic acids as phenol and *p*-fluorphenol [13]. The hydrogen bond enthalpies of other acyclic and cyclic phosphorylic derivatives (4,6,8,10) indicate very small values for ΔH_{hb} which are comparable to the size of the errors determination. This can be seen as evidence for the existence of a tautomeric form (A) for most of the compounds cited.

A more interesting situation was observed with salicylphosphoric acid (2) which in a crystalline form coexists with the (B) form, according to IR and ³¹P NMR spectro-

Table 1
Solution, hydrogen bond, and tautomeric transformation enthalpies of phosphoric acids in solutions at 298 K

Compound no.	Formula	$\Delta H_{\text{soln}}/(\text{kJ mol}^{-1})$				ΔH_{hb}^a or ΔH_{tt}^c (kJ mol^{-1})
		CCl_4	Dioxane	Nitrobenzene	<i>p</i> -Xylene	
1		-7.7	-28.1			-19.0
2				1.8	3.2	-83.0 ^b -71.0 ^c
3		0.7	-0.7			
4	$(\text{C}_3\text{H}_5\text{O})_2\text{P}(\text{O})\text{H}$	4.0	1.9			-0.6
5	$(\text{C}_3\text{H}_5\text{O})_2\text{P}(\text{O})\text{Me}$	3.7	1.2			
6		17.5	12.3			-0.6
7		24.5	19.9			
8		5.9	1.6			-1.9
9		4.7	2.3			
10		24.6	20.3			-1.2
11		5.7	2.6			

^a The uncertainties are no more than ± 0.3 – 0.8 kJ mol^{-1} ; some results have been reported previously [7,11].

^b Exothermic effect in nitrobenzene ± 3 – 5 kJ mol^{-1} .

^c Exothermic effect in *p*-xylene ± 3 – 5 kJ mol^{-1} .

scopic data [7]. On dissolution of this acid in nitrobenzene or *p*-xylene after the endothermic solution enthalpies a large exothermic effect of about 70 – 80 kJ mol^{-1} (Table 1) was observed; this case to some extent, can be accounted for as a slow tautomeric transition to a more stable form with $\text{P}=\text{O}$ and $\text{P}-\text{H}$ bonds [δ_{p} 111 and 4 ($^1\text{J}_{\text{PH}}$ 800 Hz) p.p.m.]. This has allowed us to make a more detailed thermochemical investigation of the tautomerism of hydrophosphorylic compounds with a different molecular structure.

Kabachnik and Golubeva [14] first showed that hydrophosphorylic compounds interact in solution with rhomboidal sulfur through the tautomeric form (**B**) forming

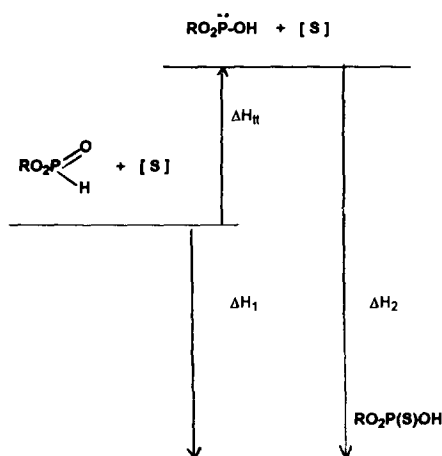
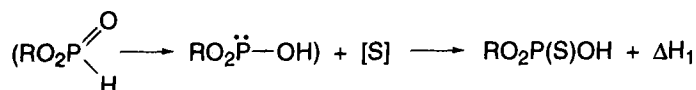


Fig. 1. Thermochemical cycle of interaction of different tautomeric forms (A and B) of hydrophosphorylic compounds towards sulfur.

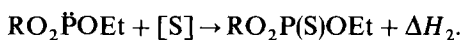
thiophosphorus acids:



The cyclic phosphoric acids react with elemental sulfur in the same manner [15]. This situation can be illustrated by a thermochemical cycle in which the enthalpy value of tautomeric transition can represent a difference between the reaction enthalpies of hydrophosphorylic compound and sulfur in the forms (A) and (B):

$$\Delta H_{\text{II}} = \Delta H_1 - \Delta H_2 \quad (2)$$

The heat of reaction (ΔH_1) of tautomer (A) with sulfur has been calorimetrically measured at 363–373 K; sulfur dissolved in *p*-xylene does not change its rhomboidal modification [16]. The interaction enthalpy of tautomer (B) with sulfur (ΔH_2) cannot be directly determined due to the instability of the enol form under such conditions therefore this energetic transformation has been modeled by the determination of the reaction heat of corresponding ethylphosphites with sulfur:



As there are some calculating values for the tautomerism energy of dialkylphosphites in the literature [4–6] it was reasonable to determine this important thermochemical parameter in the absence of the influence of solvent, i.e. in the gaseous phase. The reaction enthalpy in the gaseous phase can be expressed by Eq. (3) [10]:

$$\Delta H_r(\text{gas}) = \Delta H_r(\text{soln}) - \sum \Delta H_{\text{soln}}(\text{products}) + \sum \Delta H_{\text{soln}}(\text{reactants}) \quad (3)$$

Combining Eqs. (2) and (3), Eq. (4) is obtained; according to this the tautomeric transition enthalpy in the gaseous phase represents a difference of the heats ΔH_1 and ΔH_2 in *p*-xylene and algebraic sums of the solvation enthalpies of all products and reactants of both reactions:

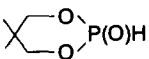
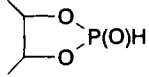
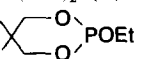
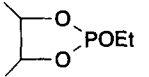
$$\begin{aligned} \Delta H_{\text{tr}}(\text{gas}) = & \Delta H_1(\text{xyl}) - \Delta H_2(\text{xyl}) - \Delta H_{\text{solv}}(\text{RO}_2\text{P(S)OH}) + \Delta H_{\text{solv}}(\text{RO}_2\text{P(S)OEt}) \\ & + \Delta H_{\text{solv}}\text{RO}_2\text{PHO} - \Delta H_{\text{solv}}\text{RO}_2\text{POEt} \end{aligned} \quad (4)$$

Because the reaction enthalpies were measured at 363–373 K, then according to Kirchoff's law it is necessary to take into consideration the heat capacities of all the participants in both processes. The absence, in the literature, of the required C_p data for all the compounds investigated does not enable compensation to be made for these values in Eq. (4) and we must suppose the calculated values of $\Delta H_{\text{tr}}(\text{gas})$ in the comparable row of substances to be acceptable. The reaction and solvation enthalpy values of phosphorus-containing derivatives are listed in Tables 2 and 3.

It can be seen from the data in Table 2 that ΔH_{tr} values for dioxaphosphorinanic and acyclic acids (**6** and **12**) are practically identical within experimental error and to a first approximation are comparable in magnitude with those of salicylphosphoric acid (**2**). Moreover, the observed values are rather close to the calculated magnitude of the tautomerism energy (90–100 kJ mol⁻¹) which has been obtained on the basis of approximate bond energies of both tautomeric forms [2]; this corresponds to the

Table 2

The reaction enthalpies (ΔH_1 and ΔH_2) of phosphoric acids and phosphites with sulfur in *p*-xylene and enthalpies of tautomeric transformation in the gaseous phase

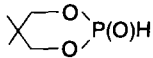
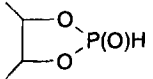
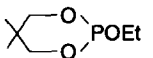
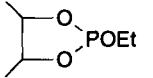
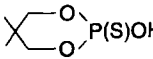
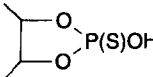
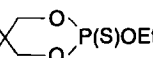
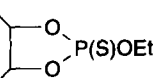
Compound no.	Formula	T/K	$-\Delta H_1$ and $-\Delta H_2$ (<i>p</i> -xylene)/ (kJ mol ⁻¹)	$\Delta H_{\text{tr}}^{\text{a}}$ (gas)/ (kJ mol ⁻¹)
6		368–373	17.6	61.4
8		368–373	20.5	37.3
12	(EtO) ₂ P(O)H	363	47.7	68.0
13		363	62.8	
14		363	27.2	
15	(EtO) ₃ P	363	91.2 ^b	

^a The uncertainties are no more than ± 3 –5 kJ mol⁻¹.

^b $\Delta H_f = -110.4$ kJ mol⁻¹ for solid sulfur and liquid phosphite [17].

Table 3

Solution, vaporization and solvation enthalpies in kJ mol^{-1} for reactants and products of reaction of acids (**6,8,12**) and phosphites (**13–15**) with sulfur^a

Compound no.	Formula	$-\Delta H_{\text{soln}}/$ (kJ mol^{-1})	$\Delta H_{\text{vap}}/$ (kJ mol^{-1})	$-\Delta H_{\text{solv}}/$ (kJ mol^{-1})
6		14.4	60.3	45.9
8		4.3	43.1	38.8
12	$(\text{EtO})_2\text{P(O)H}$	2.3	49.5	47.3
13		0.2	52.8	52.6
14		0.0	50.1	50.1
15	$(\text{EtO})_3\text{P}$	-1.2	53.0	54.2
16		43.8	121.8	78.0
17		42.0	126.6	84.6
18	$(\text{EtO})_2\text{P(S)OH}$	20.4	104.9	84.5
19		19.2	88.4	69.2
20		1.2	66.2	65.0
21	$(\text{EtO})_3\text{P(S)}$	-0.5	66.6	67.1

^a Thermochemical data for majority of compounds and methods of its determination were published previously [10,11].

existence of this kind of compound in the gaseous phase in a stable form with a tetra-coordinated phosphorus atom.

The enthalpy of tautomeric transition for five-membered cycloanalogue (**8**) represents almost a twofold reduction than for acids (**6** and **12**). This fact is in good agreement with the weaker P–H bond in phospholanic derivatives (reduced $\text{p}K_{\text{a}}$ and higher ΔH_{hb} magnitudes) and shows their easy transformation from a keto-structure to the enol form.

4. Conclusions

Thus, it follows from the experimental data of tautomerism enthalpies of hydrophosphorylic compounds of different molecular structure, that the acyclic and six-mem-

bered cyclic phosphoric acids exist in form (A) apart from salicylic derivative (2). As regards five-membered cyclic analogs a ring strain (about 25 kJ mol^{-1} [10]), an acceptor ability of 1,2-dioxyalkylenic substituents at phosphorus, and geometric factors of molecules assist their transformation from (A) into (B). The decrease of coordination number of the phosphorus atom from sp^3 to p^3 configuration is connected with the change of valence angle from 109 to 90° . The inner O–P–O angle in five membered cyclic compounds is essentially decreased (98 – 100°) compared with that in six-membered or acyclic analogs (104 – 106°) [18]. The latter circumstance makes the mentioned transformation more reasonable. The similar possibility of such “steric assistance” has been observed when investigating keto–enol tautomerism of cyclic ketones [19].

References

- [1] V.V. Ochinnikov, T.B. Makeeva, L.I. Lapteva and A.I. Kononov, *Thermochim. Acta*, 1995, in press.
- [2] R.F. Hudson, *Structure and Mechanism in Organophosphorus Chemistry*, Mir, Moscow, 1967 (in Russian).
- [3] A.J. Kirby and S.G. Warren, *The Organic Chemistry of Phosphorus*, Mir, Moscow, 1971 (in Russian).
- [4] J.P. Guthrie, *Can. J. Chem.*, 57 (1979) 236.
- [5] M.S. Gordon, J.A. Boatz and M. Schmidt, *J. Phys. Chem.*, 88 (1984) 2988.
- [6] Yu. V. Babin, V.M. Mamaev, Yu. A. Ustinyuk and V.V. Gorchakov, *Theor. Exp. Chem.*, 25 (1989) 486.
- [7] V.V. Ovchinnikov, S.V. Cheresov, R.A. Cherkasov and A.N. Pudovik, *Zh. Obshch. Khim.*, 54 (1984) 1021.
- [8] V.V. Ovchinnikov, S.V. Cheresov, V.V. Klochkov, A.V. Aganov, R.A. Cherkasov and A.N. Pudovik, *Dokl. Akad. Nauk SSSR*, 276 (1984) 144.
- [9] I.S. Antipin, R. Ph. Gareyev, V.V. Ochinnikov and A.I. Kononov, *Dokl. Akad. Nauk SSSR*, 304 (1989) 136.
- [10] V.V. Ovchinnikov, Yu. G. Safina, R.A. Cherkasov and A.N. Pudovik, *Zh. Obshch. Khim.*, 58 (1988) 2081.
- [11] V.V. Ochinnikov, V.V. Brus'ko and A.A. Sobanov, *Thermochim. Acta*, 233 (1994) 153.
- [12] E.M. Arnett, E.J. Mitchell and T.S.S.R. Murty, *J. Am. Chem. Soc.*, 96 (1974) 3875.
- [13] M.D. Joesten and L.J. Schaad, *Hydrogen Bonding*, Marcel Dekker, New York, 1974.
- [14] M.I. Kabachnik and E.I. Golubeva, *Dokl. Akad. Nauk SSSR*, 105 (1955) 1258.
- [15] V.V. Ovchinnikov, V.I. Galkin, R.A. Cherkasov and A.N. Pudovik, *Zh. Obshch. Khim.*, 47 (1977) 290.
- [16] M.G. Voronkov (Ed.), *Reactions of Sulfur with Organic Compounds*, Nauka, Novosibirsk, 1979 (in Russian).
- [17] C.L. Chernick, J.B. Pedley and H.A. Skinner, *J. Chem. Soc.*, (1957) 1851.
- [18] V.A. Naumov and L.V. Vilkov, *The Molecular Structure of Organophosphorus Compounds*, Nauka, Moscow, 1986 (in Russian).
- [19] A.N. Nesmeyanov (Ed.), *The Steric Effects in Organic Chemistry, Foreign Literature*, Moscow, 1960 (in Russian).