Solvent dependence of double proton transfer in the formic acid–formamidine complex: path integral molecular dynamics investigation

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Abstract: Solvent dependence of double proton transfer in the formic acid–formamidine (FA-FN) complex at room temperature was investigated by means of ab initio path integral molecular dynamics (AIPIMD) simulation with taking nuclear quantum and thermal effects into account. The conductor-like screening model (COSMO) was applied for solvent effect. In comparison with gas phase, double proton delocalization between two heavy atoms (O and N) in FA-FN were observed with reduced proton transfer barrier height in low dielectric constant medium (<4.8). For dielectric constant medium at 4.8, the chance of finding these two protons are more pronounced due to the solvent effect which completely washes out the proton transfer barrier. In the case of higher dielectric constant medium (>4.8), the ionic species becomes more stable than the neutral ones and the formate anion and formamidium cation are thermodynamically stable. For ab initio molecular dynamics simulation, in low dielectric constant medium (<4.8) a reduction of proton transfer barrier with solvent effect is found to be less pronounced than the AIPIMD due to the absence of nuclear quantum effect. Moreover, the motions of FA-FN complex are significantly different with increasing dielectric constant medium. Such difference is revealed in detail by the principal component analysis.

Keywords: Formic acid–formamidine complex; Path integral simulation; Nuclear quantum effect; Double proton transfer; Solvent effect