Mendeleev Commun., 1999, 9(6), 240–241

The mechanism of a diad prototropic rearrangement of hydrophosphorylic compounds

Victor M. Mamaev,*[a] Andrew V. Prisyajnuk,[b] Dmitry N. Laikov,[a] Ludmila S. Logutenko[b] and Yuri V. Babin[b]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: + 7 095 0932 8846; e-mail: vmam@nmr.chem.msu.su*

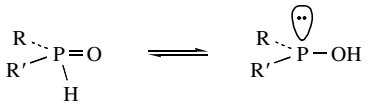
[b] *Far-East Academy of Economics and Management, 690091 Vladivostok, Russian Federation. Fax: +7 4232 40 6634; e-mail: yub@mail.primorye.ru*

A prototropic rearrangement of a number of hydrophosphorylic compounds has been found to proceed by a bimolecular mechanism with tunneling predominant at temperatures below 340 K.

Organophosphorus compounds play an important role in biochemical processes. The chemistry of phosphorus depends on the development of adequate quantum-chemical models of the electronic structure of phosphorus compounds in order to predict the structure and ways of synthesis of new phosphorus compounds.

Hydrophosphorylic compounds are the main raw materials for synthesis of different classes of chemical products such as catalysts, extractants and drugs. This paper is devoted to a theoretical study of a diad prototropic tautomeric rearrangement of hydrophosphorylic compounds.

Most of trivalent phosphorus acids are well known to be stable as hydrophosphorylic compounds **1** (R, R′ = Alk, AlkO):[1]



1 **2**

According to ICR data,[2] in the case of R, R′ = MeO, the energy of tautomerization is equal to 6.5 kcal mol^{-1}. On the other hand, for bis-pentafluorophenylphosphinic acid[3] and some cyclic esters of phosphorous acid[4] an equilibrium between **1** and **2** can be observed. If R and R′ are strong acceptor substituents (like CF_3), the equilibrium is almost completely shifted toward **2**.[5]

Since experimental determination of the mechanism and energy of tautomerization of the prototropic rearrangement in hydrophosphorylic compounds is difficult, a theoretical study of such systems is of great interest. Thus, theoretical studies of various fluorine-substituted dimethylphosphinic acids can provide an opportunity to elucidate the regularities of the prototropic equilibrium, self-association and other important aspects of acid–base interactions.[6]

We report here on calculations of the structures of the stationary points on the potential-energy surfaces of reactions (1)–(5).

$Me_2POH \rightleftharpoons Me_2P(O)H;$ (1)

$(CH_2F)_2POH \rightleftharpoons (CH_2F)_2P(O)H;$ (2)

$(CHF_2)_2POH \rightleftharpoons (CHF_2)_2P(O)H;$ (3)

$(CF_3)_2POH \rightleftharpoons (CF_3)_2P(O)H;$ (4)

$(MeO)_2POH \rightleftharpoons (MeO)_2P(O)H.$ (5)

The calculations were performed with a RHF wave function in the 6-31G** basis set with taking into account the correlation effects at the MP2 level using the GAMESS program,[7] as well as by DFT according to the PBE formula for the correlation exchange functional[8] using the program from ref. 9. We assumed the rearrangement to occur by both unimolecular and bimolecular mechanisms.

The geometry parameters of the obtained equilibrium structures are consistent with the experimental data for related compounds (Table 1). The results of the RHF + MP2 and DFT calculations are in a good agreement with each other (Table 2).

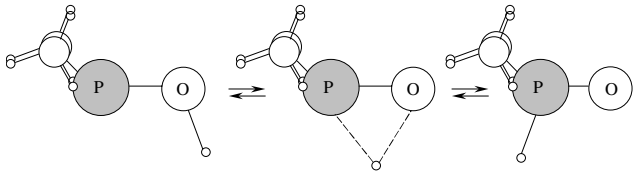
Table 1 Bond lengths in the test compounds.

Bond (reaction)	Experimental bond length[10]/Å	RHF (6-21G**) + MP2 data/Å	DFT data/Å
P-C (1)	1.844[a]	1.831	1.855
P-C (4)	1.904[b]	1.866	1.922
P-O (5)	1.620[c]	1.639	1.656
P=O (1)	1.476[d]	1.482	1.511
P-C (1)	1.809[d]	1.831	1.855
P=O (4)	1.517[e]	1.475	1.495
P-O (4)	1.5725[e]	1.610	1.620
P=O (5)	1.477[f]	1.475	1.495
P-O (5)	1.5806[f]	1.639	1.656
O-C (5)	1.4326[f]	1.443	1.450

[a]In PMe_3. [b]In $P(CF_3)_3$. [c]In $P(OMe)_3$. [d]In $O{=}PMe_3$. [e]In $O{=}P(CF_3)_3$. [f]In $O{=}P(OMe)_3$.

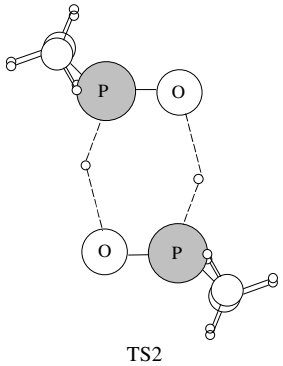
Note that the DFT reproduces the experimental value of the tautomerization energy for reaction (5).[2] According to Table 2, in the cases of (3) and (4), the reaction equilibrium in the system will be shifted toward **2**, while for (1) it will be shifted toward **1**. It is interesting that for reaction (3) both computational methods predict the reaction equilibrium to be shifted toward **2** to a greater extent than for (4).

In the case of a unimolecular mechanism of (1)–(5) the rearrangement goes from a bound state of **1** to **2** *via* a transition state (TS). All the structures have a symmetry plane:



1 TS **2**

According to DFT data, the activation barriers for (1)–(5) are as high as 50–60 kcal mol^{-1}. If we consider a bimolecular mechanism of the rearrangement, a TS of C_2 symmetry is formed (TS2). Its structure is given below:



TS2

In this case, the activation barrier is lowered by *ca*. an order of magnitude. The geometry and energy parameters of TS and

Table 2 Energies of structures **2** with respect to **1** for reactions (1)–(5)/ kcal mol^{-1}.[a]

Reaction	RHF + MP2 method	DFT[b]
1	–8.8	–3.8
2	–2.5	3.9
3	5.0	8.6
4	2.5	6.7
5	–12.0	–6.1

[a]A negative value means that form **2** is more stable than **1**. [b]With the addition of the zero point energy.

TS2 for reaction (1) are given in Table 3. Note that the replacement of hydrogen atoms with fluorine atoms changes these parameters only slightly.

The proton-transfer reactions are known to occur with an essential tunnel effect.[11] In order to evaluate the tunnel effect, we have to calculate the so-called transmission factor $\chi(T)$ (*i.e.*, the ratio of the cumulative thermal rate constant to its over-the-barrier component).[12] For the case of small tunnel corrections, we can use the Wigner expression for $\chi(T)$:[13]

$$\chi(T) = 1 + \left(\frac{h\omega^{\neq}}{24k_{\mathrm{B}}T}\right)^2,$$

where $\omega^{\neq}$ is the imaginary 'vibrational frequency' at the saddle point of TS, and k_{B} is the Boltzmann constant. If χ is equal to 2, the tunnel and activation contributions to the rate constants are equal at a given temperature. Calculations by the Wigner formula show that in the case of a unimolecular mechanism of reactions (1)–(5) $\chi \geq 2$ (*i.e.*, tunneling is predominant) at $T \leq 420$ K, while in the case of a bimolecular mechanism $\chi \geq 2$ at $T \leq 340$ K.

Thus, we can conclude that for reactions (1)–(5) the bimolecular mechanism is favourable, and tunneling contributes mainly to the rate constant at $T \leq 340$ K.

Table 3 The geometry and energy ($E^{\neq}$) parameters of TS and TS2 structures for reaction (1).[a]

Parameter	TS	TS2
P–H	1.48	1.59
O–H	1.46	1.35
P–O	1.62	1.63
$E^{\neq}$	46.9	4.5

[a]The activation barriers are counted relatively to the energies of **1** for TS, and relatively to the doubled energies of **2** for TS2. The bond lengths are given in Å, the energies are in kcal mol^{-1} with allowance for the zero point energy.

References

1 M. I. Kabachnik, in *Khimiya i primenenie fosfororganicheskikh soedinenii* (*Chemistry and Applications of Organophosphorus Compounds*), Izd. AN SSSR, Moscow, 1957, p. 18 (in Russian).
2 W. J. Pietro and W. J. Hehre, *J. Am. Chem. Soc.*, 1982, **104**, 3594.
3 D. D. Magnelly, G. Test, J. U. Lowe and W. E. McQuistion, *Inorg. Chem.*, 1966, **5**, 457.
4 E. E. Nifant'ev, A. I. Zavalishina, S. F. Sorokina and A. A. Borisenko, *Zh. Obshch. Khim*, 1976, **46**, 471 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1976, **46**, 469].
5 J. E. Griffits and A. B. Burg, *J. Am. Chem. Soc.*, 1960, **82**, 1507.
6 E. E. Nifant'ev, *Khimiya gidrofosforil'nykh soedinenii* (*Chemistry of Hydrophosphorylic Compounds*), Nauka, Moscow, 1983 (in Russian).
7 M. W. Schmidt, K. K. Balridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
8 J. P. Perdew, K. Burke and M. Ernzerhof, *J. Chem. Phys.*, 1996, **105**, 9982.
9 D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
10 V. A. Naumov and L. V. Vilkov, *Molekulyarnye struktury fosfororganicheskikh soedinenii* (*Molecular Structures of Organophosphorus Compounds*), Nauka, Moscow, 1986 (in Russian).
11 W. H. Miller, N. C. Handy and J. E. Adams, *J. Chem. Phys.*, 1980, **72**, 99.
12 D. Truhlar, W. Hase and R. Hynes, *J. Phys. Chem.*, 1983, **87**, 2264.
13 R. P. Bell, *The Tunnel Effect in Chemistry*, Chapman and Hall, London, 1980.

Received: 11th January 1999; Com. 99/1423