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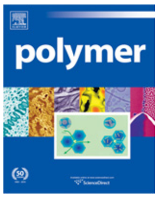

Acetone/Water as a new photoinitiating system for photografting: A theoretical study

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A R T I C L E I N F O

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Acetone can function as a high efficient photoinitiator for photografting copolymerization when it is mixed with water. The initiation mechanism of acetone/water as a new photoinitiating system for photografting copolymerization has been theoretically investigated at the B3LYP/6-31G** level. Acetone exists in the form of hydrates in its aqueous solution. Acetone dihydrate $CH_3COCH_3 \cdot 2H_2O$ is readily excited to a triplet state (T_1) under UV irradiation (254 nm) and then generates a radical $^\bullet C_3H_8O_2{}^\bullet$ involving two single electrons. The photolysis of $^\bullet C_3H_8O_2{}^\bullet$ is difficult to occur. However, the hydrogen abstraction from a polymer substrate by the ketonic oxygen of the radical is easier to take place, due to its lower energy requirement. The latter path produces a macromolecular radical that can initiate a photografting reaction easily. The photochemical reactions of acetone dihydrate produce less free radicals, leading to less termination reactions of the growing grafted chains. This study elucidates the photoinitiation mechanism of acetone/water photoinitiating system reasonably.

1. Introduction

Photo-induced grafting or photografting is a very popular technique for the surface modification of polymeric materials. Photoinitiator(s) is usually required for the initiation of photografting reaction, except for a few self-initiated photograftings. Benzophenone (BP) and its derivatives are the most commonly used photoinitiators for photografting. However, most of them are water-insoluble and hence the photografting reactions have to be carried out in organic solvents, which increase costs and induce environmental problems.

Acetone, the simplest aliphatic ketone, is usually used as a solvent rather than a photoinitiator for photografting reactions. However, in some cases, acetone can act as both a solvent and a photoinitiator. Allmer et al. reported that acetone can initiate the vapor photografting of acrylic acid (AA) onto polyethylene (PE) surface in the absence of any photoinitiators, in which acetone and AA are in the gaseous phase [1]. It is also found that acetone can function as an effective photoinitiator for liquid phase photografting when it is mixed with a proper ratio of water [2–4]. We reported that some other aliphatic ketones, such as butanone, pentanone, hexanone, etc., can also be used as photoinitiators for photografting when they are mixed with proper ratio(s) of water and alcohol (as a co-solvent) [5,6]. Therefore, these aliphatic ketones, especially acetone that is miscible with water, can be used as water-soluble photoinitiators. This finding may have important potential industrial applications.

The photodecomposition and photoinitiation mechanisms of acetone and other aliphatic ketones are proposed as follows (Scheme 1) [1,5]:

Acetone or other aliphatic ketone molecule can, after absorbing UV light, either split by a Norrish type I reaction to form radicals directly or abstract a hydrogen atom from a nearby molecule of monomer or polymer to form a monomeric (M·) or polymeric free radical (P•). The polymeric radical (P•) formed can initiate a grafting reaction, and the other radicals can initiate homopolymerization, terminate growing grafted and homopolymer chains, or recombine to produce non-active products.

The obvious drawback of this mechanism is that it does not consider the function of water in the photoinitiation effect. However, from the previous photografting work, water obviously plays a very important role in the photoinitiating effect of acetone/water or aliphatic ketone/water/alcohol systems. Therefore, understanding why and how water affects the photoinitiating effect of acetone is important for further fundamental study and industrial applications.

Until now, lots of work has been done on the photolysis of acetone in gas phase experimentally and theoretically [7–11]. For acetone aqueous solution, many studies suggest that the carbonyl group of acetone interacts with water to form hydrogen bond

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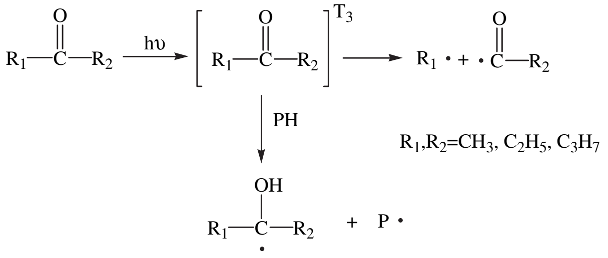


Scheme 1. Proposed photodecomposition and photoinitiation mechanism of aliphatic ketones.

[12–15]. The study of the blue shift for the n–π* transition of acetone in water shows that the hydrogen bond makes a significant contribution to the total shift [12]. However, theoretical study on acetone/water as a new photoinitiating system has not been reported.

In this work, acetone/water as a new photoinitiating system for photografting has been theoretically calculated. The purpose is to obtain the initiation mechanism and the function of water in this system.

2. Methods of calculations

For most reactions under consideration in this study, we used the density functional theory (DFT) method B3LYP [16–19] employed in the 6-31G** basis set to search for and optimize all possible geometries of transition states (TS) as well as reactants, intermediates, and products. The harmonic frequency calculations were performed at the same level to verify whether they are minima with all real frequencies or transition states with only one imaginary frequency (iw). For the dominating reaction paths, intrinsic reaction coordinates (IRC) [20] were traced to confirm the TS connecting with the corresponding two minima. In addition, TD-DFT and CIS methods were used to calculate the excitation energies of acetone in aqueous to the first excited singlet (S_1) or the first excited triplet (T_1) under UV irradiation, respectively. All calculations were performed with the Gaussian 03 package on a Pentium IV-2 G computer.

3. Results and discussion

3.1. The hydration reactions of acetone

Acetone (CH_3COCH_3) is an organic compound that is miscible with water. The reason for their mutual miscibility is that acetone forms hydrates, which have good solubility in water. Acetone can form many kinds of hydrates in water, Liao et al. [21] calculated the possible structures and energetics of different arrangements of $CH_3COCH_3\ (H_2O)_n$ ($n = 1$–3). For the simplicity of study, we only consider the hydrates of acetone with water molecule(s) directly connected to the O atom and hydrogen atoms on acetone. As the O atom of acetone has two pairs of lone electrons, it can form two hydrogen bonds with water molecules at most. The hydrates formation includes two steps (Eqs. (1) and (2)):

$$CH_3COCH_3 + H_2O \rightarrow CH_3COCH_3 \bullet H_2O \quad \Delta E = -8.7\ \text{kcal/mol} \tag{1}$$

$$CH_3COCH_3 \bullet H_2O + H_2O \rightarrow CH_3COCH_3 \bullet H_2O \quad \Delta E = -8.0\ \text{kcal/mol} \tag{2}$$

The products of the two reactions were optimized and the hydration energies of the two reactions were calculated. During the hydration process, one mole of acetone can combine with one mole of water to produce one mole of $CH_3COCH_3 \cdot H_2O$ with 8.7 kcal energy released at the same time. One mole of $CH_3COCH_3 \cdot H_2O$ continues to combine with one mole of water and generates one mole of $CH_3COCH_3 \cdot 2H_2O$, and the energy change of this reaction is −8.0 kcal/mol. The two hydration steps are both exothermic processes.

There are several isomers of $CH_3COCH_3 \cdot 2H_2O$ [21] and the two most stable configurations (A_1 and A_2) are listed in Fig. 1. Although A_1 is more stable than A_2, the two water molecules in A_1 are not directly connected to the O atom and hydrogen atoms on acetone, therefore, the following calculations are based on A_2.

Optimized geometries for acetone and its hydrates along with their energies are listed in Fig. 2. The bond lengths of the O⋯H bonds in the two hydrates are in the range of 1.94–2.38 Å, indicating both of the two hydrates have hydrogen bonding. So acetone exists largely in the form of $CH_3COCH_3 \cdot 2H_2O$ in aqueous solution. Meanwhile, the bond length of the carbonyl group of acetone increases during the hydration reaction, it is from 1.216 Å in CH_3COCH_3 to 1.223 Å in $CH_3COCH_3 \cdot H_2O$ and to 1.230 Å in $CH_3COCH_3 \cdot 2H_2O$ at last.

For the convenience of reading and understanding, all the optimized geometries and their total energies (in hartree) of the reactants, transition states and products at the level of B3LYP/6-31G** are summarized in Fig. 2, and the concerned bond lengths and bond angles, as well as the imaginary frequency (iw) of the transition states are listed, and arrows are added to indicate the reactions involved.

3.2. S_0 and T_1 of acetone in gaseous phase and in aqueous solution

The first excited triplet states (T_1) of acetone both in gaseous phase and aqueous solution have been calculated, their configurations together with ground state (S_0) of the two states were optimized at the same level. In order to confirm whether the conformations are the located minimum points of extremum, frequency analyses were performed and no imaginary frequency could be found, indicating the conformations are in equilibrium states.

Table 1 gives their vertical excitation energies and adiabatic excitation energies of S_0 and T_1 of acetone in gaseous phase and in aqueous solution.

When gaseous acetone is exited from S_0 to T_1 under UV irradiation, its total energy is raised from −193.16421 hartree to −193.04413 hartree. The bond length of C=O double bond is lengthened from 1.216 Å to 1.328 Å, which is between the length of C–O single bond (1.430 Å) and C=O double bond (1.216 Å), some other parameters also change correspondingly.

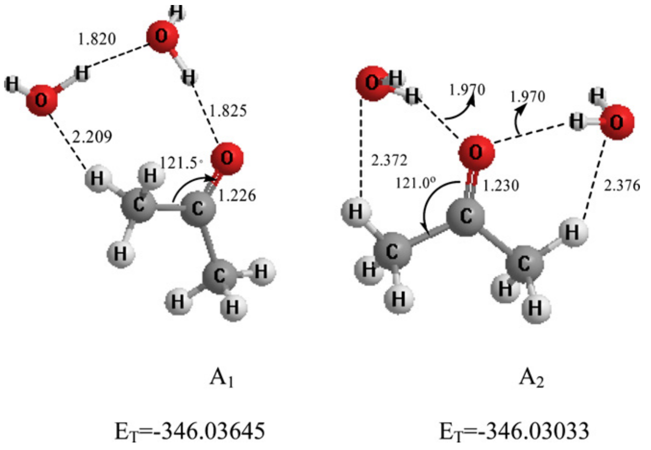


Fig. 1. Optimized geometries and their total energies of $CH_3COCH_3 \cdot 2H_2O$ at the level of B3LYP/6-31G** (bond lengths: Å; bond angles: E_T: hartree).

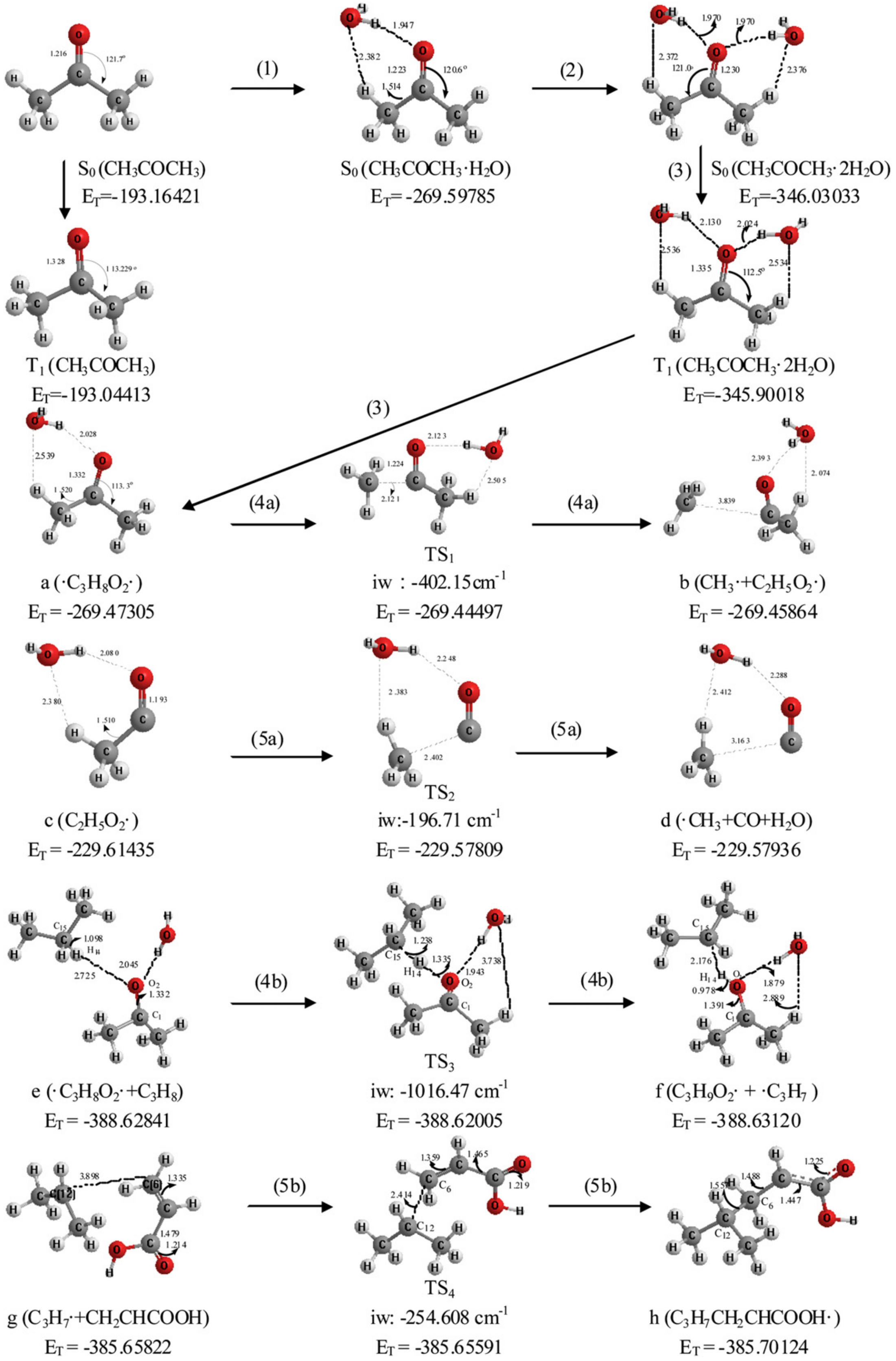
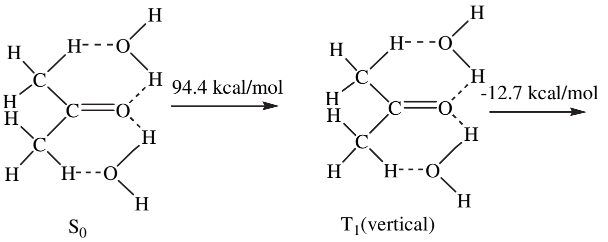


Fig. 2. Optimized geometries and their total energies for reactions at the level of B3LYP/6-31G** (bond lengths: Å; bond angles: E_T: hartree).

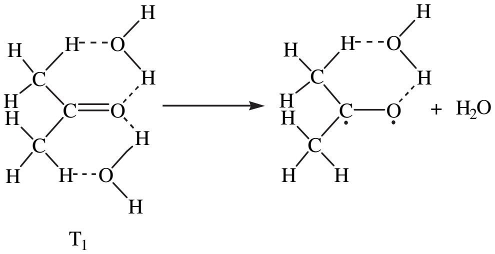
Table 1
The total energies and excitation energies of acetone in gaseous phase (CH_3COCH_3) and aqueous solution ($CH_3COCH_3 \cdot 2H_2O$) at the level of B3LYP/6-31G**.

	S_0 (hartree)	T_1 (vertical) (hartree)	T_1 (adiabatic) (hartree)	T_1 (vertical excitation) (kcal/mol)	T_1 (adiabatic excitation) (kcal/mol)
CH_3COCH_3	−193.16421	−193.02306	−193.04413	88.6	75.4
$CH_3COCH_3 \cdot 2H_2O$	−346.03033	−345.87983	−345.90018	94.4	81.7

When $CH_3COCH_3 \cdot 2H_2O$ is excited from S_0 to T_1 under UV irradiation, its total energy is raised from −346.03033 hartree of S_0 to −345.87983 hartree of $T_{1(\text{vertical})}$, the $T_{1(\text{vertical})}$ is unstable and thereafter it will release a energy of 12.7 kcal/mol and transfers to the $T_{1(\text{adiabatic})}$ with a total energy of −345.90018 hartree (Eq. (3a)). The bond length of C═O double bond is lengthened from 1.230 Å to 1.335 Å. And the lengths of O···H change correspondingly, from 1.970, 2.372, 1.970 and 2.376 Å to 2.130, 2.536, 2.024 and 2.534 Å, respectively. As a result, the hydrogen bonds of the hydrate are lengthened, and one water molecule is farther from acetone than the other one. Theoretically, during the excitation process, one pair of the isolated electrons on the O atom of C═O are excited from n to π* orbital, hence one of the hydrogen bonds disconnects at the same time. So it can be considered that a $CH_3COCH_3 \cdot 2H_2O$ molecule loses a H_2O molecule and generates a new species $\bullet C_3H_8O_2\bullet$ which has two radicals (Eq. (3b)).



(3a)



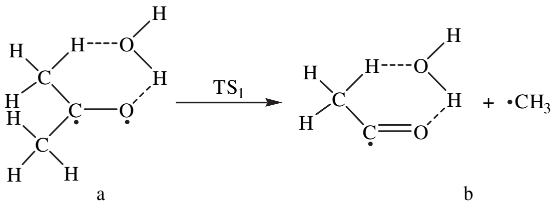
(3b)

The vertical and adiabatic excitation energies from S_0 to T_1 are calculated to be 88.6 and 75.4 kcal/mol for gaseous acetone, and 94.4 and 81.7 kcal/mol for $CH_3COCH_3 \cdot 2H_2O$, respectively. The commonly used UV lamps for photografting are medium or high-pressure mercury arc lamps which have a wide UV spectral output, however, only the output around 254 nm (112.2 kcal/mol) is usually the decisive part for photografting. The energy of UV light is much higher than the energies required for the excitation processes, thus acetone can be easily excited from S_0 to T_1 in the two states. The bond energies of ethylenic, primary, secondary and tertiary C—H bonds are 106, 100, 96 and 93 kcal/mol, respectively [22]. Therefore, the energies of the excited states of acetone in gaseous phase or in aqueous solution are sufficient for them to abstract hydrogen atoms from C—H bond(s) containing polymers directly.

Moreover, the S_1 vertical excitation energies for gaseous acetone (CH_3COCH_3) and acetone dihydrate ($CH_3COCH_3 \cdot 2H_2O$) have been calculated by CIS and TD-DFT methods, the calculated values are 122.5 kcal/mol and 129.0 kcal/mol by CIS and 101.6 kcal/mol and 106.2 kcal/mol by TD-DFT, respectively. The supplied energy is around 112.2 kcal/mol, it is feasible for them to be excited to S_1 theoretically, but it is difficult to occur under actual conditions due to the quite small energy difference. Therefore, we only consider T_1 of acetone in both gaseous phase and aqueous solution.

The total energies and C═O bond lengths of S_0 and T_1 of acetone in gaseous phase and aqueous solution are listed in Table 2. Because acetone in aqueous solution ($CH_3COCH_3 \cdot 2H_2O$) has two more molecules water than that in gaseous phase (CH_3COCH_3). When we compare their total energies, CH_3COCH_3 (in gaseous phase) plus two water molecules ($CH_3COCH_3 + 2H_2O$) is counted as one molecule.

As shown in Table 2, there are some differences in total energies and bond lengths between $CH_3COCH_3 + 2H_2O$ in gaseous phase and $CH_3COCH_3 \cdot 2H_2O$. The total energies of S_0 and T_1 are −346.00369 hartree and −345.88360 hartree for $CH_3COCH_3 + 2H_2O$ in gaseous phase, and −346.03033 hartree and −345.90018 hartree for $CH_3COCH_3 \cdot 2H_2O$, respectively. The C═O bond lengths of S_0 and T_1 are 1.230 Å and 1.335 Å for $CH_3COCH_3 \cdot 2H_2O$, respectively, they are bigger than 1.216 Å and 1.328 Å for $CH_3COCH_3 + 2H_2O$ in gaseous



(4a)

Table 2
The total energies and C═O bond lengths for S_0 and T_1 of acetone in gaseous phase ($CH_3COCH_3 + 2H_2O$) and aqueous solution ($CH_3COCH_3 \cdot 2H_2O$).

	S_0 ($CH_3COCH_3 + 2H_2O$)	S_0 ($CH_3COCH_3 \cdot 2H_2O$)	T_1 ($CH_3COCH_3 + 2H_2O$)	T_1 ($CH_3COCH_3 \cdot 2H_2O$)
E/Hartree	−346.00369	−346.03033	−345.88360	−345.90018
C═O/Å	1.216	1.230	1.328	1.335

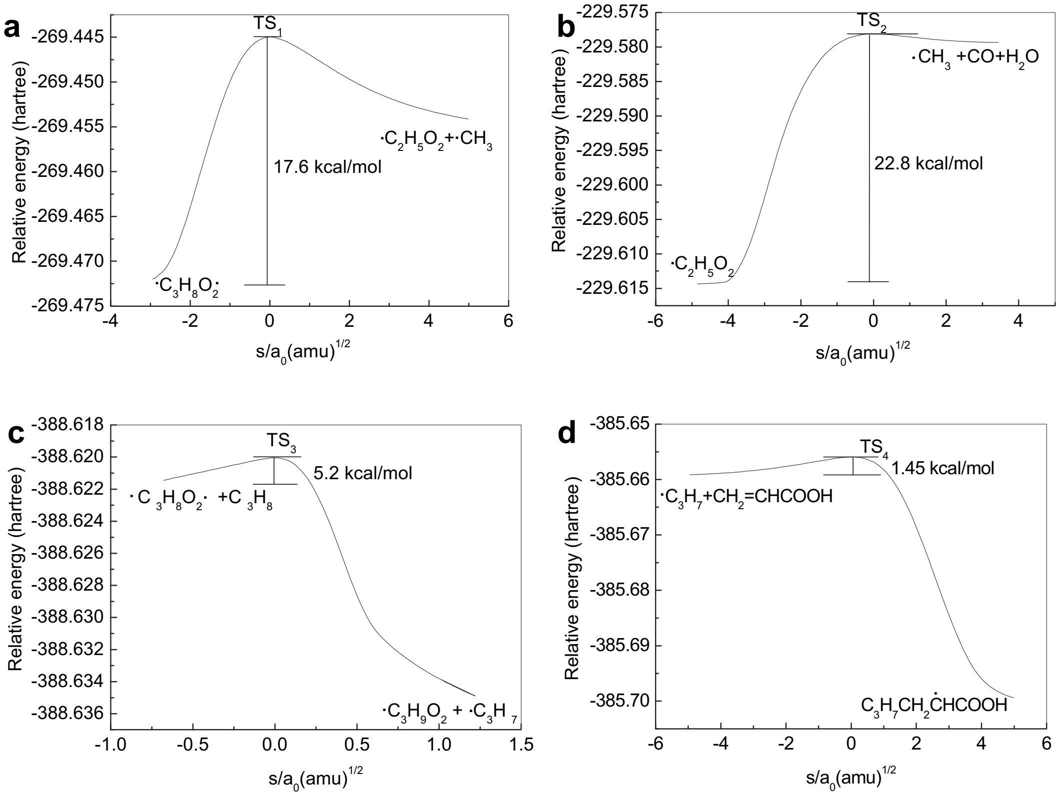


Fig. 3. The IRC for the reactions at the level of B3LYP/6-31G**.

phase. Therefore, the binding energy of C═O bond in $CH_3COCH_3 \cdot 2H_2O$ decreases, so the O atom of acetone is more active and it is easier to undergo further reactions than in gaseous phase.

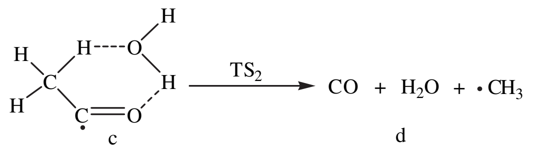
3.3. *Chemical reactions for T_1 of $CH_3COCH_3 \cdot 2H_2O$*

Under UV irradiation, acetone dihydrate in aqueous solution is excited from S_0 to T_1. The remaining energy is 30.5 kcal/mol (112.2−81.7 kcal/mol). During the excitation process, one of the hydrogen bonds connecting to the C═O double bond disconnects and forms $\cdot C_3H_8O_2\cdot$ radical which has two single electrons, one is on the carbon atom, the other is on the oxygen atom. Then the further reactions of $\cdot C_3H_8O_2\cdot$ radical are possibly important for the initiation reactions. The two most possible reaction paths of $\cdot C_3H_8O_2\cdot$ radical are as follows:

3.3.1. *Photolysis reaction of $\cdot C_3H_8O_2\cdot$*

The $\cdot C_3H_8O_2\cdot$ radical has a six-member ring formed by hydrogen bonds. The C–C single bond connected to the ring will disconnect and form $C_2H_5O_2\cdot$ and $\cdot CH_3$ radicals (Eq. (4a)).

The reactants and products are all optimized and frequency analyses were performed, they are all real, so the reactants and products are in equilibrium states. The frequency calculation was also performed for the transition state and only one imaginary frequency ($-402.15\ cm^{-1}$) was obtained. In order to confirm whether the transition state TS_1 connects the right minima, the IRC calculations were further carried out (Fig. 3a). It can be seen that $\cdot C_3H_8O_2\cdot$ radical may decompose via a transition state (TS_1) over an energy barrier of 17.6 kcal/mol, leading to $\cdot CH_3$ radical and $C_2H_5O_2\cdot$ radical. The potential barrier of the reaction 4a is 17.6 kcal/mol, which is much lower than 30.5 kcal/mol (the remaining energy after excitation), so it is easy to occur. The radicals formed are capable of initiating the homopolymerization of monomer or terminating the growing grafting polymer chains, and, certainly, the radicals can recombine to form non-active species.

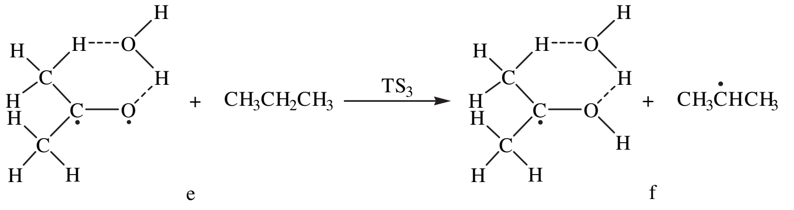


$$CO + H_2O + \cdot CH_3$$

(5a)

The first excited state of $C_2H_5O_2\cdot$ radical tends to return to its doublet of ground state with energy output. Then the doublet of ground state decomposes sequentially and generates $CH_3\cdot$, CO and H_2O (Eq. (5a)).

The optimized geometries together with some of their parameters are listed in Fig. 2. IRC calculations were carried out



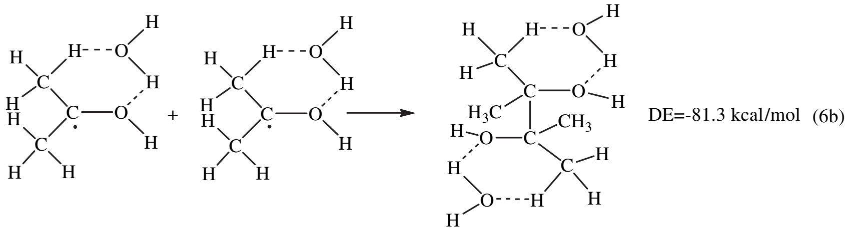
(4b)

(Fig. 3b). It shows that TS_2 (iw = −196.71 cm^{-1}) is the transition state that connects reactants and products of this reaction. The potential barrier of this reaction is as high as 22.8 kcal/mol. Therefore, the remaining energy of the first step (30.5 − 17.6 = 12.9 kcal/mol) is insufficient to achieve the second step (5a), indicating that the second step is impossible to occur.

3.3.2. Hydrogen abstraction

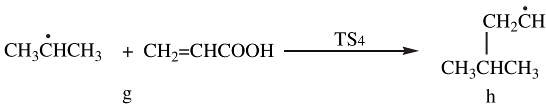
The $\cdot C_3H_8O_2\cdot$ radical can abstract hydrogen atom from polymers containing C–H bond to generate a macromolecular radical which can initiate grafting reaction. Here we used propane C_3H_8, which has a very similar chemical structure as those of the most commonly used plastics such as polyethylene and polypropylene, as a model compound to represent a polymer substrate. The reaction of $\cdot C_3H_8O_2\cdot$ radical with propane generates an isopropyl radical and a $C_3H_9O_2\cdot$ radical (Eq. (4b)).

The imaginary frequency of the transition state TS_3 is −1016.47 cm^{-1}. The geometries of all stationary points and transition states with corresponding imaginary frequencies are illustrated in Fig. 2. The bond lengths of C_{15}–H_{14} are 1.098, 1.238 and 2.176 Å for the reactant, transition state and product, respectively; and the bond lengths of O_2–H_{14} are 2.725, 1.335 and 0.978 Å for the reactant, transition state and product, respectively. So the H_{14} atom has been abstracted from propane molecule and then combines with the O atom of acetone to form an O–H bond. TS_3 has been confirmed to reach the minima at both sides of it (Fig. 3c). The energy barrier via TS_3 is 5.2 kcal/mol which is much less than the remaining energy (30.5 kcal/mol). So it is easy for $\cdot C_3H_8O_2\cdot$ radical to react with propane to form $C_3H_9O_2\cdot$ and an isopropyl radical.


DE=-81.3 kcal/mol (6b)

Although the photolysis of the $\cdot C_3H_8O_2\cdot$ radical is possible to occur, it requires more energy (17.6 kcal/mol) than the hydrogen abstraction reaction (5.2 kcal/mol), therefore, it is more possible for the hydrogen abstraction reaction to occur.

The other product of the reaction 4b, $C_3H_9O_2\cdot$ radical, has a single electron on the carbon atom of carbonyl group. It can combine with itself to form a larger molecule (Eq. (6b)).



$$\underset{g}{\mathrm{CH_3\dot{C}HCH_3}} + \mathrm{CH_2{=}CHCOOH} \xrightarrow{TS_4} \underset{h}{\begin{array}{c}\mathrm{CH_2\dot{C}HCOOH}\\ |\\ \mathrm{CH_3CHCH_3}\end{array}} \quad (5b)$$

The reaction energy for the self-combination of two $C_3H_9O_2\cdot$ radicals is −81.3 kcal/mol, so the $C_3H_9O_2\cdot$ radicals are unstable in an aqueous solution and mainly exist in the form of $C_6H_{18}O_4$.

3.4. Grafting reaction

As is well known, once macromolecular radicals are formed on a polymer substrate, the initiation of grafting reaction is very easy to occur. Here we calculated the initiation reaction of a commonly used monomer, acrylic acid, by the model radical isopropyl (Eq. (5b)).

The imaginary frequency of the transition state TS_4 is −254.61 cm^{-1}. Many bond lengths change during the process, the particular bond lengths of C_{12}–C_6 are 3.898, 2.414, 1.557 Å for the reactant, transition state and product, respectively. The C=C double bond lengths are 1.335, 1.359 and 1.488 Å for reactants, transition states and products, respectively. Actually, the C=C double bond has changed into a C–C single bond. The C=O double bond lengths are1.214, 1.219, 1.225 Å for the reactant, transition state and product, respectively. The C_6 atom approaches the isopropyl radical to form a C–C bond. The IRC calculation of this reaction was carried out. TS_4 has been confirmed to reach the minima at both sides of it (Fig. 3d). The energy barrier via TS_4 is 1.45 kcal/mol which is much less than the remaining energy (30.5 − 5.2 = 25.3 kcal/mol). So it is easy for the $C_3H_7\cdot$ radical to react with a monomer molecule to initiate the grafting reaction.

Once the grafting polymerization reaction has been initiated, the propagation of the grafting chains is very easy to occur. Since the UV-initiated free radical polymerization usually requires quite low activation energy. The grafted chains can grow until they are terminated by the recombination with other radicals or by disproportionation.

The propagation and termination mechanisms of grafting reactions are as follows [23]:

II. Propagation:

$$\mathrm{PM}\bullet + n\mathrm{M} \rightarrow \mathrm{P(M)}n\mathrm{M}\bullet \ \text{(grafting)}$$

P: polymer, M: monomer

III. Termination with a radical (R•):

$$\mathrm{P(M)}n\mathrm{M}\bullet + \mathrm{R}\bullet \rightarrow \mathrm{P(M)}n\mathrm{R}\text{(graft copolymer)}$$

As is well known, the photolysis of acetone molecule by a Norrish type I reaction forms acetyl and methyl radicals [1], both are capable of initiating the homopolymerization of monomer or terminating the growing grafted or homopolymer chains. The photolysis of acetone is easy to occur, then the formation of many low molecular weight (LMW) radicals will lead to the easy occurrence of termination of growing grafted and homopolymers chains by the radicals and hence the low extent of grafting and low homopolymerization efficiency. This is very possibly the reason for the extremely low extent of grafting or even no grafting occurs when acetone is used as the sole solvent for photografting even when a photoinitiator is present [3].

Since acetone forms hydrates with water in its aqueous solution, the direct photolysis of acetone becomes unavailable. Instead, acetone dihydrate, $CH_3COCH_3\cdot 2H_2O$, is readily excited to a triplet state (T_1) under UV irradiation and then decompose to form a radical $\cdot C_3H_8O_2\cdot$. The photolysis reaction of $\cdot C_3H_8O_2\cdot$ is possible to occur and produces $C_2H_5O_2\cdot$ and $\cdot CH_3$ radicals which can initiate the homopolymerization of monomer. However, the radical $\cdot C_3H_8O_2\cdot$, more easily, abstract a hydrogen atom from a polymer substrate to generate a propagating center. The easier occurrence of hydrogen abstraction from a polymer substrate rather than photolysis of $\cdot C_3H_8O_2\cdot$ leads to the formation of less free radicals. In addition, the radical $C_3H_9O_2\cdot$ formed by $\cdot C_3H_8O_2\cdot$ abstracting a hydrogen atom from a polymer substrate can combine with itself to form a stable compound (Eq. (6b)). With comparison to the direct photolysis of acetone, there are less LMW free radicals are formed in the photochemical reaction process of acetone dihydrate. Therefore, the growing grafted chains are difficult to be terminated. This is, very possibly, one of the reasons for the high extents of grafting using acetone/water as a photoinitiating system for the grafting of acrylic acid and methacrylic acid onto polyethylene [2,3].

The above calculations elucidate the possible photoinitiation mechanism of acetone/water photoinitiating system, the reaction paths and their energy requirements are reasonable.

4. Conclusions

The initiation mechanism of acetone/water as a new photoinitiating system for photografting has been theoretically investigated at the level of B3LYP/6-31G**. Water plays a significant role in the initiation effect of acetone in aqueous solution. Acetone dihydrate is excited to an excited triplet state under UV irradiation, and then the triplet state decomposes to form a $\cdot C_3H_8O_2\cdot$ radical (with two single electrons). The $\cdot C_3H_8O_2\cdot$ radical has two possible reaction paths: (1) Photolysis. The photolysis of $\cdot C_3H_8O_2\cdot$ is possible to occur and it generates radicals which could initiate the homopolymerization of monomer, this is the reason for the formation of some homopolymers observed in photografting reaction. (2) Hydrogen abstraction from polymer substrate by the ketonic oxygen of $\cdot C_3H_8O_2\cdot$. This path is easier to take place, due to its much lower energy requirement than the photolysis. Abstracting a hydrogen atom from a polymer substrate leads to the formation a macromolecular radical which can initiate grafting reaction of monomer easily. The photochemical reactions of acetone dihydrate also produce less free radicals that could terminate the grafting reactions. This may explain the high photoinitiation efficiency of acetone when it is mixed with water.

This study provides a new initiation mechanism for acetone in aqueous solution, and it may applicable to other aliphatic ketones in aqueous or water-borne systems. This study may provide aids for future developments of novel water-soluble photoinitiators.

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