



Theoretical Studies on the Reaction Mechanism of Vapour-Phase Carbonylation of Methoxy Group to Dimethyl Carbonate

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The reaction mechanism of vapour-phase carbonylation of methoxy group to dimethyl carbonate was investigated by using B3LYP methods with the 6-311+G(d) basis sets and reaction channels were found. Geometries of the reactants, intermediates, transition states and products were optimized and intrinsic reaction coordinate calculations were carried out. The calculated results successfully explained the conclusion of MA Xin-Bin's experimental study. From the view of bond and energy analysis, the changes of chemical bonds in the reactions were discussed, which will be helpful for the experimental research of the synthetic of dimethyl carbonate.

Key Words: Dimethyl carbonate, Reaction mechanism, Transition state.

INTRODUCTION

Dimethyl carbonate (DMC) is a new green chemicals, their toxicity is very low. In 1992, dimethyl carbonate products through the registration of non-precursor chemicals in Europe. It is the reagent of methylation and carbonylation to replace phosgene, dimethyl sulphate, halogenated methane and methyl chloride *etc.*, they are toxic or carcinogenic, dimethyl carbonate is used in organic synthesis widely, to manufacture many ramifications, to product a series of important chemicals, specialty chemicals, fine specialty chemicals, to synthesize food additives, antioxidants, dyes, pesticides, pharmaceuticals intermediates. The market prospects of dimethyl carbonate is very optimistic, there is great potential of whose application, once known as "the new cornerstone of organic synthesis of 21st century"¹⁻⁴.

Present, the main synthesis of dimethyl carbonate is phosgene method, transesterification and carbonylation of methanol, among them, the method of carbonylation of methanol received extensive attention⁵, because of wide range of sources of raw materials, low cost and low pollution, *etc.*⁵. on the catalyst surface, dimethyl ether and methanol have similar chemical properties. They will generate species of $\cdot\text{OCH}_3$. It is a new method to synthesis of dimethyl carbonate by carbonylation of dimethyl ether, the method is still in the experimental research stage. However, the mechanism of the reaction process is few, especially the reports of quantum chemical calculations from molecular level was so few. We discussed the mechanism

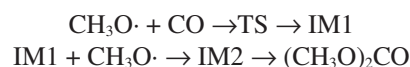
of carbonylation of methoxy group to dimethyl carbonate by the quantum chemistry, discussed the intermediates, transition states and the possible reaction channels according to the result of calculation, then compared with experiments⁶.

EXPERIMENTAL

The geometries of all compounds were optimized using the hybrid density functional B3LYP with the 6-311+G(d) 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 our 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.

The frequency analysis results of optimized transition state showed that, the transition state had only one imaginary frequency, the results: TS ($-310.5260 \text{ cm}^{-1}$).

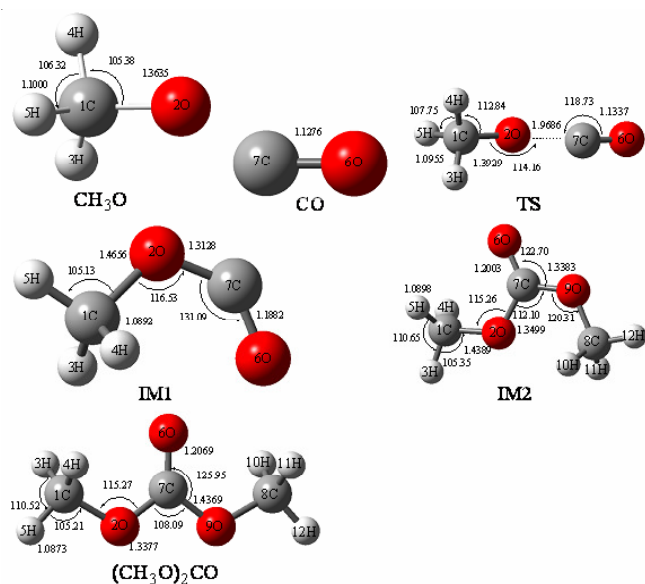


Fig. 1. Optimized geometries of the stationary points bond lengths are in nm, bond angles are in degree

The oxygen atom of methoxy group attack the carbon atom of CO, Through a transition state (TS), formation of the intermediate of IM1, carbon atoms of IM1 is close to the oxygen atoms in the $\text{CH}_3\text{O}\cdot$, they will react further, to formation of the intermediate of IM2, The bond of IM2's C-O will turn to release of energy to be more stable configuration of the product of $(\text{CH}_3\text{O})_2\text{CO}$.

Intrinsic reaction coordinate analysis of the reaction:

In order to verify the reaction mechanism, transition states were subjected to intrinsic reaction coordinate (IRC) calculations to confirm the connection between reactants and intermediates. The transition state link reactant and IM1.

The C of CO connects with the O of $\text{CH}_3\text{O}\cdot$ and the 7C-2O bond forms, the changes of the bond distances between atoms of 7C-2O with the IRC curve shown in Fig. 2. From the bond length changes, it is concluded that, the distance between the 7C and 2O reduced sharply. After the transition state structure, the curtate trend of the distance between 7C-2O become slowing down and the 7O-6H bond forms. In this process, the distance between the bond of 1C-2O and 6O-7C slightly increases.

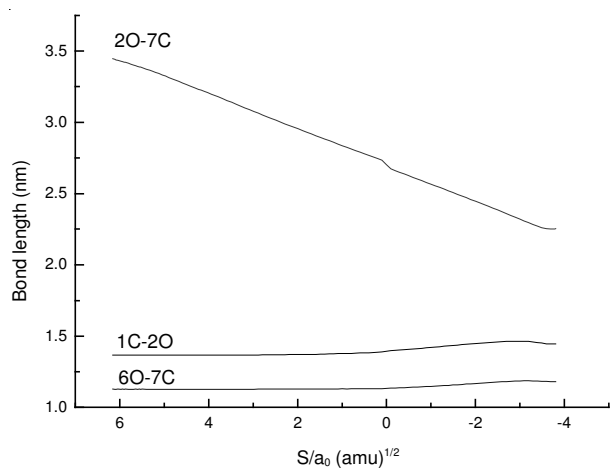


Fig. 2. Curves of bond length along reaction path $\text{CH}_3\text{O}\cdot + \text{CO} \rightarrow \text{TS} \rightarrow \text{IM1}$

Profile of potential energy: The potential energy of the reactants, transition states, intermediates and products are calculated at the B3LYP/6-311+G(d) 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 results⁷⁻⁹ 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(d) basis sets.

TABLE-1
ENERGIES FOR STATIONARY
POINTS ON THE IRC PATHWAYS

Species	E_{tot}^a (a.u.)	ΔE (KJ mol ⁻¹)
$\text{CH}_3\text{O}\cdot + \text{CO}$	-228.396034	0.0
TS	-228.388241	20.461669
IM1	-228.419374	-61.282608
$\text{IM1} + \text{CH}_3\text{O}\cdot$	-343.471398	0.0
IM2	-343.609513	-362.641275
$(\text{CH}_3\text{O})_2\text{CO}$	-343.614068	-374.601098

The potential energy curves of the reactions are given in Fig. 3. Energy change of reaction shows that, during the step of reactants $\rightarrow \text{TS} \rightarrow \text{IM1}$, reactants to the transition state only needs to overcome the energy barrier of 20.461669 KJ mol⁻¹, the step of $\text{IM1} + \text{CO} \rightarrow \text{IM2}$ is an exothermic process, it would release energy of 362.641275 KJ mol⁻¹; $\text{IM2} \rightarrow \text{product}$ is an exothermic process too, it would release energy of 11.959823 KJ mol⁻¹; so it can be judged by all the steps, the overall process of the reaction of carbonylation of methoxy group to dimethyl carbonate 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 reactants $\rightarrow \text{TS}$. So it is concluded that the step of The C of CO connects with the O of $\text{CH}_3\text{O}\cdot$ to form the bond of 7C-2O, what is the key to restricting the reaction conditions

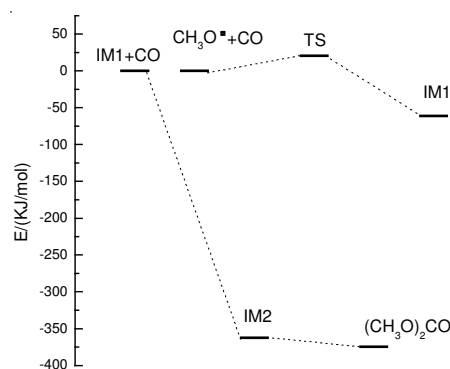


Fig. 3. Relative energies of the stationary points on the reaction path

Conclusion

It was discussed that the mechanism of carbonylation of methoxy group to dimethyl carbonate by the quantum chemistry and reaction channels were found. Compare with Ma's conclusions, who study the reaction by *in situ* infrared spectroscopy technology, our reaction pathway are more

specific. The C of CO connects with the O of CH₃O· to form the IM1, the O of the other one CH₃O· connects with the C of IM1 to form the dimethyl carbonate. The energy barrier of the reaction is lower to overcome, the overall process of the reaction is an exothermic process, what is an easy process. The only endothermic step is reactants → TS. So, we concluded that the step of the C of CO connects with the O of CH₃O· to form the bond of 7C-2O, what is the key to restricting the reaction conditions, which is useful for the experiment of carbonylation of methoxy group to dimethyl carbonate.

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