

# Theoretical study on ground-state proton/H-atom exchange in formic acid clusters through different H-bonded bridges

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**Abstract.** The ground-state triple proton/H-atom transfer (GSTPT/GSTHAT) reactions in HCOOH complexed cyclically with H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub> and mixed solvents H<sub>2</sub>O-NH<sub>3</sub>/CH<sub>3</sub>OH-NH<sub>3</sub> were studied by quantum mechanical methods in heptane. The GSTPT/GSTHAT in HCOOH-(H<sub>2</sub>O)<sub>2</sub>, HCOOH-(CH<sub>3</sub>OH)<sub>2</sub>, HCOOH-(NH<sub>3</sub>)<sub>2</sub>, HCOOH-H<sub>2</sub>O-NH<sub>3</sub>, HCOOH-NH<sub>3</sub>-H<sub>2</sub>O, HCOOH-CH<sub>3</sub>OH-NH<sub>3</sub> and HCOOH-NH<sub>3</sub>-CH<sub>3</sub>OH systems all occurred in an asynchronous but concerted protolysis mechanism. The formation pattern of the H-bonded chain was important to reduce the proton/H-atom transfer barrier. For the HCOOH-S<sub>1</sub>-S<sub>2</sub> (S<sub>1</sub>, S<sub>2</sub>: H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>) complex, the GSTPT/GSTHAT barrier height of the HCOOH-S<sub>1</sub>-S<sub>2</sub> complex, in which the H-bonded chain was formed with different solvent molecules, was lower than that of HCOOH-S<sub>1</sub>-S<sub>2</sub> complex, in which the H-bonded chain was composed of same solvent molecules. H-bonded chain consisting of mixed solvent molecules can accumulate their proton-accepting abilities and then speed up proton/H-atom transfer. When the less-basic H<sub>2</sub>O or CH<sub>3</sub>OH is connected to O-H group of HCOOH directly and the PT/HAT process is started by accepting a proton/H-atom from HCOOH, the PT/HAT reaction would be pulled by the more basic NH<sub>3</sub> along the H-bonded chain from the front. On the contrary, when the more-basic NH<sub>3</sub> is bonded to O-H group of HCOOH directly, the less-basic H<sub>2</sub>O or CH<sub>3</sub>OH hardly pulled PT/HAT process from the front. A good correlation between the proton-accepting ability (basicity) of the H-bonded chain and the GSTPT/GSTHAT barrier height was obtained.

**Keywords.** Ground-state proton/H-atom transfer; formic acid; quantum mechanical; mixed solvent; protolysis mechanism.

## 1. Introduction

Proton/hydrogen-atom transfer (PT/HAT) is the most fundamental and important reactions which take part in a large number of chemical and biological processes.<sup>1-6</sup> Therefore, modeling and understanding the mechanisms and dynamics of PT/HAT process at the atomic level are very important. PT/HAT can take place within a molecule or between different molecules depending upon the donor and acceptor groups. If the donor and acceptor groups are in different molecules, PT/HAT can occur as an intermolecular reaction. If the donor and acceptor groups are in the same molecule, and if the distance between the donor and acceptor groups are appropriate to form intramolecular H-bonds, PT/HAT can occur as an intra-molecular reaction. When the donor and acceptor groups are in the same molecule but far away from each other, PT/HAT can hardly take place. In this case, proton/H-atom can transfer with the help of protic solvent molecule, which acts as a bridge to link the donor and acceptor by forming H-bonds. The H-bonded chains between the donor and acceptor

groups provide an effective path for the long distance proton/H-atom transport process. With the assistance of solvent molecule, multiple protons/H-atoms can relay *via* a H-bonded proton-donor-acceptor bridge.<sup>7,8</sup> Such a process is called solvent-assisted PT/HAT, and is very significant in enzyme reactions.<sup>9</sup>

Many studies have been performed on the solvent-assisted PT/HAT in H-bonded complexes. For example, Kwon *et al.*,<sup>10</sup> investigated the double excited-state proton transfer (ESPT) process in the 7-azaindole-alcohol (7AI-alcohol) complexes and reported that the acidity of the bridging alcohol molecules which formed H-bonded chains in the 7AI-alcohol complexes played the key role for the PT dynamics. Kerdpol *et al.*,<sup>11</sup> simulated the PT process in 7AI with water, ammonia and mixed water-ammonia complexes to study the effect of different solvents on the PT reaction. They found that the highest proton transfer probability appeared in the 7AI-ammonia-water complex when NH<sub>3</sub> was H-bonded directly to the N-H group of 7AI. They also revealed that replacing H<sub>2</sub>O with NH<sub>3</sub> helped to lower the barrier height of the multiple PT process efficiently. Tanner *et al.*,<sup>12-14</sup>

researched 7-Hydroxyquinoine (7HQ) with mixed ammonia-water complexes in the excited state. Their results showed that the HAT along the solvent wire was terminated when one or two water molecules replaced  $\text{NH}_3$  molecule.

Daengngern *et al.*,<sup>15</sup> studied the PT process of 7-azaindole with mixed water-methanol complex in order to understand the effect of mixed solvent and the influence of different connection patterns at the proton donor site. They found that the complex, in which methanol was connected to the N-H group in the pyrrole ring of 7AI, had the lower average excited state barriers than that of the complex in which water was connected to the pyrrole of 7AI. Recently, Jang *et al.*,<sup>16</sup> investigated the triple PT dynamics in the 7-hydroxyquinoline complex, in which the hydrogen bonded chain consisted of mixed solvent molecules having different proton-donating abilities. They found that the rate constant was determined by the acidity of the alcohol, which was H-bonded to the base directly. When the less acidic alcohol, rather than the more acidic alcohol, was connected to the base directly, the rate was much faster. Riccardi *et al.*,<sup>17</sup> simulated the solvent-mediated multiple proton transfer mechanisms for enzymes by using hybrid quantum mechanical/molecular mechanical (QM/MM) methods. Their results indicated that the long-range proton relays in solutions and enzymes showed different features due to the different  $pK_a$  values of involving groups and electrostatic interactions with the environment. Mai *et al.*,<sup>18</sup> suggested that the activation energy of the long-range multiple proton relay changed with the hydroxyl molecules in the H-bonded chain. Lower the  $pK_a$  of the proton wire, faster is the rate of proton transfer. It is obvious that the features of the H-bonded chain consisting of different bridging molecules should play a vital part in the PT/HAT process.

Compared to the excited state proton/H-atom transfer (ESPT/ESHAT), the ground-state proton/H-atom transfer (GSPT/GSHAT) reaction has been rarely studied. Since the properties of the bridging H-bonded chains influenced the long-range PT/HAT process, obviously in the excited-state, we may expect that the bridging H-bonded wires may also have the same effect on the GSPT/GSHAT process. Hence, it is necessary to choose a simple model molecule having proton donor and acceptor groups to simulate long-range PT/HAT process in order to better understand the relations between the bridging H-bonded chain and the dynamics of long-range PT/HAT.

Formic acid dimer is one of the most widely studied species theoretically and experimentally<sup>19</sup> because it is one of the simplest models to exhibit PT/HAT along the two H-bonds. Especially, the exchange of

protons/H-atoms remained in an identical structure, and led to the possibility of tunneling during PT process. A large number of theoretical studies focused on the structures of the formic acid dimer and the potential energy surface for the double PT processes.<sup>20</sup> Previous studies on formic acid dimer also affirmed that double proton transfer occurred through a synchronous path in the gas phase.<sup>21</sup> For example, Miura *et al.*,<sup>22</sup> reported that the synchronous double PT time in formic acid dimer was  $\sim 5$  ps by using *ab initio* QM/MM molecular dynamics (AIMD) method. Wolf *et al.*,<sup>23</sup> reported the simultaneous PT time in formic acid dimer was 20 ps at 500~700 K by using a projected augmented wave method.

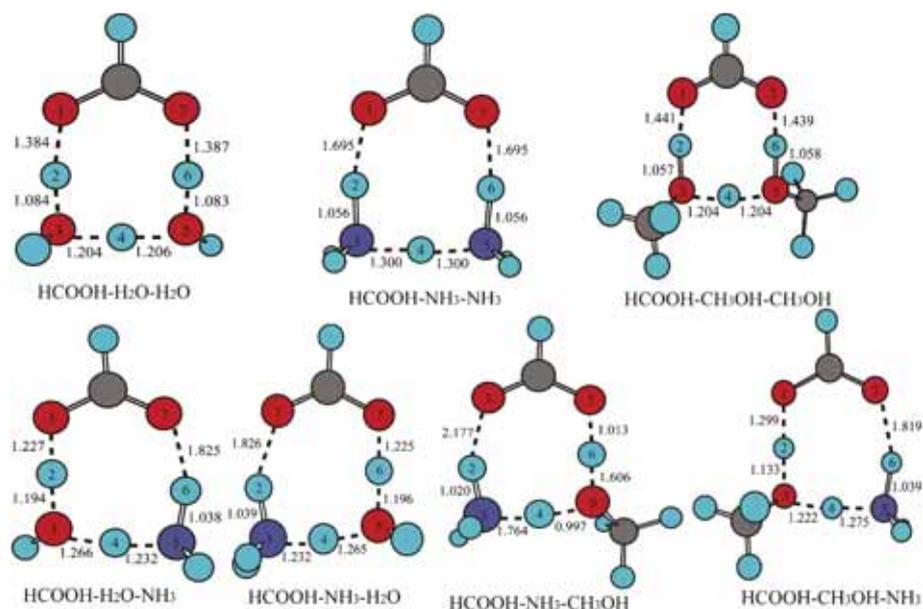
Formic acid has an O-H proton/H-atom donor site and a carbonyl O proton/H-atom acceptor site, so it is easy to form H-bonded networks with polar solvent molecules. Kohanoff *et al.*,<sup>24</sup> observed the asynchronous double PT occur in the presence of the protic solvent. Many studies on the mechanism and dynamics of PT in HCOOH-water complexes have been carried out widely.<sup>25</sup> Recently, Mackenzie *et al.*,<sup>26</sup> studied the double PT in HCOOH- $\text{HNO}_3$  complex by microwave spectroscopy and *ab initio* calculations. They found that the calculated barrier height of PT reaction was 1–2 kcal/mol larger than that of carboxylic acid dimers. And heavy atom motion was necessary to fulfill proton transfer process.

The long-range GSPT/GSHAT must be affected by the properties of bridging solvent molecules. However, no studies focusing on the effect of bridging solvent molecules to the PT/HAT in the ground-state have been reported. Therefore, we chose formic acid clusters as the target systems. Water, methanol and ammonia are the bridging solvent molecules to form the H-bonded chain with HCOOH to help proton/H-atom transfer. We aim at systematically studying the role of different solvent molecules around formic acid, and the effect of different H-bonded chain to the GSPT/GSHAT dynamics.

## 2. Computational details

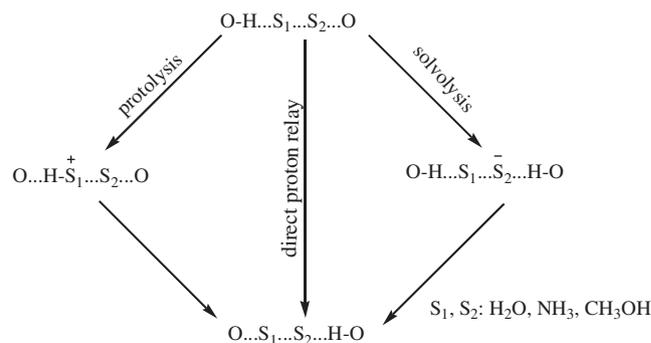
Reactant, product and transition state of GSPT/GSHAT in the HCOOH- $\text{S}_1$ - $\text{S}_2$  ( $\text{S}_1, \text{S}_2$ :  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ ) complexes were fully optimized in solution with B3LYP<sup>27</sup> and CAM-B3LYP<sup>28</sup> (Handy and co-workers' long-range corrected version of B3LYP using Coulomb-attenuation) methods, 6-311+G(d, p) basis set in the Gaussian 09 program.<sup>29</sup> The structures of all the stationary points along the potential energy surface were verified to be local minima or transition state by frequency calculations. Reactant and product had no imaginary frequency and transition state had only one imaginary





**Figure 1.** Ground-state structures of TS for PT/HAT in the HCOOH-S<sub>1</sub>-S<sub>2</sub> (S<sub>1</sub>, S<sub>2</sub>: H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>3</sub>OH) complex in heptane at the B3LYP/6-311+G(d,p) level with SMD solvent model. Bond distances are in Å.

obtained with B3LYP and CAM-B3LYP methods no matter which bridging solvent molecule was connected to the O-H group of HCOOH. In the TS obtained at B3LYP/6-311+G(d, p) level, O<sub>1</sub>-H<sub>2</sub> and O<sub>5</sub>-H<sub>6</sub> distances were 1.227 Å~1.826 Å and 1.038 Å~1.196 Å, respectively. The O<sub>1</sub>-H<sub>2</sub> distance in HCOOH-S<sub>1</sub>-S<sub>2</sub> was about 0.2~0.6 Å longer than the O<sub>5</sub>-H<sub>6</sub> distance in the same complex obviously, which indicated that H<sub>2</sub> was transferred first and moved more than halfway from O<sub>1</sub> to O<sub>3</sub> atom, H<sub>4</sub> was transferred in succession and was in the middle of O<sub>1</sub>-O<sub>3</sub> distance, H<sub>6</sub> rarely was transferred. Eigen<sup>37</sup> proposed that the solvent-assisted long-range PT happened by three ways: proton transport from acid to solvent first, subsequently proton captured by base (protolysis), proton transfer from solvent to base first, subsequently proton transfer from acid to solvent (solvolysis), and direct proton transport between acid and base (Scheme 1). It is obvious that GSTPT/GSTHAT in the HCOOH-S<sub>1</sub>-S<sub>2</sub> complex was a typical protolysis path. Only two protons/H-atoms transferred evidently, the third proton hardly moved in GSTPT/GSTHAT reaction, and we may expect an intermediate and a stepwise mechanism. However, no intermediate has been found and all attempts went towards the reactant or the product in the end. No matter how the bridging solvents (H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>) connected with HCOOH to form H-bonded chain, a concerted protolysis by asynchronous mechanism was obtained. When the long-range corrected functional CAM-B3LYP was used, the H-bonds in the reactant and product were 0.02~0.06 Å shorter than the corresponding



**Scheme 1.** Possible mechanisms of long-range proton/H-atom transfer along H-bonded water, methanol, ammonia, water-methanol and water-ammonia molecules.

B3LYP values. And CAM-B3LYP predicted quite similar TS structures and same concerted protolysis and asynchronous mechanism. All the structural parameters obtained by CAM-B3LYP method are shown in Supplementary Information (Table S1).

The TS features of proton/H-atom transfer process can be depicted with correlation plot between the hydrogen bond length and the proton/H-atom transfer coordinate. Limbach *et al.*,<sup>38,39</sup> suggested that the relationship between  $r_{AH}$  and  $r_{BH}$  in A-H...B complex could be expressed by using hydrogen bond coordinates  $q_1 = (1/2)(r_{AH} - r_{BH})$  and  $q_2 = r_{AH} + r_{BH}$  after combination the proton/H-atom transfer and hydrogen bond distance in same correlation. In A-H...B complexes, supposing that the sum of two bond orders is conserved during proton relay process,<sup>40</sup>  $n_{AH} + n_{BH} = 1$ , then the  $r_{AH}$  and

$r_{\text{BH}}$  distances satisfy the Pauling equations and correlate with each other.

$$n_{\text{AH}} = \exp\{-(r_{\text{AH}} - r_{\text{AH}}^0)/b_{\text{AH}}\} \quad (3)$$

$$n_{\text{BH}} = \exp\{-(r_{\text{BH}} - r_{\text{BH}}^0)/b_{\text{BH}}\} \quad (4)$$

where  $r_{\text{AH}}^0$  and  $r_{\text{BH}}^0$  are the bond lengths in the free AH and BH, and  $b_{\text{AH}}$  and  $b_{\text{BH}}$  are the parameters describing the decrease of bond valences with the corresponding distances in the AH and HB. When the symmetric hydrogen bonds are OHO and NHN,  $b$ 's are 0.37 Å and 0.404 Å, respectively.<sup>38,39</sup> For a linear H-bond,  $q_1$  is the distance from H to the H-bond center, and  $q_2$  is the distance from heavy atom A to B. The ‘‘bond energy bond order’’ correlation can be applied to study proton/H-atom transfer. With this type correlation, the characteristics of TS (bond order, earliness or lateness, and synchronicity) can be studied. When H is transported from A to B in the A–H...B complex,  $q_1$  raises from negative to positive and  $q_2$  locates at  $q_1 = 0$  after passing through a minimum. A positive or negative  $q_1$  value of TS means a late or early TS, respectively. And a small or large  $q_2$  value of TS means a tight or loose TS, respectively. In addition, the  $q_1$  values involving in multiple PT/HAT in TS should be similar or different in the synchronous or asynchronous mechanism, respectively.

The correlations between  $\text{O}_1\text{-H}_2$  and  $\text{H}_2\text{-O}_3(\text{N}_3)$  distances ( $\text{H}_2$  transfer),  $\text{O}_3(\text{N}_3)\text{-H}_4$  and  $\text{H}_4\text{-O}_5(\text{N}_5)$  distances ( $\text{H}_4$  transfer), and  $\text{O}_5(\text{N}_5)\text{-H}_6$  and  $\text{H}_6\text{-O}_7$  distances ( $\text{H}_6$  transfer) for the  $\text{HCOOH-S}_1\text{-S}_2$  complex at the B3LYP/6-311+G(d,p) level are shown in Figure 2. All stationary points (reactant, product and TS) were at or near the black line, which meant that the bond orders at all points were conserved. If the H-bonded chain in the  $\text{HCOOH-S}_1\text{-S}_2$  complex varied, the correlation points appeared in different positions along the solid line in the correlation plot. When the H-bonded chain consisted of the same solvent molecules, as shown in Figures 2a and 2b, the  $\text{H}_2$  and  $\text{H}_6$  points at the TS were in the upper-right and upper-left side, respectively. At the same time, the  $q_1$  values of  $\text{H}_4$  were zero and  $\text{H}_4$  correlation points were in the middle of the correlation plot. When  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  was used for  $\text{S}_1$  and  $\text{NH}_3$  was used for  $\text{S}_2$ , the  $\text{H}_2$  and  $\text{H}_4$  correlations of TS were near the center from the right side or in the center along the correlation plot, while the  $\text{H}_6$  correlation point at TS was in the left side (Figure 2c). When  $\text{NH}_3$  was used for  $\text{S}_1$  and  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  was used for  $\text{S}_2$ , the  $\text{H}_2$  correlation point at the TS was in the upper-right side, the  $\text{H}_4$  and  $\text{H}_6$  correlation points at the TS were in the center and near the center from the left side along the correlation plot (Figure 2d), respectively. Our results showed that  $\text{H}_2$  and  $\text{H}_6$  approached

$\text{O}_3/\text{N}_3$  and  $\text{O}_5/\text{N}_5$ , respectively, while  $\text{H}_4$  was in between  $\text{O}_3/\text{N}_3$  and  $\text{O}_5/\text{N}_5$ . The triple proton/H-atom transfer in the  $\text{HCOOH-S}_1\text{-S}_2$  ( $\text{S}_1, \text{S}_2: \text{H}_2\text{O}, \text{CH}_3\text{OH}, \text{NH}_3$ ) complex happened by a highly asynchronous but concerted pathway and  $[\text{S}_1\text{-H-S}_2]^+$ -like moiety emerged as part of TS. Similar correlation plots were obtained with CAM-B3LYP method and they are shown in Supplementary Information (Figure S1).

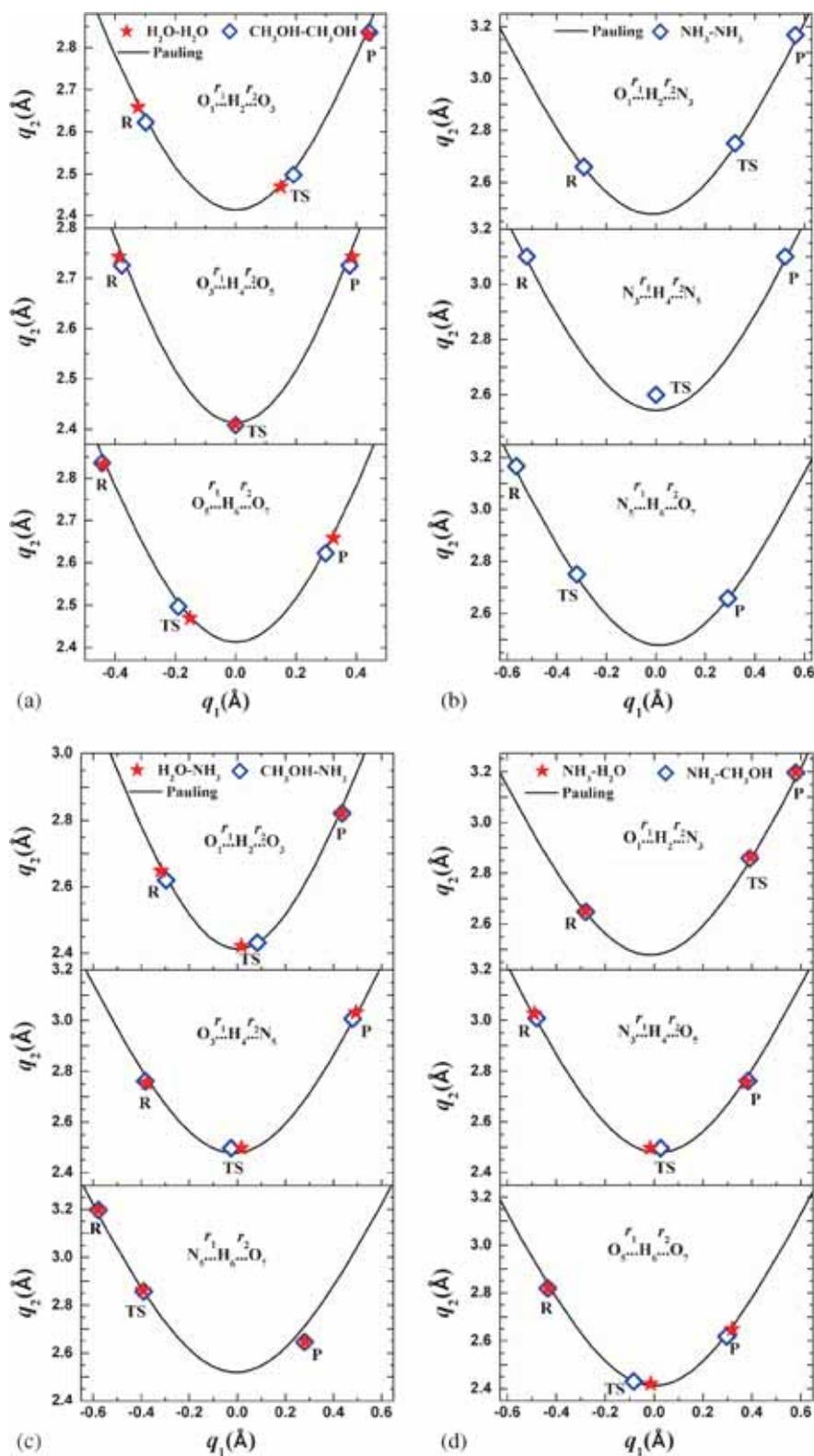
## 2.2 The energetics

The barrier heights ( $\Delta V$ ) and the rate constants for GSTPT/GSTHAT in the  $\text{HCOOH-S}_1\text{-S}_2$  ( $\text{S}_1, \text{S}_2: \text{H}_2\text{O}, \text{CH}_3\text{OH}, \text{NH}_3$ ) systems at the B3LYP/6-311+G(d,p) level are listed in Table 3. The barrier heights of  $\text{HCOOH-S}_1\text{-S}_2$  ( $\text{S}_1, \text{S}_2: \text{H}_2\text{O}, \text{CH}_3\text{OH}, \text{NH}_3$ ) without ZPE-corrections were in the range of 6.88~12.40 kcal/mol. After considering ZPE-corrections, the barrier heights decreased about 1.47~3.71 kcal/mol. The rate constants of  $\text{HCOOH-S}_1\text{-S}_2$  ( $\text{S}_1, \text{S}_2: \text{H}_2\text{O}, \text{CH}_3\text{OH}, \text{NH}_3$ ) at room temperature (25°C) were estimated by equation 1. The smaller the barrier height, the larger is the rate constant.

The imaginary frequencies of TS in the  $\text{HCOOH-S}_1\text{-S}_2$  ( $\text{S}_1, \text{S}_2: \text{H}_2\text{O}, \text{CH}_3\text{OH}, \text{NH}_3$ ) complexes were in the range of 746~1127  $\text{cm}^{-1}$ . The tunneling factor at room temperature of  $\text{HCOOH-S}_1\text{-S}_2$  ( $\text{S}_1, \text{S}_2: \text{H}_2\text{O}, \text{CH}_3\text{OH}, \text{NH}_3$ ) were estimated by Wigner tunneling approximation.<sup>31</sup> The tunneling factor were in the range of 1.54~2.24. When the long-range corrected CAM-B3LYP method was used, the barrier heights of GSTPT/GSTHAT were a little smaller than the corresponding B3LYP values. The tunneling factors at room temperature of  $\text{HCOOH-S}_1\text{-S}_2$  complex were in the range of 1.53~2.25 (The barrier height at the CAM-B3LYP level are listed in Table S2 in Supplementary Information). Therefore, the tunneling factors of GSTPT/GSTHAT in the  $\text{HCOOH-S}_1\text{-S}_2$  complex are not important, and applying classical transition state theory to calculate the rate constant is reasonable.

## 2.3 The role of H-bonded chain to the structure

With the help of protic bridging solvent, proton/H-atom in the  $\text{HCOOH}$  molecule can transfer through H-bonded chain. We chose water (W), methanol (M) and ammonia (A) as bridging solvent molecules. Kamlet-Taft acidity and basicity of solvent molecules in heptane<sup>32-36</sup> are shown in Table 1. As seen in Table 1, the proton-accepting ability (basicity) in heptane followed this order:  $\text{NH}_3 > \text{CH}_3\text{OH} > \text{H}_2\text{O}$ . Several H-bonded chains formed by two bridging solvent molecules were obtained since different solvent molecules were used



**Figure 2.** Correlation of the H-bond distances,  $q_2 = r_1 + r_2$ , with the proton/H-atom transfer coordinate,  $q_1 = (1/2)(r_1 - r_2)$ , for the  $\text{HCOOH}-\text{S}_1-\text{S}_2$  (Solvent:  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{OH}$ ) complexes in heptane. All points are for the transition states in the ground state optimized at the B3LYP/6-311+G(d,p) level. The solid lines designate the correlation that satisfies conservation of the bond order. The parameters for Pauling equations were taken from the literature.<sup>38</sup> The regions above and below the black line is where the sum of bond order is less and more than unity, respectively.

**Table 3.** Barrier heights, imaginary frequencies and rate constants without tunneling effect for the proton/H-atom transfer in the HCOOH-S<sub>1</sub>-S<sub>2</sub> (S<sub>1</sub>, S<sub>2</sub>: H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>) complex in heptane at the B3LYP level with 6-311+G(d, p) basis set. The numbers in parentheses include zero-point energies.

S <sub>1</sub>	S <sub>2</sub>	ΔV(kcal/mol)	ν <sub>TS</sub> (cm <sup>-1</sup> )	k (s <sup>-1</sup> )
H <sub>2</sub> O	H <sub>2</sub> O	12.4(8.69)	-975	2.64×10 <sup>6</sup>
H <sub>2</sub> O	NH <sub>3</sub>	7.80(4.28)	-1127	4.52×10 <sup>9</sup>
NH <sub>3</sub>	H <sub>2</sub> O	8.31(5.23)	-1127	9.09×10 <sup>8</sup>
NH <sub>3</sub>	NH <sub>3</sub>	6.88(5.41)	-1003	6.70×10 <sup>8</sup>
NH <sub>3</sub>	CH <sub>3</sub> OH	7.60(4.25)	-1024	4.75×10 <sup>9</sup>
CH <sub>3</sub> OH	NH <sub>3</sub>	7.50(3.87)	-1026	9.03×10 <sup>9</sup>
CH <sub>3</sub> OH	CH <sub>3</sub> OH	9.59(6.21)	-747	1.74×10 <sup>8</sup>

and their relative sequence in the H-bonded chain were different. It was obvious that the structural parameters of the HCOOH-S<sub>1</sub>-S<sub>2</sub> (S<sub>1</sub>, S<sub>2</sub>: H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>) complexes were influenced by the hydrogen-bonded wire formation with different solvent molecules.

For HCOOH-S<sub>1</sub>-S<sub>2</sub> (S<sub>1</sub>, S<sub>2</sub>: H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>) complexes, the H-bonds R<sub>4</sub> in reactant and R<sub>1</sub> in product were affected by S<sub>1</sub>, obviously. As shown in Table 2, when S<sub>2</sub> was same, the H-bonds R<sub>4</sub> in reactant and R<sub>1</sub> in product of the HCOOH-NH<sub>3</sub>-S<sub>2</sub> complex was on average 0.279 Å and 0.311 Å longer than those values of HCOOH-S<sub>1</sub>-S<sub>2</sub> (S<sub>1</sub>: H<sub>2</sub>O, CH<sub>3</sub>OH) complexes, respectively. At the same time, S<sub>2</sub> influenced the hydrogen bonds R<sub>6</sub> in reactant and R<sub>3</sub> in product. When S<sub>1</sub> was same, the hydrogen bonds R<sub>6</sub> in reactant and R<sub>3</sub> in product of the HCOOH-S<sub>1</sub>-NH<sub>3</sub> was on average 0.312 Å and 0.280 Å longer than those distances of HCOOH-S<sub>1</sub>-S<sub>2</sub> (S<sub>2</sub>: H<sub>2</sub>O, CH<sub>3</sub>OH), respectively. The above H-bonds elongated by 0.296 Å when NH<sub>3</sub> was one of the bridging molecules no matter how H<sub>2</sub>O or CH<sub>3</sub>OH was connected to HCOOH to form the cyclic H-bonded complex.

The structural parameters of TS were also affected by the solvent molecules. We found that the first solvent molecule (S<sub>1</sub>) influenced the structural parameters of TS, obviously. When the H-bonded chain formed with H<sub>2</sub>O and NH<sub>3</sub> molecules, R<sub>1</sub> and R<sub>2</sub> distances of HCOOH-NH<sub>3</sub>-S<sub>2</sub> (S<sub>2</sub>: H<sub>2</sub>O, NH<sub>3</sub>) were 0.455 Å longer and 0.092 Å shorter than the corresponding distances of HCOOH-H<sub>2</sub>O-S<sub>2</sub> (S<sub>2</sub>: H<sub>2</sub>O, NH<sub>3</sub>) with the same S<sub>2</sub> molecule, respectively. When NH<sub>3</sub> and CH<sub>3</sub>OH molecules formed the H-bonded chain and S<sub>2</sub> was same, R<sub>1</sub> and R<sub>2</sub> distances of HCOOH-NH<sub>3</sub>-S<sub>2</sub> (S<sub>2</sub>: CH<sub>3</sub>OH, NH<sub>3</sub>) also elongated by 0.388 Å and shortened by 0.048 Å than the corresponding distances of HCOOH-CH<sub>3</sub>OH-S<sub>2</sub>, respectively. The changes of R<sub>1</sub> and R<sub>2</sub> distances in TS could be ascribed to the higher basicity (as

**Table 4.** Mulliken partial charges of selected atoms in the TS of HCOOH-S<sub>1</sub>-S<sub>2</sub> (S<sub>1</sub>, S<sub>2</sub>: H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>) complexes obtained at the B3LYP/6-311+G(d,p) level.

S <sub>1</sub> /S <sub>2</sub>	In n-heptane			
	S <sub>1</sub>	H <sub>4</sub>	S <sub>2</sub>	S <sub>1</sub> H <sub>4</sub> S <sub>2</sub>
H <sub>2</sub> O/H <sub>2</sub> O	0.103	0.477	0.102	0.682
H <sub>2</sub> O/NH <sub>3</sub>	0.007	0.445	0.236	0.688
NH <sub>3</sub> /H <sub>2</sub> O	0.249	0.445	0.001	0.695
NH <sub>3</sub> /NH <sub>3</sub>	0.209	0.412	0.209	0.830
NH <sub>3</sub> /CH <sub>3</sub> OH	0.193	0.443	0.095	0.731
CH <sub>3</sub> OH/NH <sub>3</sub>	0.095	0.443	0.192	0.730
CH <sub>3</sub> OH/CH <sub>3</sub> OH	0.104	0.506	0.103	0.713

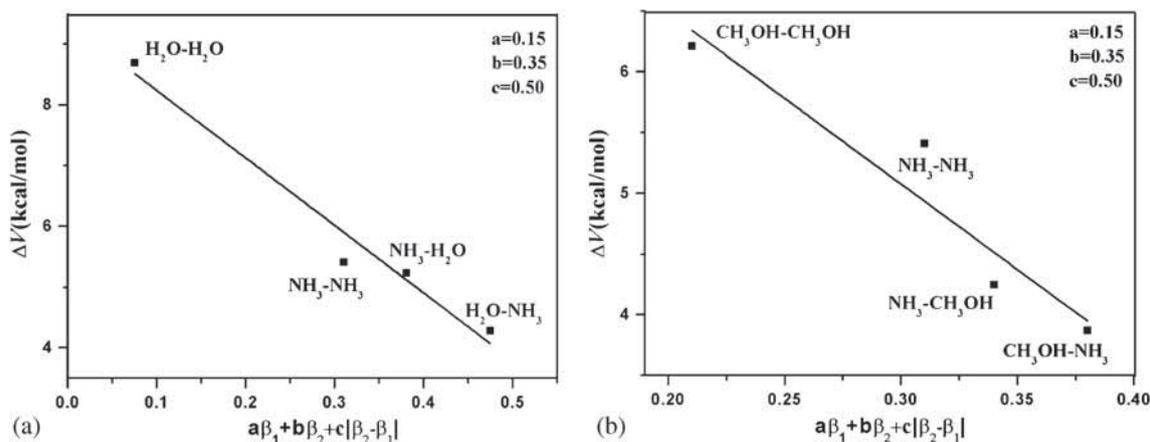
shown in Table 1) of NH<sub>3</sub> compared to H<sub>2</sub>O/CH<sub>3</sub>OH. Our results indicated that the protolysis pathway would prefer NH<sub>3</sub> to H<sub>2</sub>O/CH<sub>3</sub>OH.

The geometrical changes in the highly asynchronous transition state influenced by the second solvent molecule S<sub>2</sub> were small. When S<sub>1</sub> was same, the R<sub>5</sub> distances in the HCOOH-S<sub>1</sub>-NH<sub>3</sub> were 0.093 Å and 0.048 Å shorter than the corresponding values in HCOOH-S<sub>1</sub>-H<sub>2</sub>O and HCOOH-S<sub>1</sub>-CH<sub>3</sub>OH, respectively. The R<sub>6</sub> distances in HCOOH-S<sub>1</sub>-NH<sub>3</sub> were 0.454 Å and 0.388 Å longer than those values in HCOOH-S<sub>1</sub>-H<sub>2</sub>O and HCOOH-S<sub>1</sub>-CH<sub>3</sub>OH, respectively. As a result, NH<sub>3</sub> had larger positive charge than H<sub>2</sub>O or CH<sub>3</sub>OH had (see Table 4 and Table S3 in Supplementary Information) NH<sub>3</sub> was the better proton acceptor than H<sub>2</sub>O/CH<sub>3</sub>OH. The above changes of R<sub>5</sub> and R<sub>6</sub> in the HCOOH-S<sub>1</sub>-S<sub>2</sub> complexes due to the acidity order of the second solvent molecule were as follows: CH<sub>3</sub>OH>H<sub>2</sub>O>NH<sub>3</sub>.

#### 2.4 The role of H-bonded chain on the barrier height

The Kamlet-Taft basicities of monomeric H<sub>2</sub>O, CH<sub>3</sub>OH and NH<sub>3</sub> in heptane are different and these are listed in Table 1. Evidently, the formation pattern of the H-bonded chain played important role in increasing or decreasing the barrier height and rate constant of PT/HAT process due to different solvent molecules with different proton-accepting and donating abilities. The barrier height (ΔV) and rate constant without tunneling effect (k) of GSTPT/GSTHAT in HCOOH-S<sub>1</sub>-S<sub>2</sub> complex obtained at the B3LYP/6-311+G(d,p) level are listed in Table 3.

Proton/H-atom relay in the HCOOH-S<sub>1</sub>-S<sub>2</sub> complex occurred through the protolysis path, namely S<sub>1</sub> accepted a proton/H-atom from the acidic O-H group of HCOOH to start proton/H-atom transfer process, S<sub>2</sub> formed H-bond to S<sub>1</sub> from the back, and stabilized S<sub>1</sub>H<sup>+</sup> cation to promote proton/H-atom relay process. When the same solvent molecule was used for S<sub>1</sub> and



**Figure 3.** Correlation of the barrier height with the basicity of the H-bonded chain formed by, (a) water and ammonia, and (b) methanol and ammonia, at the B3LYP/6-311+G(d,p) level.

$S_2$ , the ZPE-corrected barrier heights were 8.69, 6.21 and 5.41 kcal/mol for  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$  and  $\text{NH}_3$ , respectively. The larger the proton-accepting ability (Kamlet-Taft basicity) of the H-bonded chain, the lower the barrier height. When different solvent molecules was chosen for  $S_1$  and  $S_2$ , such as  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , the barrier heights with ZPE-correction were 4.28 and 5.23 kcal/mol for  $\text{HCOOH}-\text{H}_2\text{O}-\text{NH}_3$  and  $\text{HCOOH}-\text{NH}_3-\text{H}_2\text{O}$ , respectively. In  $\text{HCOOH}-\text{H}_2\text{O}-\text{NH}_3$  system,  $\text{H}_2\text{O}$  started the PT/HAT process by accepting a proton/H-atom from the O-H group of  $\text{HCOOH}$ , and  $\text{NH}_3$  pulled the PT/HAT process from the front along the hydrogen bonded chain since  $\text{NH}_3$  had larger basicity than  $\text{H}_2\text{O}$ . As a result, the proton-accepting abilities of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  were accumulated, and the Mulliken partial charge of  $\text{NH}_3$  was larger than that of  $\text{H}_2\text{O}$  (as shown in Table 4), and the barrier height decreased. When the positions of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  along the H-bonded chain were switched,  $\text{H}_2\text{O}$  could not assist  $\text{NH}_3$  from the front because  $\text{NH}_3$  was basic enough to trigger the PT/HAT by accepting a proton/H-atom from  $\text{HCOOH}$ . Hence,  $\text{H}_2\text{O}$  had the smaller Mulliken partial charge than  $\text{NH}_3$  had (Table 4). The same results were obtained when  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  were used to form the mixed solvent H-bonded chain. The GSTPT/GSTHAT barrier height of  $\text{HCOOH}-\text{CH}_3\text{OH}-\text{NH}_3$  was 0.38 kcal/mol lower than the value of  $\text{HCOOH}-\text{NH}_3-\text{CH}_3\text{OH}$ . Otherwise, we found that the GSTPT/GSTHAT barrier height of the  $\text{HCOOH}-S_1-S_2$  complex, in which the H-bonded chain was formed with different solvent molecules, was lower than the value of  $\text{HCOOH}-S_1-S_2$  complex which the H-bonded chain was formed with same solvent molecules.

The proton-accepting ability (basicity) of the H-bonded chain could be denoted as  $a \times \beta_1 + b \times \beta_2 + c \times |\beta_1 - \beta_2|$  ( $a+b+c=1$ ), in which  $\beta_1$  and  $\beta_2$  are basicity of  $S_1$  and  $S_2$ , respectively. As shown in Figure 3,

when  $a=0.15$ ,  $b=0.35$  and  $c=0.5$ , a good correlation between the proton-accepting ability (basicity) of the H-bonded wire and the GSTPT/GSTHAT barrier height in the  $\text{HCOOH}-S_1-S_2$  complex were found. These results indicated that every solvent molecule along the H-bonded chain contributed to the GSTPT/GSTHAT barrier height; especially, the gap of the basicity between the two solvent molecules on the H-bonded chain had a large effect on PT/HAT process. The long-range corrected CAM-B3LYP method predicted a similar “barrier height-basicity” correlation plot (Figure S2 in supplementary information) compared with those from B3LYP method (Figure 3). The heterogeneously H-bonded chain formed by different bridging solvent molecules affects the rate constant obviously. The contribution of the H-bonded chain to the rate constant during the PT/HAT process could be authenticated experimentally. Jang *et al.*,<sup>16</sup> have successfully performed solvent-inventory experiments on the ESPT of  $7\text{HQ}-(\text{ROH})_2$  with two alcohol molecules having different proton-donating abilities. We hope that well-designed solvent-inventory experiments on PT/HAT of  $\text{HCOOH}-S_1-S_2$  complex will be tried in the future.

### 3. Conclusions

In this study, the long-range triple PT/HAT processes of  $\text{HCOOH}$  dependence on the H-bonded chain formed by  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$  and mixed solvent  $\text{H}_2\text{O}-\text{NH}_3/\text{CH}_3\text{OH}-\text{NH}_3$  were investigated using B3LYP and CAM-B3LYP methods. The proton/H-atom transfer for the  $\text{HCOOH}-S_1-S_2$  ( $S_1, S_2: \text{H}_2\text{O}, \text{CH}_3\text{OH}, \text{NH}_3$ ) systems occurred *via* an asynchronous but concerted protolysis pathway. The proton-accepting ability (basicity) of the solvent molecules had much effect on the structural parameters, barrier height and the rate constant. The changes of  $R_1$  and  $R_2$  distances of TS were related

to the basicity of  $S_1$  in the  $\text{HCOOH-S}_1\text{-S}_2$  complex, while the changes of  $R_5$  and  $R_6$  distances of TS were related to the acidity of  $S_2$  in the  $\text{HCOOH-S}_1\text{-S}_2$  complex. The larger the basicity/acidity of  $S_1/S_2$ , longer is the  $R_1/R_5$  distance of TS. We also found that the barrier height and rate constant of GSTPT/GSTHAT in the  $\text{HCOOH-S}_1\text{-S}_2$  complex changed obviously when the H-bonded chain varied. The proton-accepting ability (basicity) of the H-bonded chain could be denoted as  $a \times \beta_1 + b \times \beta_2 + c \times |\beta_1 - \beta_2|$  ( $a+b+c=1$ ,  $a=0.15$ ,  $b=0.35$ ,  $c=0.5$ ). The larger the proton-accepting ability (basicity) of the H-bonded chain, lower is the barrier height. The gap of the basicity between the two solvent molecules of the H-bonded chain had a large effect on changing the barrier height of GSTPT/GSTHAT in the  $\text{HCOOH-S}_1\text{-S}_2$  complex.

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### Supplementary Information (SI)

Bond distances of reactant, product and TS, barrier heights, imaginary frequencies, rate constants without tunneling effect and Mulliken partial charges obtained at the CAM-B3LYP/6-311+G(d,p)/SMD level are listed in three tables. The correlation of the H-bond distance with PT/HAT and correlation of the barrier height with the basicity of the H-bonded chain obtained at the CAM-B3LYP/6-311+G(d,p)/SMD level are shown in two figures. Supplementary Information is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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