

Insights into the Chalcogen Bonding Catalysis on the CO₂ Fixation with Styrene Oxide

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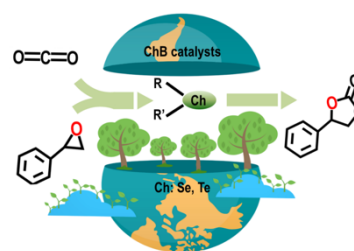
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Abstract: The fixation of CO₂ is a promising carbon-neutral approach and drawing lots of attention in the past decades. Among lots of fixation of CO₂ methods, the cycloaddition of CO₂ into epoxides (CCE) reaction is important because it could generate high value-added products. Recently, employing chalcogen bonding (ChB) catalysts for the CCE reaction has been proposed and offers significant advantages of low price, environmental friendliness, and ease of recycling. In this work, the ChB catalyzed the CCE reaction is investigated by high level theoretical calculations. The reaction can be divided into three sub-processes: ring-opening, nucleophilic addition, and formation of cyclic carbonate. Both Se- and Te-based ChB catalysts have shown the potential for catalyzing the CCE reaction, the overall catalytic performance of Te-based catalysts was superior to the Se-based ones. Overall, the most positive electrostatic potentials of the ChB catalysts, electrostatic term of the ChB binding energies, electron density at the ChB critical points, and electron density difference play important roles in the ChB catalyzed CCE reaction. This work elucidated the ChB catalyzed mechanism of the CCE reaction and provided theoretical guidance for the future development of efficient ChB catalysts for the CCE reaction.



Key words: chalcogen bonding catalysis, CO₂ fixation, density functional theory, QTAIM.

1. Introduction

Non-covalent interactions, such as halogen bonding (XB) [1-3], and chalcogen bonding (ChB) [4-5], have garnered increasing attention in organocatalysis due to their advantages, including non-toxicity, environmental friendliness, broad applicability, low cost, and high reactivity. ChB is defined as the interaction between chalcogen atoms (O, S, Se, or Te) and Lewis bases (LB) [6-7]. Compared to halogen elements, chalcogen elements have stronger positive electrostatic potential regions, characterized by enhanced σ -hole [8] interactions and a greater variety of

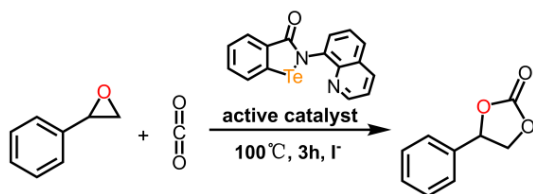
interaction sites, leading to better catalytic effects. Notably, ChB catalysis as a new catalytic strategy is a more efficient organocatalytic strategy. Matile's group first reported the application of ChB catalysis [9], which has since been applied to a range of reactions, including the Michael addition reaction [10], bromination reaction [11], and Diels-Alder reaction [12], demonstrating excellent catalytic performance. The development of efficient catalysts and the exploration of a broader range of reactions are important in chalcogen bond catalysis.

The fixation of CO₂ into economically high value-added products is one of the most important approaches to achieving

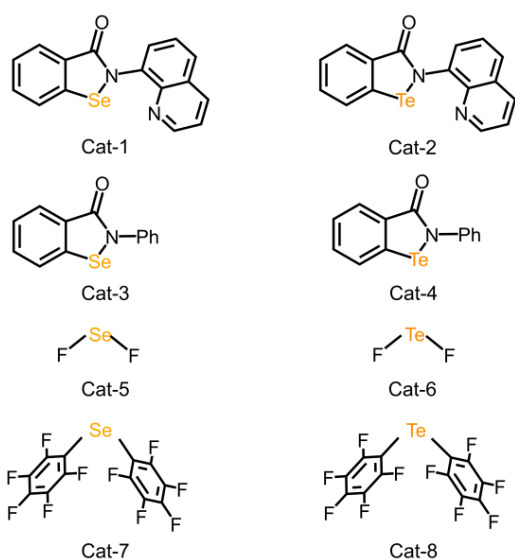
the goal of carbon neutrality [13-15]. Particularly, cyclic carbonate, which is generated by the cycloaddition of CO₂ into epoxides (CCE) reaction, is one of the most important products of the fixation of CO₂ because of their utility in the field of lithium-ion batteries, non-native polar solvents, and fuel additives, etc [16-19]. Moreover, the CCE reaction is capable of achieving 100% atom economy [20, 21], which is in line with the core concept of green chemistry [22-24]. Therefore, exploring a green, eco-friendly, and efficient catalytic method is of great significance. Recently, Kumar and colleagues have reported lots of newly synthesized Te-based catalysts, and a Te-I bond is observed in tellurenyl iodides. However, the prepared tellurenyl iodides could be transformed into another class of organotellurium molecules, namely, ebtellur, owing to the labile nature of the Te-I bond. The Te-N heterocycle ebtellur is identified as an active catalyst in the reaction of CO₂ with epoxides to afford cyclic carbonates (Scheme 1a) [25], the N-Te...O chalcogen bond efficiently catalyzes the reaction, while I⁻ primarily assists in the ring-opening step. However, the mechanistic details of the CCE reaction remain unraveled.

In this work, inspired by the work of Kumar et al., eight ChB donors as catalysts (Scheme 1b) are employed to catalyze the cycloaddition reaction of CO₂ with styrene oxide. Cat-1, Cat-3, Cat-5, and Cat-7 (the Se-based catalysts) were categorized into one category, whereas Cat-2, Cat-4, Cat-6, and Cat-8 (the Te-based catalysts) were categorized into a separate category. We aim to investigate the mechanism of CO₂ fixation with styrene oxide catalyzed by ChB catalysis, to compare the Se-based and Te-based ChB catalysis, and to explore the designing strategy of the ChB catalysts.

a. The reaction of CO₂ with styrene oxide



b. Chalcogen bonding catalysts in this work



Scheme 1. The chalcogen bonding catalysis on the reaction of CO₂ with styrene oxide.

2. Theoretical method

In this work, the M06-2X-D3/def2-TZVP level of theory was employed for all geometry optimization and electronic structure analysis [26-29]. All geometries, including reactants, catalysts, intermediates, transition states, and products, were optimized using the Gaussian 16 program package [30]. The Conformer-Rotamer Ensemble Sampling Tool (CREST) [31-33] was used for determining the lowest-energy conformers. The low-energy geometries from CREST processes were further optimized with Gaussian 16 to finally determine the lowest-energy conformers. The implicit solvation model is used during all DFT calculations. Styrene oxide solvent was used as the solvent within the IEFPCM solvation model to account for solvent effects [34]. The dielectric constant (ϵ) of styrene oxide was estimated using the Clausius-Mossotti equation and given as 2.336 [35-36]. Frequency calculations were performed at the same theoretical level to validate the optimized geometries: reactants, catalysts, intermediates, and products exhibited no imaginary frequencies, while transition states displayed only one imaginary frequency. Additionally, intrinsic reaction coordinate (IRC) calculations were conducted to confirm the connectivity of transition states with their corresponding reactants and products [37]. All Gibbs free energies, including translational entropy corrections for the solution phase, were calculated using the THERMO program [38]. The electrostatic potentials (ESPs) [39] of reactants and catalysts were calculated at 0.001 a.u. electron density isosurface. ESP, natural locational molecular orbital (NLMO) [40], and molecular formation density difference (MFDD) analyses [41-43] were performed using the Multiwfn-3.8 [44] and visualized with VMD-1.9.4 [45]. Molecular structures were rendered using CYLview 20 [46]. To quantitatively evaluate the contributions of different factors to the catalytic performance of the ChB catalysts, GKS-EDA was employed to compute intermolecular interaction energies using the modified GAMESS (2020 R2) package at the M06-2X/def2-TZVP level [47-49]. Additionally, topological analysis of electron density at bond critical points (BCPs) was performed using the AIMALL software based on the quantum theory of atoms in molecules (QTAIM) [50-52].

3. Results and discussion

3.1 Electrostatic potential analysis

Electrostatic potential (ESP) analysis has been demonstrated to be an effective method for analyzing and predicting the reactive sites for elucidating the mechanism of weak-interaction catalyzed reactions [53-54]. Therefore, the electrostatic potentials of styrene oxide and eight ChB catalysts were analyzed in this work (Figure 1). For styrene oxide, which will act as a ChB acceptor, the most negative ESP ($V_{s, \min}$) is located on the area of the O atom in the three-membered ring. On the other hand, for the eight ChB catalysts, the most positive ESP ($V_{s, \max}$) is found along the axes of the covalent bond chalcogen atom (i.e. Se/Te atom), corresponding to the “ σ -hole” region. It can be predicted that the Te/Se atom in ChB catalysts can interact with the O atom in styrene oxide to form ChB. The following discussion will show that these ChB play important roles in the CCE reaction.