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New Mechanism for the Catalyzed Thermal Decomposition of Formic Acid†

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Mechanisms for the pyrolysis of formic acid in the gas-phase catalyzed by water dimer or formic acid itself are proposed for the first time. At the B3LYP/6-311++G(3df,3pd)//B3LYP/6-311++G(d,p) level, the barrier heights for both dehydration and decarboxylation reactions are revealed to be significantly lower than previously reported values, implying the importance of the catalytic effect of $(H_2O)_2$ and HCOOH.

Introduction

Formic acid is an important intermediate in the oxidation of unsaturated hydrocarbons in combustion and in atmospheric chemistry.[1] The normal decomposition of formic acid, viz.:

$$\mathrm{HCOOH} \rightarrow \mathrm{CO} + \mathrm{H_2O}\ \text{dehydration} \tag{I}$$

$$\rightarrow \mathrm{CO_2} + \mathrm{H_2}\ \text{decarboxylation} \tag{II}$$

has been well studied experimentally and theoretically.[2−8] However, the previous results retain two questions. First, the measured activation energies (E_a) are in a wide range, i.e., $E_a^{I} = 32-66$ kcal/mol and $E_a^{II} = 48-68$ kcal/mol, while only the highest values are supported theoretically. Second, the yield ratio of CO to CO_2 is up to 10 despite the similarity between E_a^{I} and E_a^{II}. There is no convincing argument for this issue.

Such complications originate, at least in part, from the catalyzed pyrolysis of formic acid. It has been shown that both reactions I and II could be catalyzed by water molecules.[8−10] However, this mechanism only can account for the medium E_a (e.g., 40−50 kcal/mol). The worst of it is that E_a^{I} will be somewhat higher than E_a^{II}, conflicting apparently with the large CO/CO_2 ratio. Here we propose two new catalyzed mechanisms for the pyrolysis of formic acid in the gas phase. That is, water dimer [$(H_2O)_2$] and HCOOH could serve as catalysts for reactions I and II. Our findings are supported by high-level theoretical calculations.

Computations

The density functional method B3LYP, i.e., Becke's three-parameter nonlocal exchange functional[11] with the nonlocal correlation functional of Lee, Yang, and Parr,[12] as implemented in the Gaussian 94 program,[13] was used in this study. The basis set employed in geometry optimization was the split-valence, three-ζ, 6-311G-type Gaussian function, added with diffuse and polarization functions to give the 6-311++G(d,p) basis set.[14−16] Vibrational frequencies were obtained at the same level for characterization of stationary points and zero-point energy (ZPE) corrections. Zero-point energies taken from these frequency calculations can be assumed to be an upper limit due to the anharmonicity of the potential energy surface. Then the intrinsic reaction coordinate[17] calculations confirm the connections of the transition states between the designated reactants and products. Finally, the total energies were refined using the more flexible 6-311++G(3df,3pd) basis set[14−16] (with the option scf = tight) to obtain more reliable energetics. The relative energies (reaction heats and barrier heights) quoted in the present paper were considered as the difference between the total energy of the products (or transition states) and that of the separate reactants [i.e., *trans*-HCOOH, *trans*-HCOOH + H_2O, *trans*-HCOOH+$(H_2O)_2$, or two *trans*-HCOOH molecules] including the ZPE corrections (without scaling). For comparison, the normal and H_2O-catalyzed pyrolysis reactions of formic acid were also examined at the same level of theory.

Results and Discussion

Figure 1 shows the geometries of the intermediates and transition states involved in the $(H_2O)_2$ and HCOOH catalyzed reactions. The energetics of all relevant species are illustrated in Figure 2. A good agreement of the reaction heat and barrier height for the trans → cis isomerization of HCOOH with the experimental data[18,19] suggests the validity of the current B3LYP calculations. Since the results for the normal and H_2O-catalyzed reactions are consistent with those obtained previously at the G2(MP2)[9] and G2 M[10] levels, they will not be discussed except for comparative purpose.

1. $(H_2O)_2$-Catalyzed Mechanism. The water-dimer-catalyzed reactions start by the formation of the intermediates IM1 and IM2. In IM1, *trans*-HCOOH and $(H_2O)_2$ are bound with two hydrogen bondings. The water dimer acts simultaneously as a proton donor and acceptor. IM2 involves *cis*-HCOOH and $(H_2O)_2$ with only one hydrogen bonding. However, the H-bond $O^1H^1\cdots O^4$ in IM2 is ~0.25 Å shorter than the H-bond $O^3H^3\cdots O^1$ in IM1. As a result, the binding energy D_0 of IM2 is ~2.0 kcal/mol larger than that of IM1, although *cis*-HCOOH is unstable with respect to *trans*-HCOOH. This is also consistent with the fact that IM1 involves a seven-membered ring while IM2 appears to hold a *floppy* eight-membered ring.

TS1 and TS2 are the transition states for the dehydration and decarboxylation, respectively. The role of the water dimer is to serve as a proton relay. TS1 shows three concerted hydrogen transfer processes occurring anticlockwise along the ringy skeleton. The breaking of the CO^1 bond is accompanied by the H atom transfer from C to O^4 and from O^3 to O^1, forming the products CO and H_2O. The H^5 transfer from O^4 to O^3 regenerates the $(H_2O)_2$ to preserve its identity, even though the

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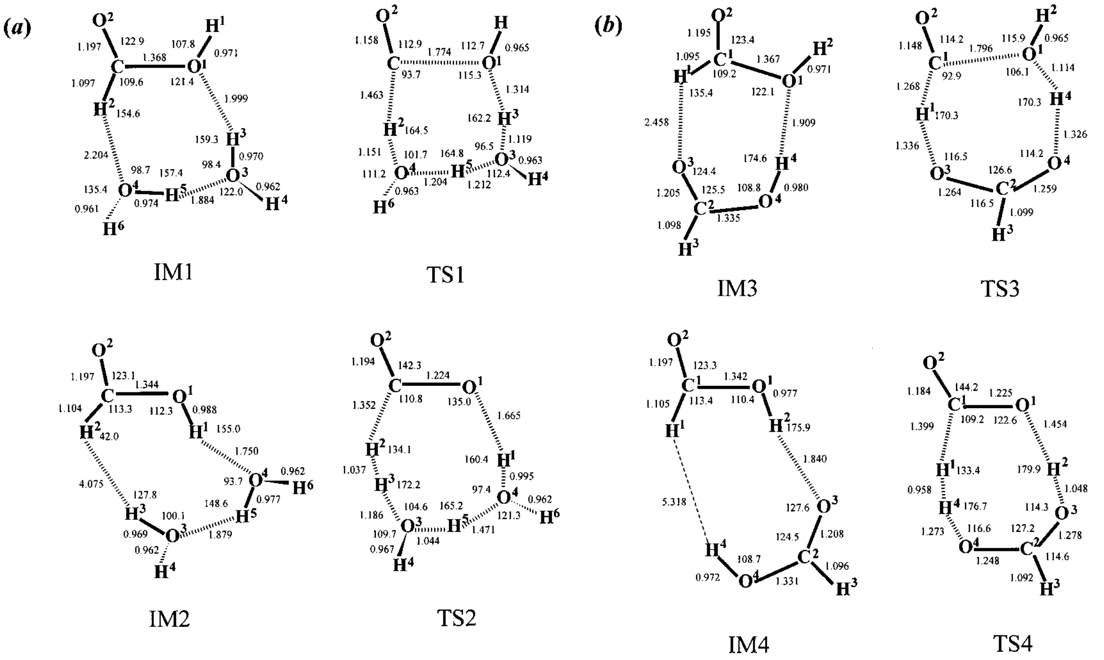

Figure 1. The B3LYP/6-311++G(d,p) optimized geometries of the intermediates and transition states for (a) $(H_2O)_2$ and (b) HCOOH catalyzed mechanisms. Bond distances are in angstroms, and angles are in degrees.

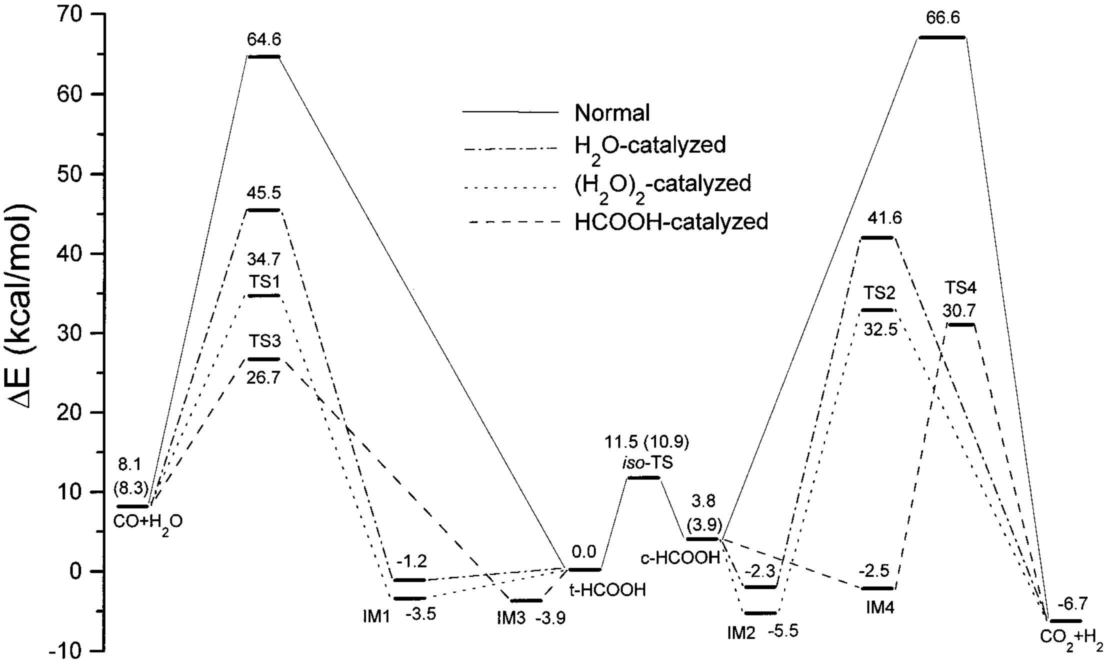

Figure 2. The profile of the potential energy surface for the dissociation of formic acid. The energetics (in kcal/mol) were calculated with respect to the *trans*-HCOOH species at the B3LYP/6-311++G(3df,3pd) level including the unscaled zero-point energy corrections at the B3LYP/6-311++G(d,p) level. The values in parentheses are the experimental data from refs 3, 18, and 19.

hydrogen bonding in this "product dimer" changes to occur between O^3 and H^5 instead of O^4 and H.[5] In TS2, the similar H atom transfer occurs but in the reverse direction. Note that the forming H^2H^3 bond is ~40% longer than its equilibrium value. With respect to the *trans*-HCOOH, the barrier heights for TS1 and TS2 are 34.7 and 32.5 kcal/mol, respectively. Thus, the catalysis of water dimer makes the barriers for reactions I and II reduced by 29.9 and 34.1 kcal/mol, respectively. In comparison with the H_2O-monomer-catalyzed mechanism, the difference is that the dimer catalyst is more effective because of the lower dissociation thresholds (Figure 2), and the similarity is that the barrier for dehydration is still somewhat higher than that for decarboxylation. It is worth noting that the barrier height for TS1 is in agreement with the experimental value of 31.7 or 40.4 kcal/mol.[4,5]

2. HCOOH-Catalyzed Mechanism. Since *trans*-HCOOH is the more stable conformer of formic acid, it acts as catalyst in this mechanism. Being similar to the $(H_2O)_2$-catalyzed reactions, two hydrogen-bonded complexes, IM3 and IM4, are formed first. IM3 has a seven-member-ring structure with two *different* hydrogen bonds. IM4 does not retain ringlike structure because the H^1H^4 distance is too long (5.318 Å). Thus, IM3 appears to be more stable than IM4 thermodynamically. The formation of IM3 should be more favorable. Turi[20] has studied recently the IM3 conformer at the MP2/D95++G(d,p) level but failed to locate IM4. The present B3LYP calculations agree well with Turi's results for IM3 in the distances of the H-bonds $O^4H^4\cdots O^1$ (1.909 vs. 1.899 Å) and $C^1H^1\cdots O^3$ (2.458 vs. 2.374 Å) and the binding energy (3.9 vs. 4.0 kcal/mol).

The IM3 and IM4 conformers can decompose readily to the products $CO + H_2O$ and $CO_2 + H_2$ via transition states TS3 and TS4, respectively. Again, the *trans*-HCOOH serves as a proton relay. In TS3, two H atom transfer processes ($C^1 \rightarrow O^3$ and $O^4 \rightarrow O^1$) occur in a concerted way with the breaking of the C^1O^1 bond to form the $CO + H_2O$ products. The catalyst HCOOH is restored to the trans conformation. Unlike IM4, TS4 turns out to be an eight-member-ring structure. The H_2 molecule is formed by the simultaneous breaking of the C^1H^1 and O^4H^4 bonds, and the accompanying transfer of H^2 from O^1 to O^3 produces CO_2 and *trans*-HCOOH. The net barrier heights are 26.7 and 30.7 kcal/mol for TS3 and TS4, respectively. Evidently these two values are the lowest data reported to date. Because of the effect of self-catalysis, E_a^{I} and E_a^{II} are lowered by 37.9 and 35.9 kcal/mol, respectively. Thus, it can be expected that the HCOOH self-catalyzed mechanism might play a significant role in the gaseous pyrolysis of formic acid.

It is noteworthy that the energy of TS3 is lower than that of TS4. The energy difference (ΔE_a) is enlarged to ~4.0 kcal/mol in comparison with ~2.0 kcal/mol in the normal mechanism. This unique result is encouraging because it might be the first proof of the dominance of dehydration. For instance, at the temperature of ~900 K, the CO/CO_2 ratio will be ~10 if the preexponential factors are the same for reactions I and II. Moreover, the lower the temperature, the more feasible the catalysis of HCOOH, and the larger the CO/CO_2 ratio. Certainly this kind of estimate is very rough and cannot be conclusive. As shown in Figure 2, the theoretical barrier heights do cover all the reported experimental values.[2-5] The kinetic modeling of pyrolysis of formic acid including all these mechanisms is apparently apposite.

It is well-known that two formic acid molecules can form a cyclic C_{2h} dimer via two *equivalent* hydrogen bondings. Its binding energy D_0 is 12−15 kcal/mol.[21,22] However, unlike IM3 and IM4, the C_{2h} dimer cannot play any role in the self-catalyzed mechanism. The barrier height for the C_{2h} dimer $\rightarrow 2CO + 2H_2O$ reaction was calculated to be 67.9 kcal/mol,[10] which is even higher than that for the normal dehydration of HCOOH. It is interesting to investigate the isomerization between the C_{2h} dimer and IM3 and IM4. This work is beyond the scope of this short article and thus is reserved for further study.

Supporting Information Available: Table S1 of Cartesian coordinates for various species in the normal and catalyzed mechanisms. Tables S2 and S3 of vibrational frequencies and total energies of various species, respectively.

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