

# Mechanism of hexaalkylguanidinium salt/zinc bromide binary catalysts for the fixation of CO<sub>2</sub> with epoxide: A DFT investigation



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## ABSTRACT

Numerous binary catalysts of IL/Lewis acid have been developed for the coupling reaction of carbon dioxide and epoxides to form cyclic carbonates with high catalytic activity under benign environment. However, the mechanism is still obscure for most of catalysts. The catalytic mechanism of the binary catalysts hexaalkylguanidinium bromide/ZnBr<sub>2</sub> is elucidated by theoretical method in this work to obtain the reason of their high catalytic activity. Owing to the complicated of the binary catalysts, there are lots of possible attack forms. Finally, it is confirmed that the electrophilic attack from the Zn complex and the nucleophilic attack from the Br<sup>-</sup> anion are the essential factors to promote the ring opening of PO. Following the most favorable route, the catalytic activity of different binary catalysts, including the ILs/ZnBr<sub>2</sub> and NBu<sub>4</sub>Br/Zn(salphen), is compared. Moreover, the influence of the bulk of hexaalkylguanidinium salt on the catalytic activity is studied. The catalytic activity is enhanced with the increased bulk of the hexaalkylguanidinium salt. It is expected that our theoretical study would provide valuable clues to further refine the binary catalysts.

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## 1. Introduction

Ionic liquids (ILs) are composed entirely of cations and anions, which have received considerable interests due to their favorable features, such as, a negligible vapor pressure, a high thermal stability, and a good solvent for a variety of materials [1]. In the early research, ILs were generally applied as solvent for catalytic reactions [2], electrolytes for Li-ion batteries [3,4] and dye-sensitized solar cells [5], engineering fluids [6], and solvents for liquid-liquid extraction processes [7,8]. Currently, ILs are found to show excellent catalytic activity for many important reactions, such as Michael addition [9,10], Beckmann rearrangement [11,12], Henry reaction [13,14], Friedel–Crafts acylation [15,16], and the fixation of carbon dioxide (CO<sub>2</sub>). The latter reaction has become the focus in recent literature [17,18].

It is well known that CO<sub>2</sub> is a main greenhouse gas, which has resulted in global warming effects and serious environmental problems. On the other hand, it is also a cheap, nontoxic, and abundant C1 building block. The synthesis of five-membered cyclic

carbonates via the cycloaddition of CO<sub>2</sub> to epoxides (PO) is regarded as one of the most promising methodologies for the fixation of CO<sub>2</sub> [19–24]. The absence of the efficient catalysts has become the roadblocks in the way of utilization of CO<sub>2</sub>. Although some catalysts have been explored, such as, alkali metal salts [25,26], metal oxides [27,28], transition-metal complexes [29,30], ILs [31–33], and others [34,35], they are still suffer from the low activity, harsh reaction conditions, the need of organic co-solvents, or a combination of these. Recently, ILs have attracted considerable attentions because of their unique properties especially due to their environmental benign and feasibility for design. The involvement of the Lewis acids, such as, ZnBr<sub>2</sub>, would dramatically enhance the catalytic activity. Moreover, it also offers the advantages of recyclability and reusability. Due to the great interest in this topic, the catalytic activity of some binary catalytic systems have been explored in experiments, including 1-butyl-3-methylimidazolium bromide ([BMIM]Br) and ZnBr<sub>2</sub> [36], choline chloride (CH) and ZnBr<sub>2</sub> [37], and hexaalkylguanidinium bromide and ZnBr<sub>2</sub> [36]. In addition to the experimental studies, the detailed mechanism of the fixation of CO<sub>2</sub> catalyzed by [BMIM]Cl/ZnCl<sub>2</sub> and CH/ZnBr<sub>2</sub> has also been studied theoretically, which is different from the proposed mechanism on the basis of the experimental result [38,39]. Thus, the theoretical investigation is desirable to obtain the reliable and accurate mechanism.

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To our best knowledge, no theoretical study has been performed on the detailed mechanism of the coupling reaction of CO<sub>2</sub> with PO catalyzed by the binary catalysts hexaalkylguanidinium bromide/ZnBr<sub>2</sub>, which is explored by the DFT method in this contribution. Furthermore, the catalytic activity of different binary catalysts with other ionic liquid cations, bulkier cations, or other Lewis acid is also theoretically determined. Our general goals are (1) to elucidate the catalyzed mechanism of bicomponent catalysts hexaalkylguanidinium bromide/ZnBr<sub>2</sub>; (2) to compare the catalytic activity of the bicomponent catalysts diethyl-tetramethylguanidinium bromide/ZnBr<sub>2</sub>, [BMIM]Br/ZnBr<sub>2</sub>, NBu<sub>4</sub>Br/ZnBr<sub>2</sub>, and PyBuBr/ZnBr<sub>2</sub>; (3) to identify the effect of the bulk of the guanidinium salt; and (4) to compare the catalytic activity of the hexabutylguanidinium bromide/ZnBr<sub>2</sub>, NBu<sub>4</sub>Br/ZnBr<sub>2</sub>, and NBu<sub>4</sub>Br/Zn (salphen).

## 2. Computational details

The equilibrium geometries of all the stationary points including reactants, products, intermediates, and transition states, were optimized by the M06 [40] function with the 6-31+G(d,p) basis set. At the same level, the vibrational frequencies were calculated at the same level to characterize the nature of the stationary point and to make the zero-point energy (ZPE) correction. The minimum corresponds to all positive frequencies and the transition state corresponds to only one imaginary frequency. On the basis of the optimized geometries, the energy is refined at the M06/6-311+G(d,p) level using a self-consistent reaction field (SCRF) method in the polarized continuum model (PCM) [41,42]. To confirm the accuracy of the transition states, the minimum-energy path (MEP) was constructed by intrinsic reaction coordinate (IRC) theory to determine that two desired minima were connected [43]. All electronic calculations were performed by the Gaussian 09 program [44].

## 3. Results and discussion

### 3.1. ZnBr<sub>2</sub> catalyst or diethyl-tetramethylguanidinium bromide catalyst

To prove the high catalytic activity of binary catalysts, the coupling reaction of CO<sub>2</sub> with PO with/without single catalyst ZnBr<sub>2</sub> or diethyl-tetramethylguanidinium bromide is firstly investigated, respectively. According to the identified results in literature [39], the preferential route in the absence/presence of ZnBr<sub>2</sub> is calculated at the M06/6-311+G(d,p) (PCM)//M06/6-31+G(d,p) level. The corresponding results are plotted in Fig. S1 and S2 of the supporting information. In previous literature [45,46], the mechanism of the fixation of CO<sub>2</sub> catalyzed by IL has been thoroughly elucidated. The three-step mechanism is more favorable than two-step mechanism. Therefore, only former mechanism is considered. In addition, the energy profile of the most favorable route catalyzed by single catalyst diethyl-tetramethylguanidinium bromide is also shown in Fig. S1. The concerted, two-step, and three-step mechanisms correspond to the uncatalyzed reaction, the reaction catalyzed by ZnBr<sub>2</sub>, and the reaction catalyzed by diethyl-tetramethylguanidinium bromide with the rate-determining barrier heights of 46.85, 49.08, and 23.67 kcal/mol, respectively. The barrier heights are dramatically decreased in presence of the diethyl-tetramethylguanidinium bromide. As expected, the catalytic activity of binary catalysts should be higher than the single catalyst. In the following section, the mechanism and rate-determining barrier height catalyzed by diethyl-tetramethylguanidinium bromide/ZnBr<sub>2</sub> are determined.

### 3.2. Diethyl-tetramethylguanidinium bromide/ZnBr<sub>2</sub> catalysts

Four possible routes catalyzed by the diethyl-tetramethylguanidinium bromide/ZnBr<sub>2</sub> catalysts are considered in the following sections. To present their difference more clearly, the proposed mechanism of the four routes is shown in Scheme S1.

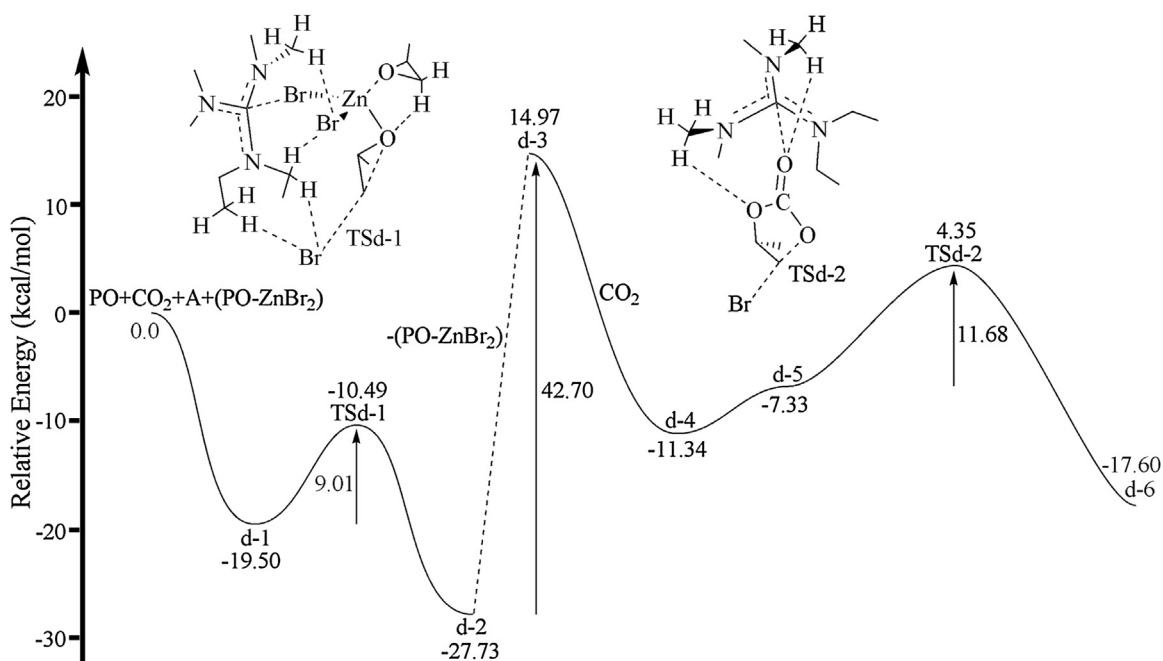


Fig. 1. Potential energy profile of route 1 for the coupling reaction of CO<sub>2</sub> with PO catalyzed by diethyl-tetramethylguanidinium bromide/ZnBr<sub>2</sub> catalysts.

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