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REGULAR ARTICLE

Theoretical studies on the reaction of pentafulvenone with water in gas phase and aqueous solvent

**Y. Liu · X. M. Pan · Z. S. Li · X. J. Jia · S. Li ·
R. S. Wang · C. C. Sun**

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Abstract In gas phase, the hydrations of pentafulvenone to generate three types of cyclopentadienyl carboxylic acids are studied theoretically at the MP2/6-311+G**//B3LYP/6-311+G** level. A water molecule attacking the C=O double bond of pentafulvenone can yield cyclopentadienyl carboxylic acids via the formation of fulvenediols, and attacking the C=C double bond of pentafulvenone can directly yield cyclopentadienyl carboxylic acid. The barriers of rate-determining transition states are 42.2 and 30.4 kcal mol^{-1}, respectively. The barriers of rate-determining transition states for two water molecules system are 20.2 and 19.6 kcal mol^{-1}, respectively. The products can isomerize to each other. In aqueous solvent, the hydrations of pentafulvenone are investigated using PCM-UAHF model at the MP2 (PCM)/6-311+G**// B3LYP (PCM)/6-311+G** and MP2 (PCM)/6-311+G**// B3LYP/6-311+G** levels. The barriers of all rate-determining transition states are decreased. The added water molecule acts as catalyst in both gas phase and aqueous solvent.

Keywords Pentafulvenone · Mechanism · Solvation effect · PCM-UAHF model · Cyclopentadienyl carboxylic acids

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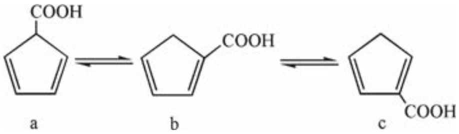
Y. Liu · X. M. Pan (✉) · X. J. Jia · S. Li · R. S. Wang
Institute of Functional Material Chemistry,
Faculty of Chemistry, Northeast Normal University,
Changchun 130024, People's Republic of China
e-mail: panxm460@nenu.edu.cn

X. M. Pan · Z. S. Li · C. C. Sun
State Key Laboratory of Theoretical and Computational Chemistry,
Institute of Theoretical Chemistry, Jilin University,
Changchun 130023, People's Republic of China

1 Introduction

The reactivities of ketene (CH_2=C=O) and its derivatives have been widely studied [1–18], including the addition and hydration reactions. Pentafulvenone and its derivatives have received particular attention because of their importance in the manufacture of integrated circuits, but have not been widely studied computationally. Experimentally Süs first described the mechanism of the photochemical ring contraction of *o*-quinone diazides and identified cyclopentadienyl carboxylic acids as the final products of photolysis in aqueous solvent [1]. Pentafulvenone generated photochemically had been detected by UV spectroscopy, and shown to react rapidly with water to form fulvene-6,6-diol as an observable but highly reactive intermediate [2]. However, direct computational determinations for the structure of pentafulvenone and the mechanism of pentafulvenone with water have not reported till now. So it is necessary to theoretically reveal the reaction mechanism of pentafulvenone with water and possible structures of the pentafulvenone, intermediates and products.

The geometric structures of the products for the reaction of pentafulvenone with water have attracted much attention [10,11]. The experimental study by Jaouen [11] showed that cyclopentadienyl carboxylic acids have three geometric structures, which are the a, b or c isomers, and it was confirmed that cyclopentadienyl carboxylic acids exist preferentially as the b isomers. Urwyler and Wirz [2] generated pentafulvenone in water and identified its product as the 6,6-fulvenediol which then tautomerized rapidly to give 1,3-cyclopentadienyl-1-carboxylic acid (denoted as b). Boule [4] and Akai [5–7] reported that a final photoproduct of 2-halogenphenol in aqua was cyclopentadienyl carboxylic acid (denoted as a), which was produced by the addition of pentafulvenone with solvent water. Bonnichon [8,9] et al. reported that the reaction of pentafulvenone with water yielded two types of cyclopentadienyl carboxylic acids (denoted as b and c) at the same time.



It is known for more than 20 years that the reaction of CH_2CO with at least two water molecules was studied theoretically [16,17], but up to now the reaction of pentafulvenone with one or two water molecules has not been investigated theoretically. Therefore, the thorough theoretical study on the reaction of pentafulvenone with water is desirable to give an understanding of the reaction mechanism.

It is necessary to study the effect of solvation, because the hydration of pentafulvenone is carried out in aqueous solvent and aqueous solvent is not only the medium but is also involved in the chemical process, and the results of the effect of solvation are of general theoretical interest. The conclusions obtained in our work help in understanding the effect of solvation for the hydration of analogous system.

2 Computational methods

The optimized geometric structures of all the reactants, complexes, intermediates, transition states and products are obtained at the B3LYP/6-311+G** level of theory. The stationary nature of structure is confirmed by harmonic vibrational frequency calculations, that is, equilibrium species possess all real frequencies, whereas transition states possess one and only one imaginary frequency. The vibrational frequencies are calculated at the B3LYP/6-311+G** level and scaled by 0.9614 scaling factor [19]. To confirm that the transition states connect designated stationary points, intrinsic reaction coordinate (IRC) calculations are carried out at the B3LYP/6-311+G** level of theory. For discussing conveniently, the energies of reactants are set zero for reference. To yield more accurate energetic information, higher level single-point energy calculations are performed at the MP2 level of theory with the same basis set [MP2/6-311+G**] using the B3LYP/6-311+G** optimized geometric structures, and the single-point energy values are further corrected for the zero-point vibrational energies (ZPVE) obtained at the B3LYP/6-311+G** level of theory. Moreover, unless otherwise specified, the MP2 single-point energies are used in the following discussions.

Dielectric continuum theories [20–22] are now widely used to describe hydration in conjunction with quantum mechanical calculations due to the relatively low cost of the calculation. PCM is one of many successful solvation models, and calculations in aqueous solvent are performed using PCM for computing the reaction more accurately.

In PCM, the solvation free energy can be expressed as:

$$\begin{aligned}\Delta G_{\mathrm{PCM}} &= \Delta G_{\mathrm{solv}} = \Delta G_{\mathrm{el}} + \Delta G_{\mathrm{non}} \\ &= \Delta G_{\mathrm{el}} + \Delta G_{\mathrm{cav}} + \Delta G_{\mathrm{dis}} + \Delta G_{\mathrm{rep}}\end{aligned}$$

ΔG_{el} is the electrostatic component of ΔG_{solv}. The nonelectrostatic component, ΔG_{non} includes three parts, which are cavitation, dispersion and repulsion energy. The cavitation term, ΔG_{cav} is the work required to create the cavity. The dispersion and repulsion terms, ΔG_{dis} and ΔG_{rep} are the solvent–solute dispersion and repulsion interaction, respectively. Electrostatic influences of the surrounding medium are expected to play an important role depending on the solvent polarity, and it is reported that for reactions involving neutral molecules, the nonelectrostatic solvation can be as important as the electrostatic one. Therefore, the nonelectrostatic contribution must be included for a quantitative prediction [23]. In PCM, the choice of cavities is important because the computed energies and properties depend on the cavity size. In our study, cavity effect in PCM approach is studied using UAHF radii set. The understanding of the effect of solvation on the hydration of pentafulvenone has been tackled by employing two different approaches. First, aqueous solvent internal energies and free energies are calculated using a recent version of the polarizable continuum model (PCM) developed by Cammi and Tomasi [24,25], which are implemented in the GAUSSIAN03 program [26,27]. Relevant gas-phase geometric structures are full re-optimized in aqueous solvent at the B3LYP (PCM)/6-311+G** level. Furthermore, single-point energy calculations are done at the MP2 (PCM)/6-311+G** level by using the B3LYP (PCM)/6-311+G** optimized geometric structures. Second, only single-point energy calculations are performed using B3LYP (PCM)/6-311+G** and MP2 (PCM)/6-311+G** levels based on gas-phase geometric structures. It is suspected that B3LYP method is used to estimate activation energies for several reactions [28], therefore, we investigate the aqueous solvent internal energies using MP2 method. All the calculations are carried out using the GAUSSIAN98 and GAUSSIAN03 programs [26,27].

3 Results and discussion

3.1 Addition of a water molecule

The reaction of pentafulvenone with a water molecule may proceed along two different attacking modes, one is a water molecule attacking the C=O bond and the other is to attack the

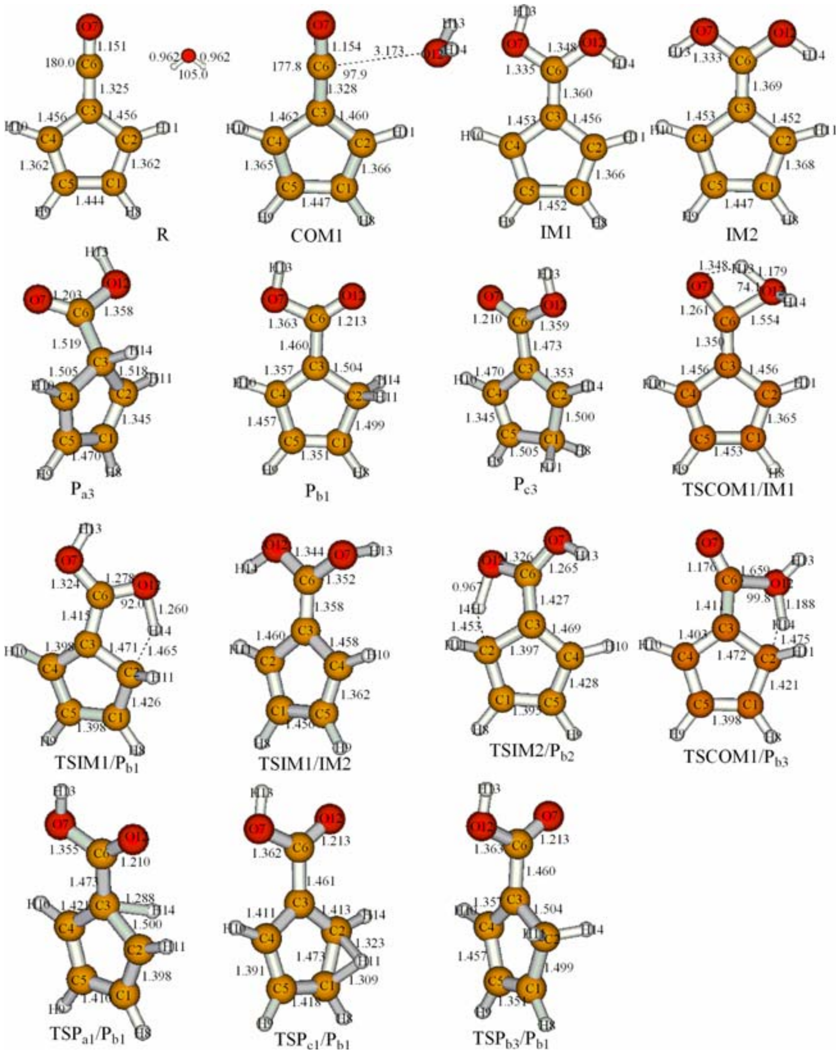


Fig. 1 The optimized geometrical parameters for reactants, complex, intermediates, more stable products and primary transition states of the reaction of pentafulvenone with a water molecule at the MP2/6-311+G**//B3LYP/6-311+G** level of theory

C=C bond of pentafulvenone. Figure 1 gives the optimized geometric structures for reactants, complex, intermediates and products at the MP2/6-311+G**//B3LYP/6-311+G** level of theory for the reaction of pentafulvenone with a water molecule. Figure 2a describes the potential energy profile, which will be used to illustrate the reaction mechanism. In the potential energy profile for the reaction of pentafulvenone with a water molecule, 1 complex, 2 intermediates, 12 products and 25 transition states are located. The calculated relative energies of the stationary points and all transition states along the reaction channels are given in Table 1.

Our theoretical results show that if the reaction of pentafulvenone with a water molecule can proceed, it should go through via an initial complex denoted as **COM1** with energy of $-3.1\,\text{kcal mol}^{-1}$. It should be pointed out that in the theoretical investigations for the ketene reaction systems, Skancke [17] reported that the reaction of CH_2CO with a water molecule yielded a weak bound complex. Fang et al. [29] studied the mechanism of the formation of pentafulvenone–pyridine ylide, and pointed out that a complex was formed first, which was then converted to the ylide via a transition state. In the Fang [29] and Skancke [17] studies, the energies of those initial complexes are -3.65 and $-4.4\,\text{kcal mol}^{-1}$, respectively.

From the information of the lowest unoccupied molecular orbital (LUMO) of **COM1**, the initial interaction between pentafulvenone and a water molecule originates from a weak attractive intermolecular force between lone pair of electrons of oxygen and the LUMO of pentafulvenone that has a dominant contribution from C_α (C6). The equilibrium distance between O12 of water and C_α is found to be 3.173 Å in **COM1**, which is close to those of the complex formed between pentafulvenone and pyridine (3.006 Å) [29] and the complex formed between CH_2CO and a water molecule (3.020 Å) [17].

Now let us discuss the reaction mechanism. One possible reaction pathway is that a water molecule attacks the

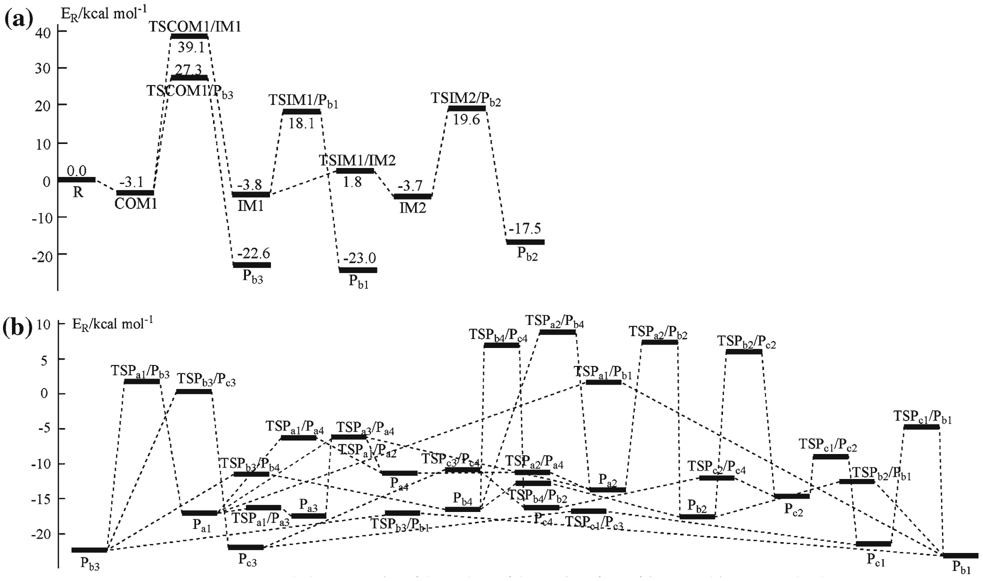


Fig. 2 **a** The potential energy profile for the reaction of pentafulvenone with a water molecule. **b** The interconversion of the products of the reaction of pentafulvenone with a water molecule

Table 1 Relative energies E_R (in kcal mol^{-1}) of all stationary points and transition states for the reaction of pentafulvenone with a water molecule at MP2 level with 6-311+G** basis set

Species	E_R	Species	E_R	Species	E_R
R	0.0	P$_{c3}$	−21.4	TSP$_{a1}$/P$_{a3}$	−16.4
COM1	−3.1	P$_{c4}$	−16.0	TSP$_{a2}$/P$_{b2}$	6.6
IM1	−3.8	TSCOM1/IM1	39.1	TSP$_{b1}$/P$_{b2}$	−12.5
IM2	−3.7	TSIM1/P$_{b1}$	18.1	TSP$_{b2}$/P$_{c2}$	5.5
P$_{a1}$	−16.6	TSIM1/IM2	1.8	TSP$_{c1}$/P$_{c2}$	−9.4
P$_{a2}$	−14.3	TSIM2/P$_{b2}$	19.6	TSP$_{b3}$/P$_{b4}$	−11.1
P$_{a3}$	−16.9	TSCOM1/P$_{b3}$	27.3	TSP$_{a2}$/P$_{b4}$	9.4
P$_{a4}$	−11.2	TSP$_{a1}$/P$_{b1}$	2.0	TSP$_{b2}$/P$_{b4}$	−13.2
P$_{b1}$	−23.0	TSP$_{c1}$/P$_{b1}$	0.2	TSP$_{b3}$/P$_{c3}$	0.3
P$_{b2}$	−17.5	TSP$_{b3}$/P$_{b1}$	−16.8	TSP$_{c1}$/P$_{c3}$	−16.5
P$_{b3}$	−22.6	TSP$_{a1}$/P$_{b3}$	2.2	TSP$_{c3}$/P$_{c4}$	−10.6
P$_{b4}$	−16.2	TSP$_{a1}$/P$_{a4}$	−6.0	TSP$_{c2}$/P$_{c4}$	−13.1
P$_{c1}$	−21.0	TSP$_{a1}$/P$_{a2}$	−5.8	TSP$_{b4}$/P$_{c4}$	6.6
P$_{c2}$	−14.9	TSP$_{a3}$/P$_{a4}$	−5.8	TSP$_{a2}$/P$_{a4}$	−10.9

carbon–oxygen double bond of pentafulvenone. The first step is the formation of intermediate *trans*-6, 6-fulvenediol **IM1**, which has been detected experimentally [2,3,8,9,30], via **TSCOM1/IM1**(1658i) with a barrier of 42.2 kcal mol^{-1}. **IM1** belongs to *Cs* symmetry, and the relative energy of **IM1** is −3.8 kcal mol^{-1}.

It is worth mentioning that **TSCOM1/IM1** is a four-membered ring transition state, which is similar to a water molecule attacking the C=O bond of CH_2CO [17,18]. In **TSCOM1/IM1**, the formed C6–O12 bond length is 1.554 Å. The vibrational normal mode analyses describe a transfer of H13 between O12 of water and O7 of pentafulvenone, which will lead to the rupture of O12–H13 bond and the formation of O7–H13 bond.

The second step is the conversion of **IM1** to cyclopentadienyl carboxylic acid **P$_{b1}$** via **TSIM1/P$_{b1}$** (1742i) with a barrier of 21.9 kcal mol^{-1}, which proceeds through the intramolecular H14 migration from **IM1** to form **P$_{b1}$** with an exothermicity of 23.0 kcal mol^{-1}.

Our calculated barriers of **TSCOM1/IM1** and **TSIM1/P$_{b1}$** for the reaction of pentafulvenone with a water molecule are 42.2 and 21.9 kcal mol^{-1}, respectively. The calculated barriers for the corresponding transition states **TSCOM1/IM1** and **TSIM1/P$_{b1}$** are 40.6 and 47.7 kcal mol^{-1} calculated by Skancke [17] at the MP2/6-31G* level, and 38.2 and 45.3 kcal mol^{-1} calculated by Duan [18] with the G2 method, respectively. The barriers of corresponding **TSCOM1/IM1** given by Skancke, Duan and the present authors are closer, however, the barrier of **TSIM1/P$_{b1}$** for the reaction of pentafulvenone with water decreases obviously. The reason is that **TSIM1/P$_{b1}$** is a five-membered ring transition state for pentafulvenone, and the transition states for CH_2CO reaction system are four-membered rings. The structure of five-membered ring transition state is more stable than that of four-membered ring transition state. Thus, the transformation from **IM1** to **P$_{b1}$** via **TSIM1/P$_{b1}$** is easier than the conversion from enediol to acetic acid, and the pentafulvenone and CH_2CO are different systems with respect to the proton transfer steps. Moreover, **IM1** can easily transform to cyclopentadienyl carboxylic acid, which is agreement with the results of many experimental studies [2,3,8,9,30].

By comparing the structural parameters of **IM1** to those of $\mathbf{P_{b1}}$, we can infer that C6–O12 single bond transforms to double bond, C3–C6 double bond changes to single bond and O12–H14 bond is completely broken. In the cyclopentadienyl ring, we find the alterations between carbon–carbon double bonds and the corresponding single bonds.

The previous studies for the reaction of CH_2CO with a water molecule mentioned one type of enediol [17,18]. In our study we find two types of fulvenediols and study the interconversion of the two fulvenediols, that is, from **IM1** to form *cis*-6,6-fulvenediol **IM2** via **TSIM1/IM2**(455i). The process is just the rotation of O7–H13 bond, and the barrier of **TSIM1/IM2** is 5.6 kcal mol^{-1}.

Subsequently, the process of **IM2** to form $\mathbf{P_{b2}}$ via $\mathbf{TSIM2/P_{b2}}$ (1741i) with a barrier of 23.3 kcal mol^{-1} is through the intramolecular H14 migration from O12 to C2, and then $\mathbf{P_{b2}}$ is formed with an exothermicity of 17.5 kcal mol^{-1}.

The processes from the reactants to cyclopentadienyl carboxylic acids via 6,6-fulvenediols have been identified experimentally [2,3,8,9,30].

The other reaction pathway is found by a water molecule attacking the carbon–carbon double bond of pentafulvenone to form cyclopentadienyl carboxylic acid $\mathbf{P_{b3}}$ via $\mathbf{TSCOM1/P_{b3}}$ (1425i) with a barrier of 30.4 kcal mol^{-1}.

Compared with the calculated barriers of the corresponding transition states given by Skancke [17] and Duan [18] for a water molecule attacking the C=C bond of CH_2CO, our result is much less than their barriers (45.2 and 42.0 kcal mol^{-1}, respectively). The reason is similar to that of $\mathbf{TSIM1/P_{b1}}$, which is due to a five-membered ring formed in $\mathbf{TSCOM1/P_{b3}}$ for pentafulvenone. It is found that the alterations of carbon–carbon double bonds and the corresponding single bonds in the cyclopentadienyl ring.

3.2 Stabilities and interconversions of cyclopentadienyl carboxylic acids

3.2.1 Stabilities of cyclopentadienyl carboxylic acids

In many experimental studies, the products for the reaction of pentafulvenone with water only have different types of cyclopentadienyl carboxylic acids [2–9]. In our theoretical study, we find three types of cyclopentadienyl carboxylic acids, that is, the a, b and c isomers, similar to that suggested by Jaouen [11]. For each type of product there are four isomers, denoted as a1–a4, b1–b4, c1–c4. More stable products are presented in Fig. 1 and other products are in Fig. A of Supporting Information. The energy orders are a3 (−16.9) < a1 (−16.6) < a2 (−14.3) < a4 (−11.2), b1 (−23.0) < b3 (−22.6) < b2 (−17.5) < b4 (−16.2) and c3 (−21.4) < c1 (−21.0) < c4 (−16.0) < c2 (−14.9). The energy values in the parentheses are in kcal mol^{-1}. From the information of these energies, it can be found that the reaction of pentafulvenone with water is exothermic, and $\mathbf{P_{b1}}$ and $\mathbf{P_{b3}}$ are the most stable products in the three types of cyclopentadienyl carboxylic acids, and this conclusion has been confirmed by experimental fact [2,3]. For the c isomers, $\mathbf{P_{c3}}$ and $\mathbf{P_{c1}}$ are the second most stable products, which may be observed in experiments. In terms of the energies of $\mathbf{P_{b1}}, \mathbf{P_{b3}}, \mathbf{P_{c1}}$ and $\mathbf{P_{c3}}$, their stabilities are comparative, so the b and c isomers should be detected simultaneously by experimental investigations, which have been proved by Bonnichon and coworkers [8,9].Compared with those of the b and c isomers, the energies of the a isomers are higher and it may be difficult for them to be observed in experimental studies, only Boule [4] and Akai [5–7] reported the existence of the a isomers. The a isomers are energetically high-lying isomers, but the formations are exothermic, so they are kinetically stable. Thus, it is necessary to investigate the interconversions of cyclopentadienyl carboxylic acids further.

3.2.2 Interconversions of cyclopentadienyl carboxylic acids

The interconversions of cyclopentadienyl carboxylic acids include two types of processes, which are the interconversions between the different cyclopentadienyl carboxylic acids (a⟶b, c⟶b) and each cyclopentadienyl carboxylic acid itself (a↔a, b↔b, c↔c), presented in Fig. 2b. For simplicity, we always take the processes of interconversions to the most stable product $\mathbf{P_{b1}}$ as examples to illustrate the interconversions between the cyclopentadienyl carboxylic acids, and other processes are not presented in details.

$\mathbf{P_{a1}}$ isomerizes to $\mathbf{P_{b1}}$ via $\mathbf{TSP_{a1}/P_{b1}}$ (1127i), and the relative energy of $\mathbf{TSP_{a1}/P_{b1}}$ is 2.0 kcal mol^{-1}. The vibrational frequency analyses show that the normal mode associated with the only one imaginary frequency describes a transfer of H14 between C2 and C3, which will lead to the rupture of C3–H14 bond and the formation of C2–H14 bond. $\mathbf{P_{c1}}$ isomerizes to $\mathbf{P_{b1}}$ via $\mathbf{TSP_{c1}/P_{b1}}$ (1122i), and the relative energy of $\mathbf{TSP_{c1}/P_{b1}}$ is 0.2 kcal mol^{-1}.

From the discussion mentioned above, we consider that the interconversions from the a and c isomers to the b isomers are possible under certain conditions.

In the processes of interconversions for each type of cyclopentadienyl carboxylic acid itself, there are two types of channels, that is, direct and indirect channels. We take the interconversion from $\mathbf{P_{b3}}$ to $\mathbf{P_{b1}}$ as an example to illustrate the channels. Channels **(I)** and **(II)** can lead to the most stable product $\mathbf{P_{b1}}$ via the direct and indirect channels, respectively. Channels **(I)** and **(II)** are depicted as follows:

$$\text{Channel}(\mathbf{I})\text{:}\mathbf{P_{b3}}\xrightarrow{\mathbf{TSP_{b3}/P_{b1}}}\mathbf{P_{b1}}$$

$$\text{Channel}(\mathbf{II}) : \mathbf{P_{b3}}\xrightarrow{\mathbf{TSP_{b3}/P_{b4}}}\mathbf{P_{b4}}\xrightarrow{\mathbf{TSP_{b4}/P_{b2}}}\mathbf{P_{b2}}\xrightarrow{\mathbf{TSP_{b2}/P_{b1}}}\mathbf{P_{b1}}$$

The direct channel is much more favorable than the indirect one, so we just describe the direct channel. $\mathbf{P_{b3}}$ isomerizes to $\mathbf{P_{b1}}$ via $\mathbf{TSP_{b3}/P_{b1}}$, and the barrier is 5.8 kcal mol^{-1}. The process is just the rotation of C3–C6 bond.

From the information of the energies of transition states, the interconversions for each cyclopentadienyl carboxylic acid itself are much easier than those between the different cyclopentadienyl carboxylic acids.

The low-lying and very high kinetic stability indicate that both $\mathbf{P_{b3}}$ and $\mathbf{P_{b1}}$ should be observable in laboratory.

3.3 Addition of two water molecules

In this case the interaction between pentafulvenone and two water molecules is initiated by weak intermolecular attractions. Two water molecules attacking the carbon–oxygen double bond of pentafulvenone form six-membered ring complex, denoted as **COM2**, and attacking the carbon–carbon double bond of pentafulvenone form seven-membered ring complex, denoted as **COM3**. The relative energies of **COM2** and **COM3** are −8.3 and −11.7 kcal mol^{-1}, respectively, so **COM3** is more stable than **COM2**. In the Skancke's study [17], their calculation gave two six-membered ring complexes for the reaction of CH_2CO with two water molecules, one involving the C=O bond and the other involving C=C bond of CH_2CO, and the energy values are −8.0 and −6.9 kcal mol^{-1} calculated at the MP2/6-31G* level, respectively. In the Nguyen's study, the energy values of the two complexes formed by CH_2CO with two water molecules calculated at the MP2/6-31G* level are −11.7 and −11.5 kcal mol^{-1}, respectively, and are −7.4 and −7.2 mol^{-1} calculated at the MP2/6-311++G** level, respectively [12]. Figure 3 gives the optimized geometric structures for reactants, complexes, intermediate, transition states and products at the MP2/6-311+G**//B3LYP/6-311+G** level, and Fig. 4 describes the potential energy profile for the reaction of pentafulvenone with two water molecules. The calculated total and relative energies of the stationary points and all transition states along the reaction channels are given in Table A of Supporting Information.

In **COM2** and **COM3**, the distances between O12 and C_α(C6) are 3.160 and 2.975 Å, respectively, and the angles of C3–C6–O12 are 98.0 and 94.0°, respectively. Therefore, we can infer that O12 of the two water molecules almost vertically attack C_α of pentafulvenone. In **COM3** the distance between C2 and H13 is found to be 2.406 Å and in **COM2** the distance between O7 and H13 is found to be 2.273 Å.

As shown in Fig. 4, each of the two attacking modes begins with a pre-associative complex. With the weak bound complex **COM2** as the starting point, the two water molecules attacking the carbon–oxygen double bond of pentafulvenone proceeds through $\mathbf{TSCOM2/IM'}$(894i) with a barrier of 20.2 kcal mol^{-1} to form intermediate $\mathbf{IM'}$. It is worth mentioning that $\mathbf{TSCOM2/IM'}$ is a six-membered ring transition state, which is similar to two water molecules attacking the C=O bond of CH_2CO [16,17]. The vibrational normal mode analyses describe a transfer of H13 between O15 and O7, which will lead to the rupture of O15–H13 bond and the formation of O7–H13 bond.

The energy value of $\mathbf{IM'}$ is −12.1 kcal mol^{-1}. In $\mathbf{IM'}$, O12–H16 bond is broken, O15–H16, O7–H13 and a hydrogen bond of O15–H13 are formed, and H17–O15–H16 forms a new water. The intermediate $\mathbf{IM'}$ is formed between fulvenediol and the new water with the hydrogen bond O15–H13 (1.745 Å). In the Nguyen's study, the energy value of the corresponding intermediate formed by enediol with a water molecule is −14.8 kcal mol^{-1} at the MP2/6-31G* level [16].

The second step is the conversion of $\mathbf{IM'}$ to complex **COM4** via $\mathbf{TSIM'/COM4}$ (1710i) with a barrier of 20.4 kcal mol^{-1}, which proceeds through the intramolecular H14 migration from O12 to C2 associated with O12–H14 bond rupture and C2–H14 bond formation. The energy value of **COM4** is −31.2 kcal mol^{-1}. **COM4** can further dissociate to the product $\mathbf{P_{b1}}$ and the newly formed water via the direct O15–H13 bond rupture with the barrier of 8.2 kcal mol^{-1}, and with an exothermicity of 23.0 kcal mol^{-1}.

With the weakly bound complex **COM3** as the starting point, the other reaction pathway is found by two water molecules attacking the carbon–carbon double bond of pentafulvenone via the cleavage of O12–H14 and O15–H13 bonds accompanied by the formation of C6–O12, C2–H13 and O15–H14 bonds through transition state **TSCOM3/COM5** (789i) with a barrier of 19.6 kcal mol^{-1} to form complex **COM5**. From Fig. 3, it is easily seen that O15–H13 bond is completely broken, a hydrogen bond of O12–H14 is formed and H14–O15–H17 forms a new water in **COM5**. The energy value of **COM5** is −26.1 kcal mol^{-1}. In addition, the hydrogen bond rupture of **COM5** to form the product $\mathbf{P_{b3}}$ and the newly formed water becomes possible after overcoming the dissociation energy of 3.5 kcal mol^{-1}, and with an exothermicity of 22.6 kcal mol^{-1}.

Our calculated barriers of the rate-determining transition states $\mathbf{TSCOM2/IM'}$ and **TSCOM3/COM5** are 20.2 and 19.6 kcal mol^{-1}, respectively. In the Nguyen's study, the barriers of the corresponding transition states for the reaction of CH_2CO with two water molecules calculated at the MP2/6-311++G** level are 22.9 and 27.2 kcal mol^{-1}, respectively [16].

Now let us turn our attention to the catalytic effect of the second water molecule. Comparing the barriers of transition states of two water molecules attacking pentafulvenone with that of a water molecule attacking pentafulvenone, the rate-determining barriers decrease obviously. This means that in the reaction the second water acts as catalyst to promote the reaction easily. Moreover, we infer that in the water environment the rate-determining barriers decrease, and it will

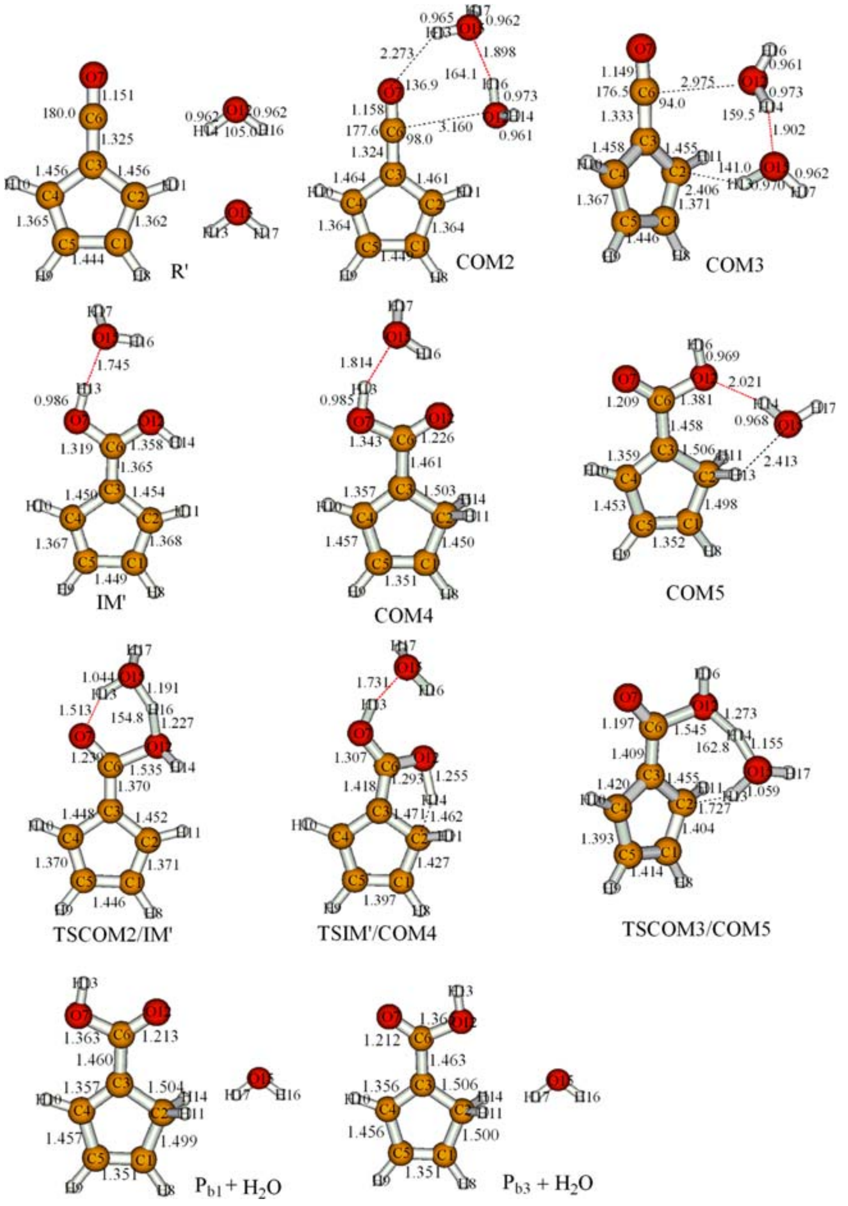


Fig. 3 The optimized geometrical parameters for reactants, complexes, intermediate, transition states and products of the reaction of pentafulvenone with two water molecules at the MP2/6-311+G**//B3LYP/6-311+G** level of theory

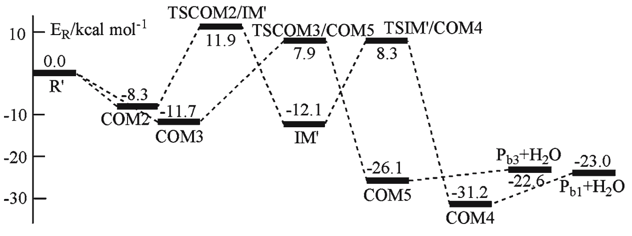


Fig. 4 The potential energy profile for the reaction of pentafulvenone with two water molecules

lead to the hydration of pentafulvenone quickly, which is consistent with the experimental conclusion that is its high reactivity to water [2,3,5,6,8,9].

3.4 Solvation effect

3.4.1 Solvation effect on the reaction of pentafulvenone with a water molecule

To get a better description of the change of geometric structures, it would be necessary to re-optimize the gas-phase geometric structures in PCM. The result is that aqueous solvent has slight effect on the geometric structures, which are shown in Fig. 5.

In addition, we have also investigated the solvation effect on energies and mechanisms. Apparently, the polar aqueous solvent significantly decreases the activation internal energies by preferentially stabilizing transition states. Table 2 shows the relative energies calculated for the reaction in

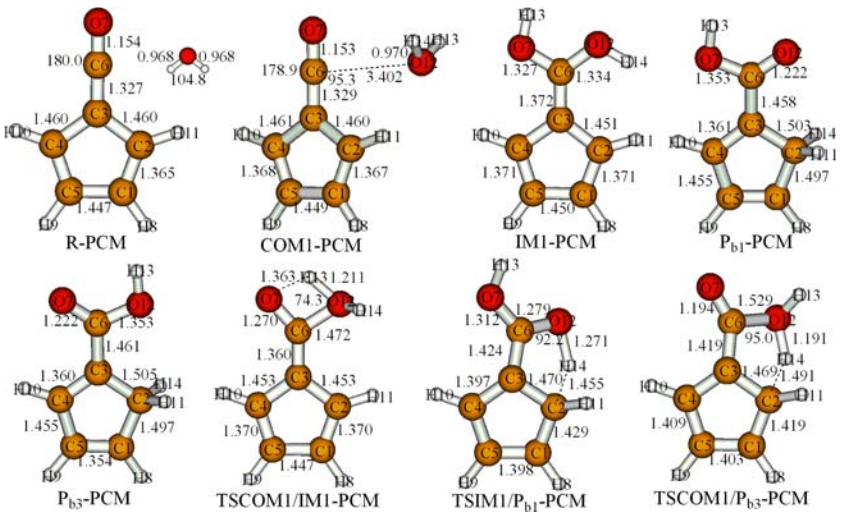


Fig. 5 The optimized geometrical parameters for reactants, complex, intermediates, more stable products and primary transition states of the reaction of pentafulvenone with a water molecule at the MP2 (PCM)/6-311+G**//B3LYP(PCM)/6-311+G** level of theory

Table 2 Relative energies and free energies (in kcal mol^{-1}) of stationary points and transition states for the reaction of pentafulvenone with a water molecule in aqueous solvent at the B3LYP(PCM)/ 6-311+G**//B3LYP(PCM)/6-311+G** and MP2 (PCM)/ 6-311+G**//B3LYP(PCM)/6-311+G** levels

Species	$E_{\text{B3LYP-PCM}}$	ZPVE$_{\text{B3LYP-PCM}}$	$E_{\text{MP2-PCM}}$	ΔG°_{g} [a]	ΔG°_{aq} [b]	$\Delta\Delta G_{\text{PCM}}$
R-PCM	0.0	0.0	0.0	0.0	0.0	0.0
COM1-PCM	0.3	0.7	−1.1	−2.6	1.0	3.57
IM1-PCM	−7.6	3.4	−7.5	−8.1	−12.2	−6.45
P$_{b1}$-PCM	−24.3	3.4	−23.6	−27.3	−29.0	−2.32
P$_{b3}$-PCM	−24.1	3.4	−23.4	−26.9	−28.8	−2.77
TSCOM1/IM1-PCM	36.2	0.5	36.0	38.5	34.8	−6.30
TSIM1/P$_{b1}$-PCM	19.8	0.6	15.5	18.9	17.6	−2.01
TSCOM1/P$_{b3}$-PCM	29.4	−0.2	25.1	29.7	28.3	−3.91

[a] B3LYP/6-311+G**// B3LYP/6-311+G**

[b] B3LYP (PCM)/6-311+G**// B3LYP(PCM)/6-311+G**

PCM. In aqueous solvent, the activation internal energies of rate-determining transition states **TSCOM1/IM1-PCM** (1737i) and **TSCOM1/P$_{b3}$-PCM** (1530i) are 36.0 and 25.1 kcal mol^{-1}, respectively, and in gas phase the activation internal energies of rate-determining transition states **TSCOM1/IM1** and **TSCOM1/P$_{b3}$** are 39.1 and 27.3 kcal mol^{-1}, respectively, therefore, after considering the solvation effect, the activation internal energies are reduced by ca. 8%. Note that the aqueous solvent effect stabilizes the transition state **TSCOM1/IM1-PCM** more than it does **TSCOM1/P$_{b3}$-PCM**. However, the difference between **TSCOM1/IM1-PCM** and **TSCOM1/P$_{b3}$−PCM** is still considerable, 10.9 kcal mol^{-1}. These results illustrate that the solvation effect promotes the easy and feasible reaction, and the barrier of the rate-determining transition state for the a water molecular attacking the C=C double bond of pentafulvenone is always less than that of attacking the C=O double bond.

Tuning to the free energies in solution, for discussing conveniently, the free energies of reactants are set zero for reference. Aqueous solvent effect stabilizes reactants, intermediate, transition states and products. Table 2 shows that solvation effect stabilizes transition states **TSCOM1/IM1-PCM**, **TSIM1/P$_{b1}$-PCM** (1789i) and **TSCOM1/P$_{b3}$-PCM** by −6.30, −2.01, and −3.91 kcal mol^{-1}, respectively. For **TSCOM1/IM1-PCM** cavitation, dispersion and repulsion energies are 15.97, −16.59 and 2.93 kcal mol^{-1}, respectively, and for **TSCOM1/P$_{b3}$-PCM** cavitation, dispersion and repulsion energies are 15.48, −17.35 and 3.74 kcal mol^{-1}, respectively, which are presented in Table B, C and D of Supporting Information. Therefore, nonelectrostatic contributions are found to increase the free energies of **TSCOM1/IM1-PCM** and **TSCOM1/P$_{b3}$-PCM** by 2.32 and 1.87 kcal mol^{-1}. Thus, electrostatic solvent–solute interaction is a dominant factor in such a lowering of the energies. Further support for this statement is owing to a significantly large charge separation in electronic structures of the rate-determining transition states. When going from gas phase to aqueous solvent, for **TSCOM1/IM-PCM**, the dipole moment is increased from 4.2 to 5.0 D, and for

Table 3 Relative energies and free energies (in kcal mol^{-1}) of stationary points for the reaction of pentafulvenone with a water molecule in aqueous solvent at the B3LYP(PCM)/ 6-311+G**//B3LYP/6-311+G** and MP2 (PCM)/ 6-311+G**//B3LYP/6-311+G** levels

Species	$E_{\text{B3LYP}-\text{PCM}-\text{SP}}$	$\text{ZPVE}_{\text{B3LYP}-\text{PCM}-\text{SP}}$	$E_{\text{MP2}-\text{PCM}-\text{SP}}$	$\Delta G^{\circ\,\text{a}}_{\text{g}}$	$\Delta G^{\circ\,\text{b}}_{\text{aq}}$	$\Delta\Delta G_{\text{PCM}}$
R-PCM	0.0	0.0	0.0	0.0	0.0	0.0
COM1-PCM	1.2	0.6	0.0	−2.6	1.5	3.19
IM1-PCM	−9.4	3.1	−9.0	−8.1	−13.7	−4.35
P_{b1}-PCM	−26.1	3.4	−25.5	−27.3	−31.0	−2.21
P_{b3}-PCM	−25.0	3.4	−23.9	−26.9	−29.8	−1.40
TSCOM1/IM1-PCM	34.8	0.3	34.8	38.5	33.6	−3.95
TSIM1/P_{b1}-PCM	14.8	0.5	13.1	18.9	12.0	−4.54
TSCOM1/P_{b3}-PCM	25.6	−0.7	23.8	29.7	24.4	−3.37

[a] B3LYP/6-311+G**// B3LYP/6-311+G**

[b] B3LYP (PCM)/6-311+G**// B3LYP/6-311+G**

TSCOM1/$\mathbf{P_{b3}}$-PCM, the dipole moment is increased from 2.3 to 3.5 D.

The gas-phase relative free energy of **IM1** is −8.1 kcal mol^{-1}, the relative free energy of **IM1-PCM** is −12.2 kcal mol^{-1} in aqueous solvent, and **IM1-PCM** is more stabilized by 4.1 kcal mol^{-1} in free energy. After consideration of solvation effect, **$\mathbf{P_{b1}}$-PCM** is 1.7 kcal mol^{-1} lower in free energy than **$\mathbf{P_{b1}}$**, and **$\mathbf{P_{b3}}$-PCM** is 1.8 kcal mol^{-1} lower than **$\mathbf{P_{b3}}$** in free energy, moreover, **$\mathbf{P_{b1}}$-PCM** is more stable than **$\mathbf{P_{b3}}$-PCM** in aqueous solvent, which is consistent with the result in gas phase.

The second approach is employed to understand the effect of solvation on the hydration of pentafulvenone, that is, only single-point energy calculations in PCM using the gas-phase geometric structures are performed, which is shown in Table 3. When the solvent reaction field is included, the activation internal energies of the rate-determining transition states **TSCOM1/IM1-PCM** (1676i) and **TSCOM1/$\mathbf{P_{b3}}$-PCM** (1509i) are 34.8 and 23.8 kcal mol^{-1}, respectively, at the MP2 (PCM)/6-311+G**// B3LYP/6-311+G** level, which represent reductions of, respectively, 4.3 and 3.5 kcal mol^{-1} relative to the corresponding gas-phase barriers at the MP2/6-311+G**// B3LYP/6-311+G** level. The relative internal energy values of **IM1-PCM**, **$\mathbf{P_{b1}}$-PCM** and **$\mathbf{P_{b3}}$-PCM** are −9.0, −25.5 and −23.9 kcal mol^{-1}, respectively, at the MP2 (PCM)/6-311+G**// B3LYP/6-311+G** level, and at the MP2 (PCM)/6-311+G**// B3LYP (PCM)/6-311+G** level, the corresponding values are −7.5, −23.6 and −23.4kcal mol^{-1}, respectively. It turns out that the MP2 (PCM)/6-311+G** results using gas-phase geometric structures do not differ significantly from the MP2 (PCM)/6-311+G** results based on geometric structures optimized in PCM.

Because the structural parameters change slightly in going from gas phase to aqueous solvent, the cost of calculation time is high, and the energy discrepancies are small between using gas-phase geometric structures and geometric structures optimized in PCM; therefore, for the reaction of pentafulvenone with two water molecules, only single-point energy calculations are done using B3LYP (PCM)/6-311+G** and MP2 (PCM)/6-311+G** levels based on gas-phase geometric structures.

3.4.2 Solvation effect on the reaction of pentafulvenone with two water molecules

The internal energy values of **COM2-PCM**, **COM3-PCM**, **COM4-PCM** and **COM5-PCM** are −4.5, −6.2, −26.3 and −25.3 kcal mol^{-1}, respectively, relative to reactants in aqueous solvent, which are increased compared to the corresponding values in gas phase. However, the internal energy values of **IM′-PCM** and products $\mathbf{P_{b1}{+}H_2O-PCM}$ and $\mathbf{P_{b3}+H_2O-PCM}$ are −12.5, −25.5 and −23.9 kcal mol^{-1}, respectively. The results indicate that the stabilities of intermediate and products are increased in aqueous solvent. Table 4 shows the relative energies calculated for the reaction in PCM.

The activation internal energies of rate-determining transition states $\mathbf{TSCOM2/IM'{-}PCM}$ (918i) and **TSCOM3/COM5-PCM**(764i) are 11.3 and 7.5 kcal mol^{-1}, respectively, and in gas phase the activation internal energies of rate-determining transition states $\mathbf{TSCOM2/IM'}$ and **TSCOM3/COM5** are 11.9 and 7.9 kcal mol^{-1}, respectively, therefore, after considering the solvation effect, the activation internal energies are reduced. Comparing the activation internal energies of rate-determining transition states of two water molecules attacking pentafulvenone with that of a water molecule attacking pentafulvenone in aqueous solvent, the activation internal energies decrease obviously (**TSCOM1/IM1-PCM** and **TSCOM1/$\mathbf{P_{b3}}$-PCM** are 34.8 and 23.8 kcal mol^{-1}, respectively), which is consistent with the trend in gas phase. The added water molecule still plays an active catalytic role. As reported by Nguyen [16] for the

Table 4 Relative energies and free energies (in kcal mol^{-1}) of stationary points for the reaction of pentafulvenone with two water molecules in aqueous solvent at the B3LYP(PCM)/ 6-311+G**//B3LYP/6-311+G** and MP2 (PCM)/ 6-311+G**//B3LYP/6-311+G** levels

Species	$E_{\mathrm{B3LYP-PCM-SP}}$	$\mathrm{ZPVE}_{\mathrm{B3LYP-PCM-SP}}$	$E_{\mathrm{MP2-PCM-SP}}$	$\Delta\Delta G^{\mathrm{a}}_{\mathrm{PCM}}$	$\Delta\Delta G^{\mathrm{b}}_{\mathrm{PCM}}$
R′-PCM	0.0	0.0	0.0	−0.49	−1.21
				−14.40	−15.42
COM2-PCM	−2.5	2.5	−4.5	−4.40	−5.03
COM3-PCM	−2.2	2.9	−6.2	−3.16	−4.09
COM4-PCM	−26.7	5.7	−26.3	−6.74	−7.49
COM5-PCM	−24.9	4.9	−25.3	−9.77	−11.11
IM′-PCM	−11.7	5.1	−12.5	−11.26	−12.35
$\mathrm{P_{b1}} + \mathrm{H_2O}$-PCM	−26.1	3.4	−25.5	−17.09	−18.40
$\mathrm{P_{b3}} + \mathrm{H_2O}$-PCM	−25.0	3.4	−23.9	−16.29	−17.89
TSCOM2/IM′–PCM	12.1	3.2	11.3	−11.98	−13.90
TSIM′/COM4-PCM	16.2	2.6	13.1	−6.46	−7.34
TSCOM3/COM5-PCM	11.5	2.8	7.5	−11.67	−13.88

[a] B3LYP (PCM)/6-311+G**// B3LYP/6-311+G**

[b] MP2 (PCM)/6-311+G**// B3LYP/6-311+G**

mechanism of CH_2CO with water, we can infer that the further incorporation with more than two water molecules induces energetic improvements for the rate-determining barriers of the reaction of pentafulvenone with water.

4 Conclusions

The main results are summarized as follows.

1. For the hydrations of pentafulvenone, there are two feasible pathways, which are water molecules attacking the C=O bond and C=C bond of pentafulvenone. The calculated barriers of the rate-determining transition states are 42.2, 30.4, 20.0 and 19.6 kcal mol^{-1}, respectively, in gas phase, and in aqueous solvent those of the rate-determining transition states are 34.8, 23.8, 15.8 and 12.0 kcal mol^{-1}, respectively.
2. Along with the numbers of water molecules increasing from one to two, the rate-determining barriers decrease, which is interpreted as the catalytic effect of the second water molecule, and after considering the solvation effect, the energies and barrier heights for the hydrations of pentafulvenone decrease.
3. Three types of cyclopentadienyl carboxylic acids should be observed. Their structures and stabilities are identified in our theoretical study. Among these products, $\mathbf{P_{b1}}$ and $\mathbf{P_{b3}}$ are the most stable products. Under certain conditions the a and c isomers always isomerize to the b isomers.

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