C-PCM Based Calculation of Energy Profiles for Proton Transfer in Phosphorus-Containing Acid–*N*,*N*-Dimethylformamide Complexes

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Received May 12, 2015

Abstract—Proton transfer along the hydrogen bond in complexes of DMF with H_3PO_4, H_3PO_3, $CH_3H_2PO_3$, and their dimers has been investigated by the B3LYP/6-31++G** method in combination with the C-PCM model. When the $O_{acid}\cdots O_{DMF}$ distance (R) in the scanning procedure is not fixed, the energy profile in all cases has a single well. When this distance is fixed, there can be a proton transfer in all of the complexes in the gas phase at $R > 2.6$ Å; if solvation is taken into account, proton transfer can take place at $R > 2.4$ Å ($R > 2.5$ Å for DMF complexes with $CH_3H_2PO_3$ and its dimer). The height of the energy barrier to proton transfer increases with increasing R. Proton transfer is energetically most favorable in the DMF–phosphoric acid complexes. The structural and energetic characteristics of the hydrogen-bonded complexes calculated on the basis of the solvation model are compared with the same parameters for the complexes in the gas phase.

Keywords: phosphoric acid, phosphonic acid, methylphosphonic acid, DMF, hydrogen bond, proton transfer, quantum chemical calculation, C-PCM model.

DOI: 10.1134/S003602441602014X