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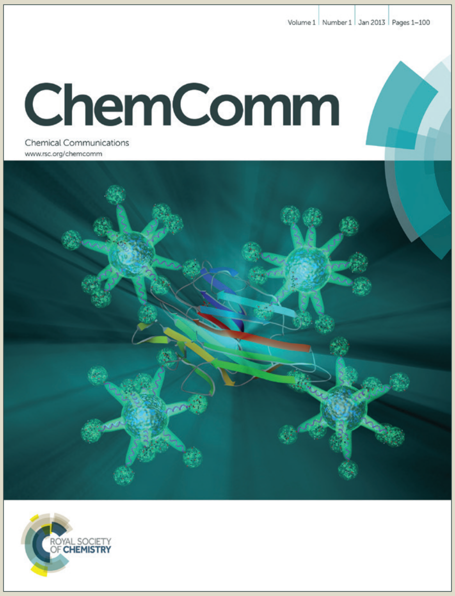

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ARTICLE TYPE

Computational Study of the Mechanism of the [(Salen)Cr + DMAP]-Catalyzed Formation of Cyclic Carbonates from CO_2 to Epoxide

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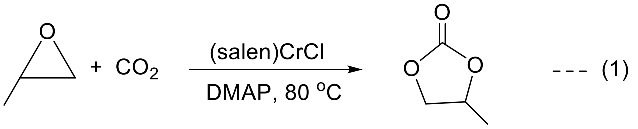
Epoxide and CO_2 coupling reaction catalyzed by (salen)Cr^{III}Cl has been modeled computationally to contrast a monometallic vs. bimetallic mechanism. A low-energy CO_2 insertion step into the metal-alkoxide bond has also been located.

Utilizing carbon dioxide as a feed stock chemical to prepare useful products in an efficient manner is attractive in part because it may provide a sustainable solution for recycling CO_2 from the environment.[1-5] To this end, the last two decades have witnessed a resurgence of interests in CO_2 utilization chemistry, with many catalyst systems reported for the conversion of CO_2 to feedstock chemicals such as cyclic carbonates,[6] which have many uses: as pharmaceutical and fine chemical intermediates, as monomers for the production of polycarbonates, and as aprotic polar solvents. In particlular, several salen-based complexes of Cr, Mn, Co Al, Zn have been found to be remarkably efficient in this conversion,[6] with (salen)Cr(III) catalyst being quite selective and efficient in the presence of a (4-dimethylamino)pyridine (DMAP cocatalyst (Eq. 1).[7] The reaction proceed under mild conditions and have a scope that broadly spans over many terminal epoxides. The presence of DMAP cocatalyst is critically important, as the reaction does not occur in its absence and the catalyst activity is reduced when weaker Lewis bases are used as cocatalysts.[8]



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The mechanism of the asymetric ring opening of meso epoxides with trimethylsilyl azides catalyzed by (salen)Cr complexes has been extensively studied by Jacobsen and coworkers.[9] A second-order dependence on catalyst concentration was found, leading to the proposal that the epoxide and azide reactants are activated by two different catalyst molecules simulataneously.[10] Based on these reports, we initially suggested that a similar bimetallic mechanism may be operating in our [(salen)Cr + DMAP]-catalyzed cyclic carbonate formation (eq 1) where one metal center activates the epoxide for attack by a nucleophilic CO_2 that has been activated separately by a second, DMAP-coordinated metal center.[7] Subsequently, others have also proposed analogous bimetallic mechanisms for the (salen)Cr-catalyzed copolymerization of propylene oxide (PO) with CO_2[11, 12] and for the (salen)Al-catalyzed ring-opening polymerization of epoxides.[13] Interestingly, in the [epoxide + CO_2] copolymerization, mechanistic studies have suggested that in the absence of a Lewis base (LB) cocatalyst such as DMAP, only a single (salen)Cr center is involved in the propogation step.[14] Similar monometallic mechanistic arguments were also suggested in other studies employing (salen)Cr and Co catalysts where the metal center activates the epoxide for attack by an external LB coctalyst.[15-18] In view of these reports, we decided to carry out a series of quantum chemical simulations to fully elucidate the mechanism for the [(salen)Cr + DMAP]-catalyzed cyclic carbonate formation. As reported herein, our study suggests that the observed reactivity for this system can indeed be explained through a bimolecular pathway where a Lewis-acid-activated epoxide is ring-opened by an external DMAP cocatalyst before ring-closing to the cyclic carbonate regenerates the two catalyst components (Figure 1) .

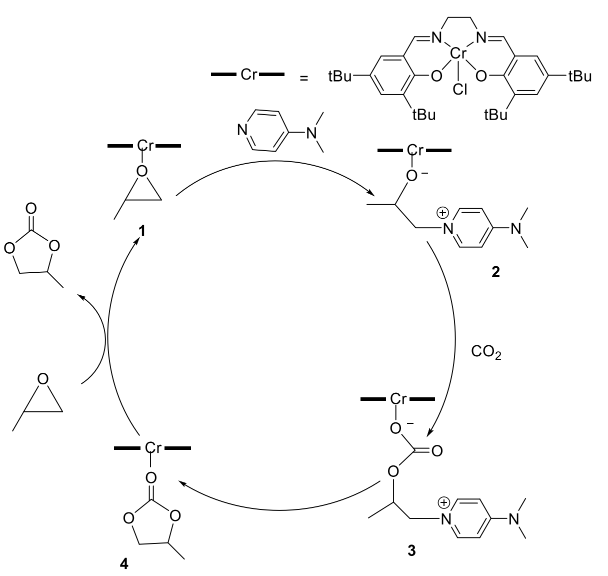

Figure 1. Mechanistic sheme for cyclic carbonate formation from epoxide and CO_2 in presence of a cocatalyst.

Figures 1 and 2 summarize our computational investigations of reaction 1, incorporating all of our previous experimental observations and extensive computational modeling. The catalytic cycle starts with the epoxide substrate binding to the Cr(III)-center of the catalyst to afford the reactant complex **1**, in which the C–O bond of the epoxide becomes slightly elongated by 0.02 Å compared to the free substrate. This process is slightly uphill with a solution phase binding free energy of 4.7 kcal/mol. Next, the sterically less hindered carbon of the epoxide is attacked by the basic cocatalyst DMAP in a nucleophilic fashion to give the ring-opened intermediate **2** at a relative energy of 11.3 kcal/mol traversing the transition state **1-TS**. The barrier for this first step is 27.8 kcal/mol. As will be detailed below, this sequence of epoxide opening differs notably from that of a bimetallic mechanism proposed by Jacobsen, which assumed concurrent activation of epoxide and cocatalyst by two different Cr-complexes.[9]

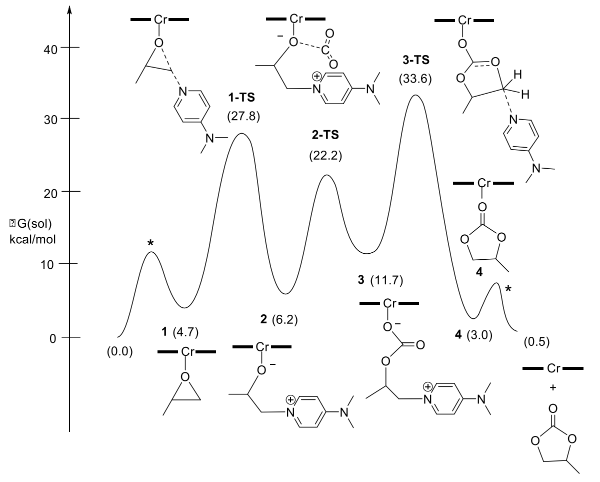

Figure 2. Reaction profile for cyclic carbonate formation from CO_2 and epoxide. The transition state marked * was not located and is shown for illustrative purposes only. Free energy values have been corrected for excess concentration of substartes. For enthalpy results please see section S4, page S2 in SI)

Considering the bimetallic mechanism we tried to ring open the activated epoxide with another molecule of (salen)Cr(III)Cl acting as a nucleophile. This attempt failed and we were unable to obtain reasonable molecular structures in our geomertry optimizations despite significant efforts (see Supporting Inoformation for details). Although tandem activation of both nucleophile and electrophile was considered previously[19] in few cases of epoxide and CO_2 copolymerization, our theoretical investigation suggests that activation of the nucleophile is not necessary as long as the epoxide substrate is activated by binding to the Lewis acidic Cr(III) center. In principle, binding of epoxide to the metal center can be competitively inhibited by coordination of the Lewis base cocatalyst but the equilibrium is mostly shifted towards the epoxide owing to its significantly higher concentration compared to DMAP (1500 equivalents to the cocatalyst). Computationally, a barrier of epoxide ring opening by DMAP was found to be 27.8 kcal mol^{-1} at a temperature of 80 ^{o}C. . Because this energetic requirement can be achieved under the reaction condition, we did not attempt to further optimize the trajectory of the incoming DMAP nucleophile and search for the lowest energy pathway. (Such optimization would require expensive MD calculations that is not necessary for the purpose of illustrating the overall mechanism.) Following the epoxide ring opening by the nucleophilic DMAP, CO_2 is inserted into the resulting Cr-alkoxide bond. The transition state for the intermolecular CO_2 insertion reaction was located at 22.2 kcal mol^{-1}. Salient features of the TS involves elongated Cr–O bond (from 1.96 Å in **2** to 2.12 Å) as well as bent CO_2 molecule (OCO angle is 146.7°) (Figure 3). Our calculations reveal that no prior activation of CO_2 by coordination to the Lewis acidic Cr(III) center is required. The lack of CO_2 coordination and subsequent activation is easy to understand given the coordinatively saturated nature of the Cr-center. As a result, the O–C and Cr–O bonds involving the CO_2 form synchronously (step **2**→**3**). Luinstra *et al.* proposed salen-ligand detachment to create a free coordination site before CO_2 insertion based on computational results.[20] Our Attempts toward creating unsaturation at Cr(III) center by either losing the chloride or detaching oxygen/nitrogen ligation of salen backbone resulted in significant energy penalties leading to the conclusion that such step is not possible in this case. CO_2 insertion in a coordinatively saturated metal center has been experimentally verified by Bergman and others.[21-23]

Previously, we speculated that a Cr(III)-DMAP complex may be involved and activate CO_2 by reduction and the resulting Cr-bound η^1-carbonate species may be attacked by the epoxide ring at the less sterically hindered position.[7] Our calculations suggest that the Cr-bound carbonate species is very high in energy. The considerably higher energy penalty in reducing CO_2 can be understood considering the difficulty involved in two electron oxidation of the Cr(III)-center. Overall, the nucleophilic chromium bound carbonato species is not predicted to form under the experimental condition.

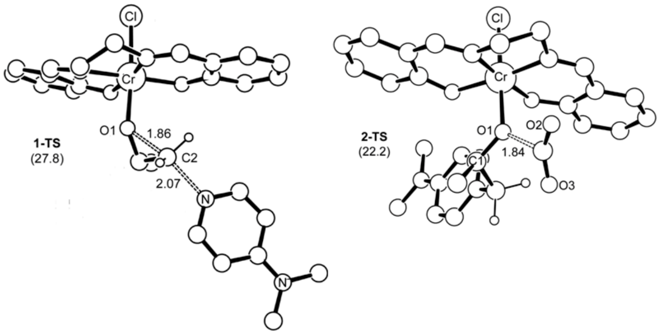

Figure 3. Calculated structures of transition states **1-TS** and **2-TS**. Hydrogens are ommited for clarity except for those bound to C2.

The CO_2 inserted intermediate **3** exposes two nucleophilic sites, one at the alkoxide oxygen bound to metal center labeled O1 in Figure 4 and the other at the carbonyl oxygen

O3, which can both engage in nucleophilic attack at the carbon atom of the cocatalyst moiety. The electronic energy barrier for alkoxide attack is 25.8 kcal mol^{-1} (**3→4**) compared to 31.7 kcal mol^{-1} for carbonyl mediated attack (see SI, Figure S1). We surmise that the carbonyl oxygen requires significant rearrangement and rehybridization, as the oxygen lone pair points into a wrong direction making this process less facile compared to the alkoxide attack where no such electronic rearrangement is necessary. Further analysis of the solution phase free energy surface reveals that the nucleophilc attack performed by the carbonyl group is energetically favored by 4 kcal mol^{-1} over the alternative path where alkoxide acts as the nucleophile. The transition state for cyclic carbonate formation, **3-TS**, displays features of a classical S_N2 type transition state with an almost linear arrangement of the O–C–N bond vector as illustrated in Figure 4. The carbon atom adopts a trigonal bipyramidal structure, as expected for a S_N2 transition state. The computed barrier for forming the five membered cyclic carbonate is 33.6 kcal mol^{-1}, slightly higher than what may be expected for a reaction that completes at 80 ^{o}C. Overall, the reaction is thermoneutral with a free energy of the reaction of only 0.5 kcal mol^{-1}. Whereas formation of the cyclic carbonate is electronically favored by 13.9 kcal mol^{-1}, it is fully compensated by entropy loss due to the trapping of a gaseous reagent $CO_{2.}$

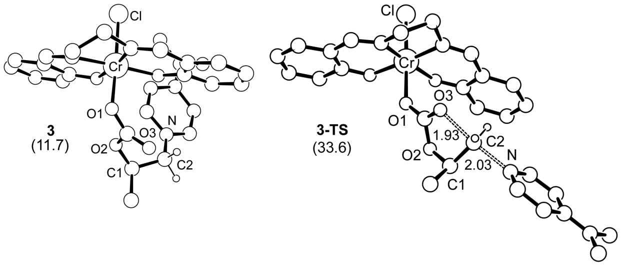

Figure 4. Calculated structures of the intermediate **3** and transition state **3-TS**. Hydrogens are ommited for clarity except for those bound to C2.

Conculsions

This computational work provides convincing evidence for the role of (salen)Cr^{III}Cl complex as a dedicated Lewis acid which promptly activates the epoxide ring promoting its opening by an external nucleophile. We did not find evidence for a bimetallic pathway or simultaneous activation of both the epoxide and basic cocatalyst for cyclic carbonate formation reaction, which had been speculated upon previously.

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Notes and references

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