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Theoretical study of diad prototropic rearrangement in fluorinated methylphosphonic acid *N*,*N*-dimethylamides

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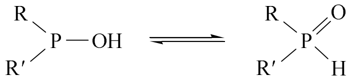
The DFT calculations of fluorinated methylphosphonic acid *N*,*N*-dimethylamides revealed that they exist as a mixture of two tautomeric forms at ~400 K.

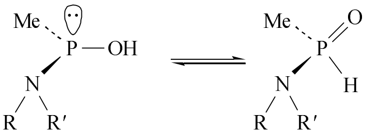
Organophosphorus compounds including hydrophosphoryl compounds (HPC) are widely used in industry, agriculture and medicine. Many HPC are used as complexing and extracting agents, as well as corrosion and saline deposition inhibitors.[1,2]

From a theoretical point of view, it is interesting to study the mechanism of diad prototropic rearrangement in HPC, as well as the structures of equilibrium HPC tautomers.



Earlier, we studied prototropic rearrangement in HPC[3–5] and confirmed the experimental data that electron-accepting groups attached to the phosphorus atom shift the equilibrium towards tautomer I. According to the quantum-chemical models of the rearrangement in hypophosphoric acid dimethylamides, the equilibrium is shifted toward species I in the course of consecutive fluorine substitution for hydrogen in the methyl groups.[5] We determined the DFT approach to be accurate in the computation of the geometry and electronic structures of HPC.

In this work, we consider the tautomeric rearrangement in the fluorinated methylphosphonic acid *N*,*N*-dimethylamides:



I **II**

where R and R′ are CH_nF_{3-n}, $n = 0$–3.

The quantum-chemical calculations were carried out using the DFT technique in a triple-zeta AO basis. We used the PBE formula for the correlation-exchange function,[6] and the software was described in ref. 7.

The Gibbs energies and equilibrium constants of the process at 400 K are listed in Table 1. We used the reaction isotherm $K_p = \exp(-\Delta G_0/RT)$ to calculate K_p. Here, $\Delta G_0 = G_{II} - G_I$ denotes the change of the Gibbs energy in the course of reaction at 298 K. Under laboratory conditions, the processes in HPC usually occur at ~400 K.[2]

Table 1 Changes in the Gibbs energy in the course of the process (ΔG/kJ mol^{-1}), the equilibrium constants K_p of the tautomeric rearrangement **I** → **II** at $T = 400$ K, bond orders of the P=O and O–H bonds (B_{PO}, B_{OH}) in struc-tures **II** and **I**, respectively, and the charges at the P and O atoms of structures **II**, at the O and H atoms of the hydroxyl groups of structures **I** (in atomic charge units).

R	R′	ΔG	K_p	Structure **II**			Structure **I**		
				B_{PO}	q_P	q_O	B_{OH}	q_O	q_H
Me	Me	–3.7	105	1.77	0.96	–0.71	0.87	–0.62	0.30
CH_2F	CH_2F	–3.6	94	1.78	0.95	–0.69	0.86	–0.61	0.31
CHF_2	CHF_2	–4.1	174	1.75	0.93	–0.70	0.85	–0.59	0.32
Me	CH_2F	–4.4	240	1.75	0.97	–0.71	0.86	–0.60	0.30
Me	CHF_2	–0.8	2.58	1.79	0.91	–0.68	0.85	–0.62	0.31
Me	CF_3	–0.7	2.40	1.84	0.91	–0.65	0.85	–0.60	0.32
CH_2F	CF_3	–1.0	1.38	1.84	0.89	–0.65	0.85	–0.60	0.32
CH_2F	CHF_2	–0.5	1.95	1.85	0.89	–0.65	0.85	–0.60	0.32
CF_3	CF_3	1.6	0.12	1.85	0.89	–0.65	0.85	–0.59	0.33

According to Table 1, the tautomeric equilibrium is shifted towards the derivatives of type II, unlike the compounds considered previously.[5] The successive fluorine substitution for hydrogen atoms causes the equilibrium to shift towards tautomer I, similarly to the derivatives of dimethylphosphite.[3]

The data in Table 1 are indicative of a decrease in the thermodynamic stability of form II compared to tautomer I in the course of successive fluorination of the N-methyl group. The simultaneous growth of the P=O bond strength in the corresponding structure is also observed. The order of the P=O bond gains a more covalent character as the absolute values of charges at the P and O atoms decrease. Surprisingly, the P=O bond length remains nearly the same in all considered tautomers and is equal to 1.50 Å.

Thus, the strength of the P=O bond in form II of the fluorinated derivatives of the phosphonic acid does not determine the ratio between forms I and II in the mixture of tautomers. The growth of the stability of form I should be ascribed to other factors. For instance, we can observe an increase in the O–H acidity of structures I in the course of consecutive fluorine substitution for methyl hydrogens. As the hydrogens are replaced with fluorine, the charge at the H atom increases, and the order of the OH bond decreases to facilitate OH bond dissociation, *i.e.*, increases the acidity (Table 1).

On the basis of the calculated equilibrium constants, one can expect that HPC like $N(CF_3)(Me)P(Me)OH$, $N(CF_3)(CH_2F)$-$P(Me)OH$, $N(Me)(CHF_2)P(Me)OH$ and $N(CH_2F)(CHF_2)P(Me)OH$ occur as a mixture of two tautomeric forms at temperatures about 400 K in a gas phase.

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