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Prototropic rearrangement in fluorine-substituted hypophosphoric acid dimethylamides

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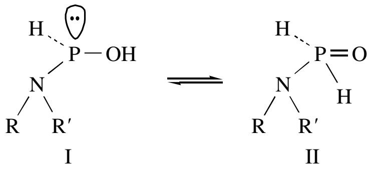
The prototropic rearrangement equilibrium of fluorine-substituted hypophosphoric acid dimethylamides in a gas phase has been found to be displaced towards the formation of a three-coordinated phosphorus atom, in contrast to the rearrangement of dimethyl phosphite derivatives.

Organic phosphorus compounds are of importance in biochemical processes. Hydrophosphorous compounds (HPC) are the precursors of chemical products such as catalysts, extractants and drugs.[1,2] Previously,[3,4] we studied the rearrangements of fluorine-substituted dialkyl phosphites to form dialkylphosphine oxides and possible mechanisms of such processes.

Here, we report on a theoretical study of the tautomeric rearrangement of fluorine-substituted hypophosphoric acid dimethylamides into dimethylaminophosphine oxides (Scheme 1).



R, R′ = CH_nF_{3-n} (n = 0–3)
Scheme 1

The quantum-chemical calculations were performed using the DFT technique in a triple-zeta AO basis. We used the PBE formula for the correlation-exchange functional[5] and the software described in ref. 6. Previously,[3,4] we found that DFT quantitatively represents the geometry and energy parameters of fluorine-substituted dimethylphosphites and dimethylphosphine oxides.

Kostyanovsky *et al.*[7] studied a tautomeric equilibrium between bis(1-aziridinyl)phosphinic acid and bis(1-aziridinyl)phosphine oxide and found a shift toward bis(1-aziridinyl)phosphinic acid. Our test DFT calculations are in agreement with these data.

The Gibbs energies and equilibrium constants of the reaction at 400 K are given in Table 1. We used the reaction isotherm $K_p = \exp(-\Delta G_0/RT)$ to compute K_p. Here, $\Delta G_0 = G_{II} - G_I$ is the change in the Gibbs energy in the course of reaction at 298 K.

We computed the energies of the molecular structures at 400 K since similar rearrangements can be observed in solutions at such temperatures.

Table 1 suggests that the reaction equilibrium in all considered rearrangements in a gas phase must be shifted towards the derivatives of hypophosphoric acid dimethylamides (I), in contrast to the rearrangement of dimethyl phosphite derivatives.[3]

This result is consistent with published data.[7] Successive hydrogen replacement with fluorine atoms causes the equilibrium to shift further (this is in accordance with published data[3]). Note that the change in the Gibbs energy grows abruptly when the total number of fluorine atoms n_F in methyl moieties becomes greater than the number of hydrogen atoms n_H: at $n_F > n_H$, ΔG = = (18.9–23.6) kJ mol^{-1}, and at $n_F < n_H$ ΔG = (6.6–9.3) kJ mol^{-1} (Table 1).

The most important geometry parameters of structures (I) and (II) are given in Table 2. It should be noted that the values are conserved when one successively replaces the methyl hydrogen atoms with fluorine atoms. An analysis of the geometry parameters of the molecular systems revealed the shifting of the equilibrium toward II to be followed by shortening in the P–O bond by ~0.2 Å in any case. This is related to an increase in the contribution of the 3*p* AO of the phosphorus atom in the bonding molecular orbitals formed by the 3*s* AO of a phosphorus atom and the 2*s* AO of an oxygen atom.

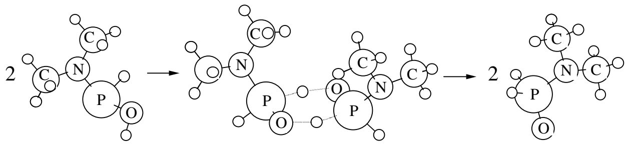
Table 1 Changes in the Gibbs energy in the course of reaction ΔG/kJ mol^{-1}, the barrier heights E_A^{400}/kJ mol^{-1} and the equilibrium constants K_p of the tautomeric rearrangement I → II at 400 K.

R	R′	ΔG	E_A^{400}	K_p
Me	Me	6.6	55.9	0.1
CH_2F	Me	9.3	43.2	0.06
CHF_2	Me	8.2	39.0	0.08
CF_3	Me	8.5	53.9	0.08
CF_3	CH_2F	22.7	68.4	0.001
CF_3	CHF_2	20.0	68.0	0.002
CF_3	CF_3	18.9	71.3	0.003
CH_2F	CH_2F	7.6	55.5	0.1
CHF_2	CHF_2	23.6	55.0	0.0008

Table 2 Geometry parameters of structures (I) and (II).

Structure (I)			Structure (II)			
r(P–N)/Å	r(P–O)/Å	β(POH)/°	r(P–N)/Å	r(P=O)/Å	r(P–H)/Å	β(POH)/°
1.71	1.71	108	1.70	1.50	1.44	113

We assumed[3] that the rearrangement occurs by a bimolecular mechanism like the rearrangement of dimethylphosphite derivatives *via* a transition state of C_{2v} symmetry:



Scheme 2

Like the dialkylphosphite → dialkylphosphine oxide rearrangement, in the structure of the transition state the six atoms (H–O–P–H–O–P) are in the same plane to form a nearly rectangular figure [β(POH) ≈ 104°, β(PHO) ≈ 154°].

An essential difference from the rearrangement of dimethylphosphite derivatives is that the height of the activation barrier of intermolecular proton transfer E_A^{400} for the I → II rearrangement changes in a wider region (Table 1). We cannot observe a clear correlation between the number of fluorine atoms and the potential-barrier height. It appears to be related to the asymmetry of the fluorine-substituted methyl fragments.

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