



## Theoretical Studies on the Reaction Mechanism of Photocatalytic Degradation of Acetone

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The reaction mechanism of photocatalytic degradation of acetone by TiO<sub>2</sub> was investigated by using B3LYP methods with the 6-311++G (3df, 3pd) basis sets and reaction channels were found. Geometries of the reactants, predicted that the intermediate product is CH<sub>3</sub>COOH, last products of reaction is CO<sub>2</sub> and H<sub>2</sub>O. Intermediates, transition states and products were optimized and intrinsic reaction coordinate calculations were carried out. The calculated results successfully explained the conclusion of Huang's experimental study. From the view of bond length and energy analysis, the changes of chemical bonds in the reactions were discussed, the potential energy of the reaction was low, which will be helpful for the experimental research of the photocatalytic degradation of acetone.

**Key Words:** Acetone, Photocatalysis degradation, Reaction mechanism, Transition state.

### INTRODUCTION

Because of the wide application of material, insecticide, aromatic, *etc.*, it is very serious in pollution to the indoor air. The high energy-conservation take a breath insufficiently, make the indoor air pollution aggravate<sup>1-4</sup>. Because acetone is used in the manufacture of organic solvent, dyestuffs and rubber extensively, it generally exist in the building materials, renovation material and furniture material, release in the surrounding environment constantly, it is regarded as the typical air pollutant of organic compounds (volatile organic compounds), very harmful to human health. It is a hot problem to solve the pollution of acetone<sup>5,6</sup>.

There was some method to eliminate acetone of indoor air, such as active charcoal adsorption method, condensation and photocatalysis degradation, *etc.*<sup>7</sup>. The photocatalysis degradation already becoming an important technology to improvement indoor environmental. It had obvious advantages, such as energy-conservation, high-efficient and to degrades the pollutant completely and the condition of reaction was so mild, apparatus was simple, secondary pollution was little and easy to operation. TiO<sub>2</sub> was a high-efficient semiconductor as catalyzes materials to photocatalysis, it has a good effect to get rid of low density pollutants and gaseous phase pollutants. Recent years<sup>8-11</sup>, there were some reports of reactions to degraded acetone with TiO<sub>2</sub><sup>12-14</sup>. However, the mechanism of the reaction process is relatively less, especially the reports of quantum chemical calculations from molecular level was so few. Huang *et al.*<sup>14</sup> study the process of photocatalytic degra-

tion of acetone in the TiO<sub>2</sub> surface *in situ* infrared spectrum technical, capture reaction's intermediates CH<sub>3</sub>COOH.

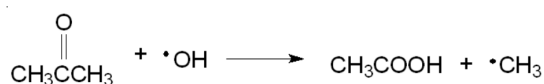
We discussed the mechanism of photocatalytic degradation reaction of acetone in the TiO<sub>2</sub> by the quantum chemistry, discussed the intermediates, transition states and the possible reaction channels according to the result of calculation, then compared with experiments.

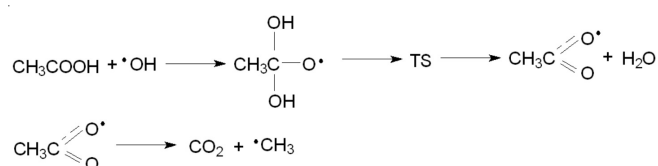
### EXPERIMENTAL

The geometries of all compounds were optimized using the hybrid density functional B3LYP with the 6-311++G (3df, 3pd) basis set. Harmonic vibrational frequencies calculated at the same level were used for characterization of stationary points as a minimum or a saddle point and for zero-point energy (ZPE) corrections. Transition states were subjected to intrinsic reaction coordinate (IRC) calculations to confirm the connection between reactants, intermediates and decomposition products. All quantum calculations were performed with the Gaussian 03 program.

### RESULTS AND DISCUSSION

**Stability configurations and reaction channels:** The results of the calculation indicate that the possible reaction channels as follows:





The geometry parameters of the reactants, products, potential intermediates and transition states are shown in Fig. 1.

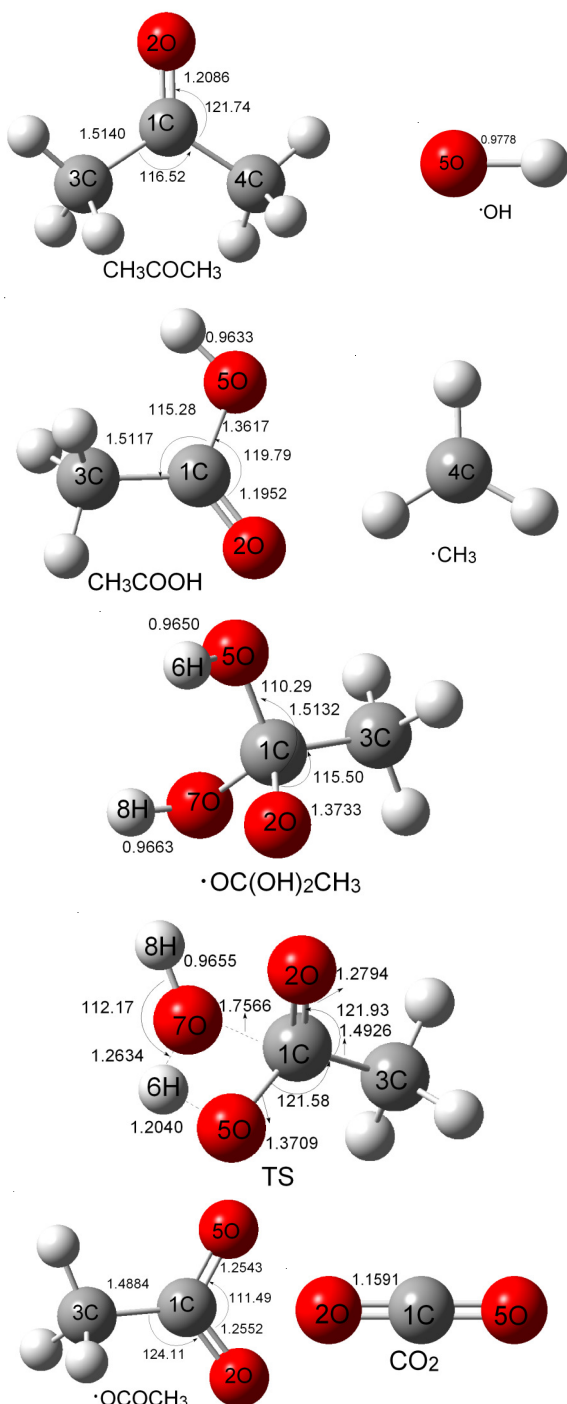


Fig. 1. Optimized geometries of the stationary points bond lengths are in nm, bond angles are in degree

The frequency analysis results of optimized transition state showed that the transition state had only one imaginary frequency, the resulting transition state (*ca.* 1820  $\text{cm}^{-1}$ ).

Oxygen of  $\cdot\text{OH}$  attack the carbonyl carbon of  $\text{CH}_3\text{COCH}_3$  (by light irradiation, the water molecules is oxidated to  $\cdot\text{OH}$  by catalyst of  $\text{TiO}_2$ ), while breaking of the C-C bond between one  $\cdot\text{CH}_3$  and carbonyl carbon, formation of  $\text{CH}_3\text{COOH}$  and free radicals of  $\cdot\text{CH}_3$ ; further, oxygen of the other one  $\cdot\text{OH}$  attack the carbonyl carbon of  $\text{CH}_3\text{COOH}$ , then formation of free radicals of  $\cdot\text{OC}(\text{OH})_2\text{CH}_3$ ; through a transition state (TS), formation of the intermediate of  $\cdot\text{OCOCH}_3$  and  $\text{H}_2\text{O}$ ;  $\cdot\text{OCOCH}_3$  is unstable, whose C-C bond will be broken to formation of the products of  $\cdot\text{CH}_3$  and  $\text{CO}_2$ .

#### Intrinsic reaction coordinate analysis of the reaction:

In order to verify the reaction mechanism, transition states were subjected to intrinsic reaction coordinate calculations to confirm the connection between reactants and intermediates.

The 7O (who in connect with the 1C in  $\cdot\text{OC}(\text{OH})_2\text{CH}_3$ ) away from the 1C, at the same time, The 7O connected with the 6H (6H is a H of one hydroxyl's who in connect with the 1C in  $\cdot\text{OC}(\text{OH})_2\text{CH}_3$ ) and four-member ring transition state (TS) structure of 1C-5O-6H-7O have been found in the reactions studied. The TS link the free radical of  $\cdot\text{OC}(\text{OH})_2\text{CH}_3$  and ( $\cdot\text{OCOCH}_3 + \text{H}_2\text{O}$ ). In the reaction process, the changes of the bond distances between atoms of 1C-7O, 5O-6H, 1C-5O and 7O-6H with the intrinsic reaction coordinate curve shown in Fig. 2.

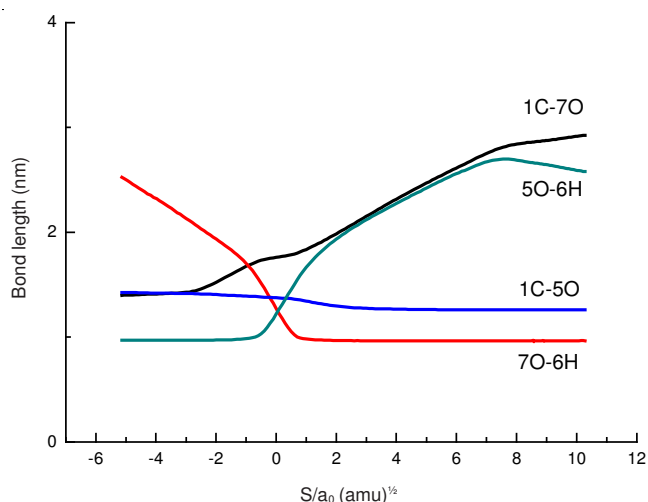


Fig. 2. Curves of bond length along reaction path of  $\cdot\text{OC}(\text{OH})_2\text{CH}_3 \rightarrow \text{TS} \rightarrow \text{CH}_3\text{CO}_2 + \text{H}_2\text{O}$

From the bond length changes, it is concluded that the distance of 1C-7O of  $\cdot\text{OC}(\text{OH})_2\text{CH}_3$  increases rapidly until the bond is broken, at the same time, the distance between the 7O and 6H reduced sharply. after the transition state structure, the curtare trend of the distance between 7O-6H become slowing down and the 7O-6H bond forms. The distance between atoms of 7O and 6H remain unchanged; In this process, because of 7O bond with 6H, it form structure of  $\text{H}_2\text{O}$ , it is a more stable structure, so 6H away from 5O gradually, after the transition state structure, the distance between the bond of 5O-6H increases rapidly, until the bond is broken; in this process, the distance between the bond of 1C-5O slightly shorten.

**Profile of potential energy:** The potential energy of the reactants, transition states, intermediates and products are calculated at the B3LYP/6-311+G (3df, 3pd) level with thermal

corrections and summarized in Table-1 and the energies are corrected by zero-point energy (ZPE) corrections. The method of B3LYP includes the exchange of energy and related gradient correction, in the past, many similar calculation of the study achieved better results<sup>15,16</sup> and consider of higher synthesis efficiency of this method, it's calculation time is shorter, so we adopted the results of the B3LYP methods and 6-311++G(3df,3pd) basis sets.

| Species                                 | $E_{\text{tot}}^a$ (a.u.) | $\Delta E$ (KJ mol <sup>-1</sup> ) |
|---|---------------------------|------------------------------------|
| CH <sub>3</sub> COCH <sub>3</sub> + •OH | -268.906853               | 0.0                                |
| •CH <sub>3</sub> + CH <sub>3</sub> COOH | -268.94071                | -88.896540                         |
| CH <sub>3</sub> COOH + •OH              | -304.869857               | 0.0                                |
| •OC(OH) <sub>2</sub> CH <sub>3</sub>    | -304.875825               | -15.669863                         |
| TS                                      | -304.830455               | 103.455754                         |
| •OCOCH <sub>3</sub> + H <sub>2</sub> O  | -304.897346               | -72.176418                         |
| •OCOCH <sub>3</sub>                     | -228.454146               | 0.0                                |
| •CH <sub>3</sub> + CO <sub>2</sub>      | -228.47732                | -60.846750                         |

The potential energy curves of the reactions are given in Fig. 3. Energy change of reaction shows that, the step of CH<sub>3</sub>COCH<sub>3</sub> + •OH → •CH<sub>3</sub> + CH<sub>3</sub>COOH is an exothermic process, it would release energy of 88.896540 KJ mol<sup>-1</sup>. The reaction CH<sub>3</sub>COOH + •OH → •OC(OH)<sub>2</sub>CH<sub>3</sub> is an exothermic process too, it would release energy of 15.669863 KJ mol<sup>-1</sup>; during the step of CH<sub>3</sub>COOH → TS → •OCOCH<sub>3</sub> + H<sub>2</sub>O, reactants to the transition state only needs to overcome the energy barrier of 119.125617 KJ mol<sup>-1</sup> and the whole process is exothermic, it would release energy of 56.506555 KJ mol<sup>-1</sup>

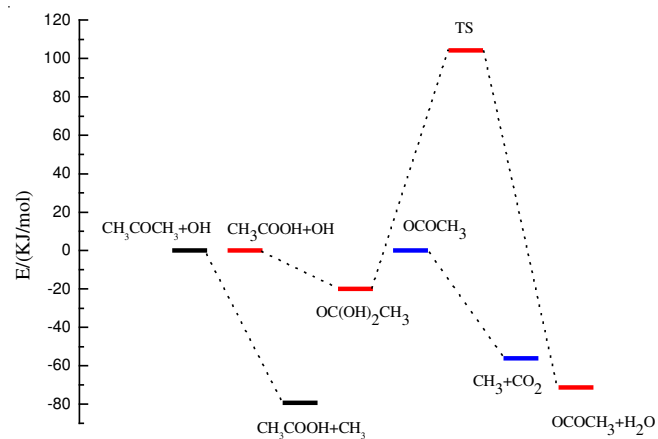


Fig. 3. Relative energies of the stationary points on the reaction path

and the step of •OCOCH<sub>3</sub> → •CH<sub>3</sub> + CO<sub>2</sub> would release energy of 60.846750 KJ mol<sup>-1</sup>. So it can be judged by all the steps, the overall process of the reaction of photocatalytic degradation of acetone is an exothermic process and the energy barrier of the reaction is lower to overcome, this is an easy process. The only endothermic step is •OC(OH)<sub>2</sub>CH<sub>3</sub> → TS. So, we concluded that the step of the bond breaking of the 7O and 1C of •OC(OH)<sub>2</sub>CH<sub>3</sub> and the 7O connected with the 6H at the same time, it is the key to restricting the reaction conditions.

## Conclusion

We discussed the reaction mechanism of photocatalytic degradation of acetone by TiO<sub>2</sub>, by quantum chemical method. The calculated values of the geometry parameters and potential energy of the reactants, transition states, intermediates and products validated the Huang's, who capture the intermediates of the reaction by *in situ* infrared spectroscopy technology. It is displayed that the potential energy surface of the channel were low, therefore, it is predicted that acetone is degraded to H<sub>2</sub>O and CO<sub>2</sub> easily, which is useful for the experiment to elimination of acetone in the air pollution of indoor.

## ACKNOWLEDGEMENTS

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