QUANTUM-CHEMICAL STUDY OF ENERGY SURFACE AND THE MINIMUM-ENERGY REACTION PATH OF THE PROTON TRANSFER ALONG O—H···N HYDROGEN BOND IN ACETIC ACID–IMIDAZOLE x 2 H_2O SYSTEM

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The semi-empirical quantum-chemical PCILO method has been used for calculation of the energy surface of the proton transfer along the O—H···N hydrogen bond in acetic acid–imidazole . 2 H_2O system. The PCILO calculations gave the energy surface with two minima. The most stable minimum corresponds to the O—H···N hydrogen bond and has been found at the distances $R_{H...N} = 0{\cdot}149$ nm and $R_{O-N} = 0{\cdot}107$ nm. According to the PCILO calculations the proton transfer is accompanied by significant changes in the O···N distance. The second energy minimum corresponding to the proton transfer $O^-{\cdots}NH^+$ complex has been found at $R_{H...N} = 0{\cdot}10$ nm and $R_{O...N} = 0{\cdot}30$ nm.

The approximative minimum energy reaction path for the proton transfer has been calculated by the procedure developed by Müller and Brown. The calculated energy barrier represents a value 376·15 kJ/mol. The second energy minimum lies higher by 246 kJ/mol.

Existence of hydrogen bonds is a well known fact in chemistry and biology. Experimental studies[1] showed that many of these hydrogen bonds are proton-transfer hydrogen bonds. The interaction type in these hydrogen bonds depends on acid-base properties of the interacting components and specific solvation of the complex by the solvent molecules.

The especially large number of hydrogen bonds formed by the polar groups inside the protein molecules can provide extremely suitable conditions for the proton transfer. Hydrogen bonds between carboxylic and histidine residues in proteins were observed in refs[2–7]. The experimental study[8] of hydrogen bonds in model systems carboxylic acid/N-base showed that the hydrogen bonds type $O{-}H{\cdots}N = O^-{\cdots}H{-}N^+$ can have two-minimum potential functions.

Theoretical PCILO calculations of the proton potential functions of the systems acetic acid–pyridine[9] and acetic acid–imidazole[10] at two O···N distances (the equilibrium distance and a somewhat longer one, $R_{O...N} = 0{\cdot}30$ nm) indicated that the proton transfer is accompanied by significant fluctuations in the O···N distances. Increasing hydration of these systems (within the framework of supermolecular approach) results in deepening of the proton-transfer minimum and lowering of energy barrier between the hydrogen-bond and proton-transfer minima[9,10].

With the aim of a deeper theoretical study of the proton transfer process this paper gives results of the PCILO calculations of the total energy surface for the proton transfer in O—H···N hydrogen bond of the system acetic acid–imidazole hydrated by two water molecules.

CALCULATIONS

For calculation of the energy surface and the minimum-energy reaction path we used the PCILO method[11]. The energy surface for the proton transfer along the O—H···N hydrogen bond in the system acetic acid–imidazole . 2 H_2O was obtained by variation of the R_{O-H} and $R_{H...N}$ distances. Hydration of the system studied was considered similarly as in ref.[10] (Fig. 1). The calculations were carried out with experimental geometries of imidazole[12], acetic acid[13], and water[14] using a Siemens 4004/150 computer (Computer centre of Comenius University) and the QCPE No 220 program.

RESULTS AND DISCUSSION

The results of the PCILO calculations of energy surface of the proton transfer along O—H···N hydrogen bond in acetic acid–imidazole . 2 H_2O system are given in Fig. 2. The potential energy of this proton-transfer process was calculated as a func-

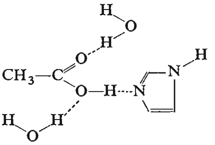

FIG. 1

Model of hydrogen bond and specific hydration of acetic acid–imidazole system

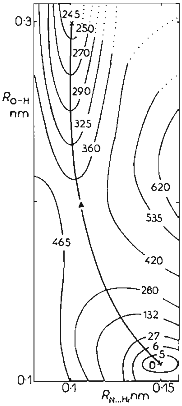

FIG. 2

The PCILO calculated energy surface of the proton transfer in acetic acid–imidazole . 2 H_2O system. Isoenergetic curves in kJ/mol with respect to the global energy minimum taken as zero energy. The minimum-energy reaction path (heavy line) represents the path of reaction valley. ▲ the saddle point tion of two parameters (distances R_{O-H} and $R_{H...N}$). According to the PCILO calculations the energy surface has two energy minima. The lower one corresponding to the hydrogen-bond complex was found at $R_{O-H} = 0{\cdot}107$ nm and $R_{H...N} = 0{\cdot}149$ nm distances. The second minimum calculated at $R_{O...H} = 0{\cdot}30$ nm and $R_{H...N} = 0{\cdot}10$ nm is higher by 245 kJ/mol and corresponds to the proton transfer complex $O^- \cdots NH^+$.

A theoretical approach to the proton-transfer process necessitates determination of the transition state and its approximate localization, *i.e.* determination of the saddle point at the energy surface. In our case the localization of the saddle point was carried out by the procedure developed by Müller and Brown[15,16]. This procedure makes use of generation of ascending valley points for the localization of the saddle point. Then the approximative minimum-energy reaction path was calculated by generating a series of descending path points[15,16]. The potential barrier was calculated from position of the saddle point, its value being 376·15 kJ/mol.

Lindemann and Zundel[8] studied in detail the system acetic acid–imidazole using IR spectroscopy. They found that addition of 2–6 water molecules to the acetic acid–imidazole complex does not cause dissociation of hydrogen bonds but causes an increase in population of the $O^- \cdots NH^+$ structure. Addition of further amount of water molecules causes dissociation of the $O^- \cdots NH^+$ bonds. Our previous PCILO calculations[10] of the system acetic acid–imidazole . n H_2O ($n = 2, 4$) at two $R_{O...N}$ distances showed in accordance with experiment that the water molecules lower the energy barrier between the minima, decrease the second minimum of the potential function, and shift it towards longer R_{O-H} distances. These PCILO calculations of the complete energy surface for the proton transfer in the O—H···N bond

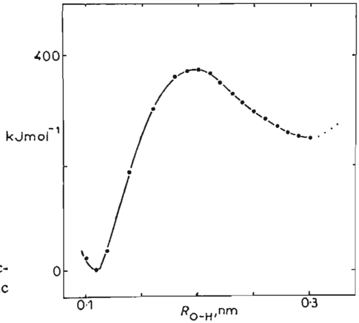

FIG. 3

The PCILO calculated minimum-energy reaction path for the proton transfer in the acetic acid–imidazole . 2 H_2O system of acetic acid–imidazole . 2 H_2O system gave a clear evidence for the fact that the proton-transfer process is connected with considerable change of the $O \cdots N$ distance. ($R_{O...N}$ = 0·256 and 0·40 nm for the hydrogen-bond and the proton-transfer complexes, respectively.) Plotting the two-dimensional energy minima against the R_{O-H} distance gives the curve represented in Fig. 3. This curve represents the minimum-energy reaction path of the proton transfer in dependence on the reaction coordinate (R_{O-H} length). According to this graph the proton transfer in the system studied represents an endothermic reaction. However, such PCILO calculations suffer from the main disadvantage that the perturbation expansion is diverging at great distances, and the second minimum cannot be completely calculated (dashed lines in Figs 2 and 3). To surmount these difficulties the problem necessitates the MC-SCF or the variation CI procedure[17]. Thus the PCILO method can only be used for a semiquantitative description of the proton-transfer processes in hydrogen bonds.

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