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Theoretical Studies on the Reaction Mechanism of Photocatalytic Degradation of Ethylene in Gas Phase Over TiO_2

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The reaction mechanism of photocatalytic degradation of ethylene in gas phase over titanium dioxide (TiO_2) was investigated by using B3LYP methods with the 6-311G basis sets and reaction channels were found. Geometries of the reactants predicted that the intermediates with the structure of hydrogen bonds, last products of reaction is CO_2 and H_2O. Intermediates and products were optimized and frequency were carried out. The calculated results successfully explained the conclusion of Huang Yali's experimental study. From the view of energy analysis, the reaction is a process to reduce energy, the reaction can be carried out under mild conditions from the theoretical studies. This will be helpful for the experimental research of the photocatalytic degradation of ethylene in gas phase.

Key Words: Ethylene, Reaction mechanism, Gas photocatalytic reaction, Degradation.

INTRODUCTION

TiO_2 is a catalyst of photocatalytic oxidation in gas phase, it is advanced and widely used for photocatalytic degradation of organic pollution with a strong catalytic activity, the ideal end product of degradation (some compounds can be directly degraded to carbon dioxide and water), stable, light corrosion resistance, simple to operating, cheap materials, non-toxic, chemically inert and bio-inert *etc.*[1-5]. It gradually developed into environmental pollution control technology in a new technology. There are number of reports[6-8] about the reaction mechanism of photocatalytic degradation of ethylene in gas phase over TiO_2. But, it is not enough about a systematic study of the unstable intermediate by the process of degradation produced.

We discussed the mechanism of carbonylation of ethylene photocatalytic degradation in gas phase over TiO_2, discussed the intermediates and the possible reaction channels according to the result of calculation and then compared with experiments[9].

EXPERIMENTAL

The geometries of all compounds were optimized using the hybrid density functional B3LYP with the 6-311G basis set. Harmonic vibrational frequencies calculated at the same level were used for characterization of stationary points as a minimum point and for zero-point energy (ZPE) corrections. All quantum calculations were performed with the Gaussian 03 program.

RESULTS AND DISCUSSION

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

$$CH_2CH_2 + 2OH \longrightarrow IM1$$
$$IM1 + 2OH \longrightarrow IM2$$
$$IM2 + 2OH \longrightarrow IM3$$
$$IM3 + 2OH \longrightarrow IM4$$
$$IM4 + 4OH \longrightarrow IM5$$
$$IM5 \longrightarrow 2CO_2 + 8H_2O$$

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

The reaction mechanism is predicted, by light irradiation. The water molecules is oxidized to $^{\bullet}OH$ by catalyst of TiO_2, oxygen of two $^{\bullet}OH$ attack the unsaturated carbon of CH_2CH_2, respectively, addition reaction occurred and formation of IM1; then oxygen of two $^{\bullet}OH$ attack the IM1, respectively and take away the H who is connected with the C in IM1, to form H_2O, at the same time, there are hydrogen bonds between the H_2O and the OH of IM1, it is the structure of IM2; the Next step, oxygen of two $^{\bullet}OH$ attack the unsaturated carbon of IM2, respectively, addition reaction occurred and formation of IM3; then oxygen of two $^{\bullet}OH$ attack the IM3, respectively and take away the H who is connected with the C in IM3, to form H_2O. At the same time, there are hydrogen bonds between the H_2O

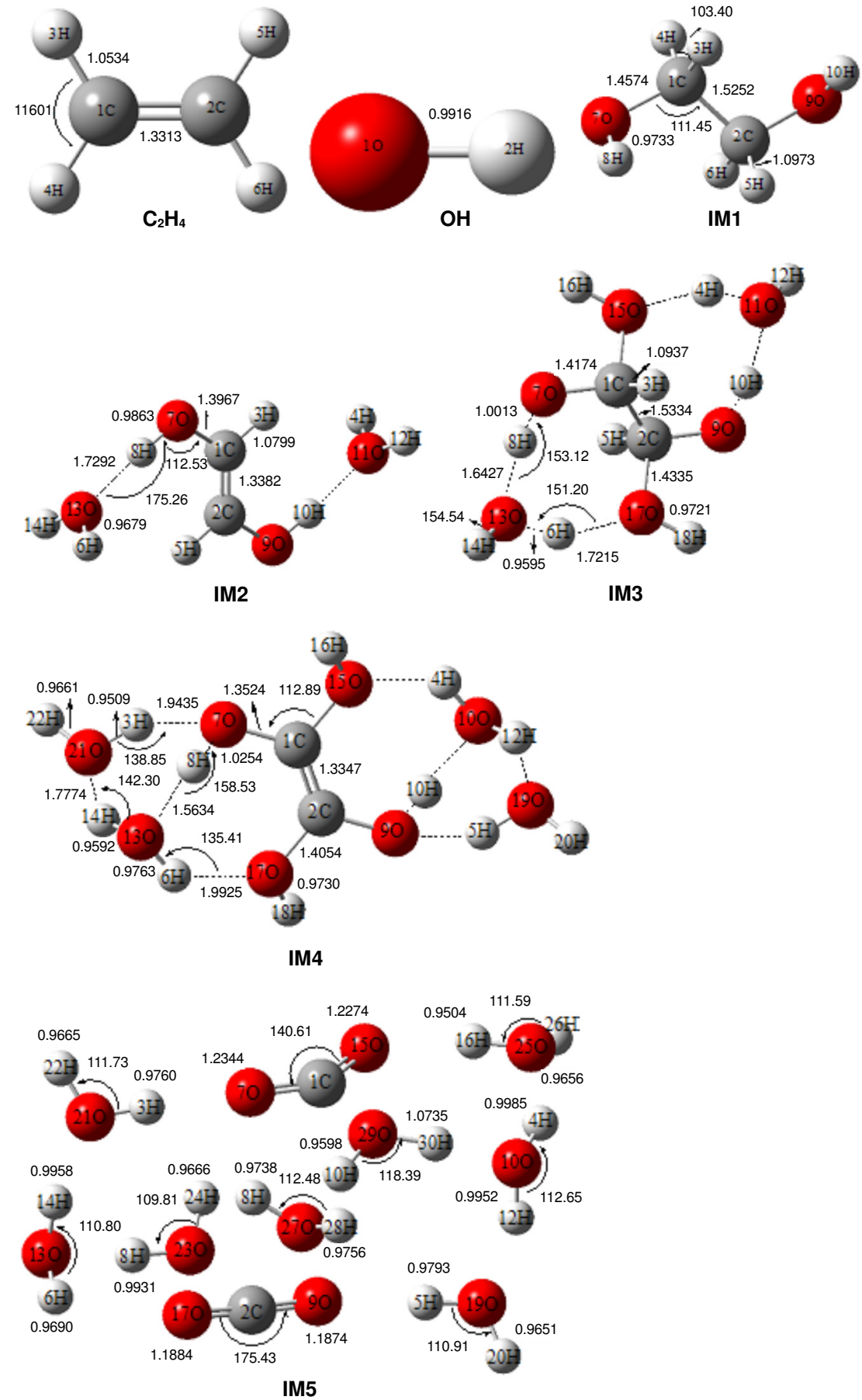

Fig. 1. Optimized geometries of the stationary points bond lengths are in nm, bond angles are in degree

and the OH of IM3, it is the structure of IM4; four •OH attack the IM4, respectively and take away the H of OH who is connected with the C in IM4, to form H_2O and CO_2. At the same time, there are hydrogen bonds between the O and the H, it is the structure of IM5. As the photocatalytic reaction of nano-TiO_2, ethylene was broken down into H_2O and CO_2 eventually.

Profile of potential energy: The potential energy of the reactants, transition states, intermediates and products are calculated at the B3LYP/6-311G 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[10-12] and consider of higher synthesis efficiency of this method, its calculation time is shorter, so we adopted the results of the B3LYP methods and 6-311G basis sets.

TABLE-1
ENERGIES FOR STATIONARY POINTS ON THE PATHWAYS

Species	E_{tot} [a] (au)	ΔE (KJ mol^{-1})
CH_2CH_2+2•OH	-229.996989	0.0
IM1	-230.153805	-411.743504
IM1+2•OH	-381.610189	0.0
IM2	-381.774337	-430.994750
IM2+2•OH	-533.230721	0.0
IM3	-533.431960	-528.382634
IM3+2•OH	-684.888344	0.0
IM4	-685.048104	-419.473410
IM4+4•OH	-987.960872	0.0
IM5	-988.430156	-1232.174260
$8H_2O + 2CO_2$	-988.243692	489.588695

The energy change of reaction shows that, the all step of the •OH reacted with reaction are strong exothermic process and there is not detection of the transition state in the whole process. All of the spatial structures have higher symmetry of the products after reaction with •OH of every step. There are a large number of hydrogen bonds, so these structures low-energy and stable. So it can be judged by all the steps, the overall process of the reaction of photocatalytic degradation of ethylene is an exothermic process. The effect of degradation to eliminate contamination of ethylene is better. IM5 is the intermediate be combined by hydrogen bonding of CO_2 and H_2O molecules, its energy is lower than the sum of the energy of free CO_2 and H_2O molecules corresponding. Therefore if one wishes to detect the product of degradation of ethylene in gaseous form, it is necessary to heat to desorption the CO_2 and water vapor from the surface of the catalyst. The generation of gaseous product is increasing as the increase of temperature.

Conclusion

We discussed the reaction mechanism of photocatalytic degradation of ethylene by TiO_2, by quantum chemical method, and calculated the geometry parameters and potential energy of the reactants, intermediates and products. The hydrogen bonding is important form in the intermediate product. The overall process of the reaction of ethylene photocatalytic degradation is an exothermic process. Therefore, it is predicted that ethylene is degraded to H_2O and CO_2 easily, which is useful for the experiment to elimination of ethylene in the air pollution.

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