



Catalytic influence of water and formic acid molecules on hydration of methylglyoxal in atmosphere



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ABSTRACT

The hydration of methylglyoxal [CH₃C(O)CHO, MG] in the atmospheric condition has been explored at the CBS-QB3 level of theory. Special attention was paid to the influence of additional water and formic acid molecules. The calculated results show that the reaction of MG with water could take place through the water-mediated keto-enol isomerization mechanism, in contrast to the previously proposed addition mechanism producing germinal diol. The enol products of the former mechanism are vital for the oligomerization of MG which is the critical process of secondary organic aerosols (SOA) formation initiated by MG. On the other hand, the catalytic effects of additional water and formic acid molecules are significant, although the hydration mechanism is favored over the water-mediated keto-enol isomerization. Moreover, the catalytic effect of formic acid is much more effective than that of water molecules. The present study provides fundamental mechanism framework for the hydration of MG in atmosphere, which is of great of significance to understand the atmospheric chemistry of MG.

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1. Introduction

Methylglyoxal (C₃H₄O₂, MG) is one of the most abundant α -dicarbonyl compounds in the atmosphere, which is produced in high yield from oxidation of anthropogenic and biogenic volatile organic compounds (VOCs), including isoprene, acetone, and xylenes [1–3]. The atmospheric chemistry of MG has attracted considerable attention, since it has been proven to be a precursor of secondary organic aerosols (SOA) [4–8]. Fu et al. [9] estimated the amount of SOA formed from MG as 8 Tg.C.yr⁻¹, which was a quarter of the total SOA amount produced and three times the amount of SOA generated from aldehydes in the adopted model. Unfortunately, the mechanism of SOA formation initiated from MG is combined by very complicate physical and chemical processes. Generally speaking, this process occurs via MG uptake into the aqueous phase of an aerosol particle or cloud droplet, followed by aqueous-phase chemistry leading to the formation of low-volatility oligomer products, such as acetal and hemiacetal. Therefore, the oligomerization of MG, especially the dimerization is of critical importance. There are only a few studies on the mechanism of MG oligomerization [4,9]. The results revealed that the oligomerization is a two-step process combined by (a) hydration

of MG, and (b) aldol reaction of hydrated MG as shown in Fig. 1 [10]. It is worth to point out that Krizner et al. [11] explored the thermodynamics and kinetics of methylglyoxal dimer and glyoxal dimer formation, and discovered that these two processes are distinct because there isn't α -H in glyoxal molecule so that Aldol condensation couldn't take place. It suggested that the enol structure is critical for the reaction of C₃H₄O₂ oligomerization. It is interesting that Alagona et al. [12] revealed that water molecules can catalyze the keto-enol isomerization of pyruvic acid and acetylacetone. These results inspired us to evaluate whether water molecules can catalyze the isomerization of MG to the enol form which will benefit the dimerization of MG in gas phase.

In fact, the catalytic effect of water on various atmospheric reaction is far from well understood, although there are several reviews very recently [9,10]. To the best of our knowledge, whether the water-mediated isomerization of MG could compete with the hydration is still unclear. The insight into the effects of water molecules on the dimerization of MG will provide fundamental comprehension to the atmospheric chemistry of MG.

On the other hand, formic acid (HCOOH) is a carboxylic acid present in the atmosphere in large amounts [13–19], being reported to effectively reduce the energy barrier of some atmospheric chemical reactions [20–27]. Hazra et al. investigated the catalytic effect of HCOOH on the gas-phase hydrolysis of formaldehyde (HCHO) [27], finding that HCOOH can significantly reduce the

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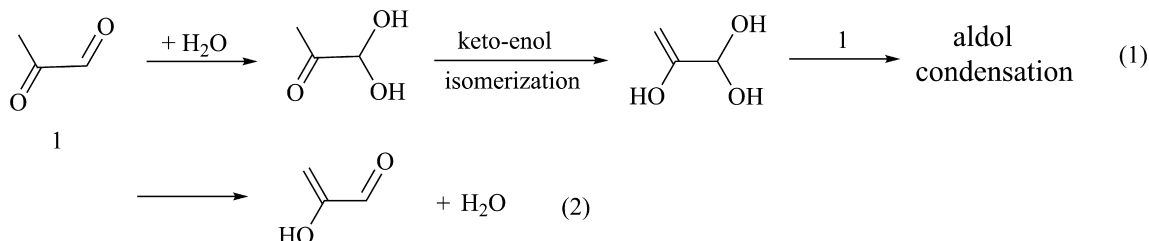


Fig. 1. Proposed mechanism for the reaction of MG with H₂O. (1) Hydration of MG, (2) water-mediated isomerization.

corresponding energy barrier. The product of this reaction, methanediol [CH₂(OH)₂], is also an important species for the formation of SOA. Moreover, Hazra and co-workers [5] explored the catalytic effect of formic acid on the hydrolysis of glyoxal in water-restricted environments, and the results indicated that formic acid is more efficient than water as a catalyst in the hydrolysis of glyoxal. These results further inspire us to explore the influence of formic acid on the dimerization of MG in atmosphere. The present study will provide systemic insight into the dimerization mechanism of MG, especially the catalytic effect of water and formic acid in water-restricted environments.

2. Computational methods

All reactant complexes (RC, PC) and transition states (TS) were optimized using the density functional theory B3LYP [28–30] and 6-311G(d,p) basis set. The vibrational frequencies of all optimized structures were calculated at the same theoretical level to confirm the intermediate and transition states. In addition, the intrinsic reaction coordinate (IRC) [31] calculations were carried out to verify that the predicted transition states connect the reactants and products. To confirm the reliability of the B3LYP/6-311G(d,p) method, MP2/6-311G(d,p) [32–35], B3LYP/aug-cc-pVTZ, wB97XD/aug-cc-pVTZ [36–38], and other methods were adopted to calculate some important structures, as shown in Fig. S1. The structural parameters calculated by the B3LYP/6-311G(d,p) method were very close to those obtained by other methods, indicating the reliability of the B3LYP/6-311G(d,p) method. To obtain more accurate energy data, single-point energies of all species were calculated using the CBS-QB3 [39,40] method. All computations were performed using the Gaussian 09 program [41].

3. Results and discussion

3.1. Reactions of MG + H₂O

The reactions of MG + H₂O result in either water addition or H₂O-catalyzed keto-enol isomerization, with the species involved in these reactions listed in Fig. 2. The corresponding zero-point energies (ZPE) and single-point energies are listed in Table S1, and the potential energy profiles of these reactions are shown in Fig. 3.

The addition of H₂O to MG can involve either the aldehyde or the keto carbonyl group, with the transition states of these mechanisms denoted as TS1 and TS2, respectively (see Fig. 2). In the addition mechanism, the O–H bond of water breaks, and the dissociated H reacts with the oxygen of the C=O bond, while the OH fragment forms a new bond with the carbonyl carbon to form a geminal diol. Fig. 2 shows that the structures of TS1 and TS2 are very similar, both containing a four-membered ring unit and showing very similar lengths of the newly formed C–O and O–H bonds (maximum difference of only 0.05 Å). The addition of H₂O to the ketone C=O group is expected to exhibit a higher energy barrier

due to the steric hindrance of the methyl group. However, as seen from Fig. 3, the energy of TS2 is ~1 kcal/mol lower than that of TS1, probably because the energy barrier is calculated for the gas-phase reaction. Fig. 3 also shows that the energy difference between TS1 and product P1 is slightly larger than that between TS2 and P2, in agreement with the results of Krizner et al. [21].

All four isomerization mechanisms depicted in Fig. 3 feature water-mediated hydrogen migration. Fig. 2 shows that RC3, RC4, RC5, RC6, and other pre-reaction complexes comprise a ring structure formed by two hydrogen bonds. Although the sizes of the formed cycles are different, the hydrogen bonds forming the rings are similar, resulting in similar relative energies of these complexes (with the largest relative energy of 4.81 kcal/mol observed for RC3). However, the energy barrier of the subsequent heterogeneous processes involving these complexes is subject to significant variation. For example, the energy barrier corresponding to TS4 and TS5 exceeds 50 kcal/mol, while that corresponding to TS6 equals ~42 kcal/mol, and that related to TS3 is relatively low (36.90 kcal/mol), as shown in Fig. 3. Obviously, only the RC3 → TS3 → PC3 heterogeneous process can compete with the two addition processes. Notably, among the four products of water-catalyzed hydrogen transfer processes, only PC3 contains an enol structure as shown in Fig. 2, which is a key factor for the MG dimerization reaction. Thus, the above dimerization may also be initiated by the water-catalyzed isomerization of MG to the corresponding enol.

3.2. Influence of water molecules on the MG + H₂O reaction

In view of the above discussion, the isomerization of MG into the corresponding enol can compete with the hydration reaction due to the catalytic action of water molecules. However, in the hydration reaction, the water molecule acts only as a reactant. Therefore, it is necessary to discuss the catalytic effect of additional H₂O molecules on the MG + H₂O reaction. To facilitate this discussion, the species involved in the reaction are denoted as W_x-c/s-RC (TS, PC), where W_x represents the total number of water molecules involved in the reaction, and c/s represents the catalyst (c) or spectator (s) role in the reaction.

3.2.1. MG + 2H₂O reaction

The structures of various reactant complexes and transition states involved in two addition reactions and one isomerization reaction are shown in Fig. 4. The reaction potential energy curve is plotted in Fig. 5, and the zero- and single-point energies are listed in Table S2.

When one additional water molecule is involved in the MG + H₂O addition reaction as a catalyst, the water molecule acting as the reactant directly attacks the carbonyl carbon atom to form a new C–O bond, and H is transferred to the carbonyl oxygen by the water molecule acting as the catalyst, with a six-membered ring structure formed (W2-c-TS1 and W2-c-TS2 in Fig. 4). When the H₂O molecule is involved in the MG + H₂O addition reaction as a spectator, the structure of the transition state is different. In

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