

A computational study of the mechanism of the [(salen)Cr + DMAP]-catalyzed formation of cyclic carbonates from CO₂ and epoxide†

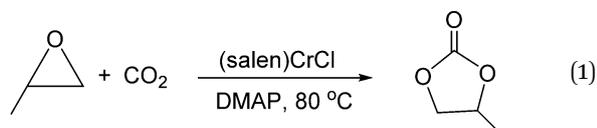
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Epoxide and CO₂ coupling reactions catalyzed by (salen)Cr^{III}Cl have been modeled computationally to contrast a monometallic vs. a bimetallic mechanism. A low-energy CO₂ insertion step into the metal–alkoxide bond was located.

Utilizing carbon dioxide as a feedstock chemical to prepare useful products in an efficient manner is attractive in part because it may provide a sustainable solution for recycling CO₂ from the environment.^{1–5} To this end, the last two decades have witnessed a resurgence of interests in CO₂ utilization chemistry, with many catalyst systems reported for the conversion of CO₂ 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 particular, several salen-based complexes of Cr, Mn, Co, Al, and Zn have been found to be remarkably efficient catalysts for this conversion,⁶ with (salen)Cr(III) being quite selective and efficient in the presence of a (4-dimethylamino)pyridine (DMAP) cocatalyst (eqn (1)).⁷ Reaction 1 proceeds under mild conditions and have a scope that broadly spans over many terminal epoxides. The presence of the 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



The mechanism of the asymmetric 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 simultaneously.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 (eqn (1)) where one metal center activates the epoxide for attack by a nucleophilic CO₂ 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 CO₂^{11,12} and for the (salen)Al-catalyzed ring-opening polymerization of epoxides.¹³ Interestingly, in the [epoxide + CO₂] 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 propagation 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 cocatalyst.^{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 (Fig. 1).

Fig. 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^{–1}. 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

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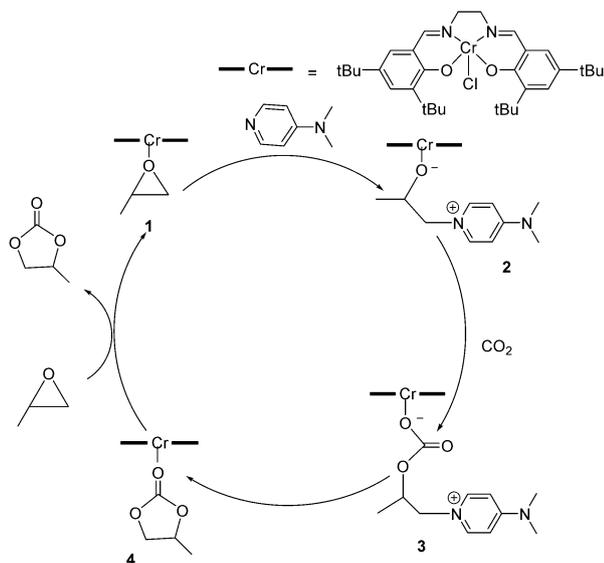


Fig. 1 Proposed mechanistic scheme for cyclic carbonate formation from epoxide and CO₂ in the presence of a cocatalyst.

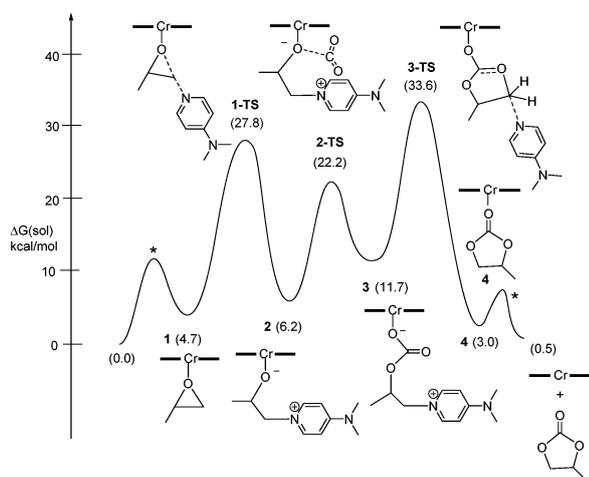


Fig. 2 Reaction profile for cyclic carbonate formation from CO₂ and epoxide. The transition state marked * was not located and is shown for illustrative purposes only. Free energy values have been corrected for excess concentration of substrates. For enthalpy results please see Section S4, page S2, in the ESI.†

intermediate **2** at a relative energy of 6.2 kcal mol⁻¹ traversing the transition state **1-TS**. The energy barrier for this first step is 27.8 kcal mol⁻¹. As will be detailed below, this sequence of epoxide opening differs notably from the bimetallic mechanism proposed by Jacobsen *et al.*, which assumed concurrent activation of the epoxide and the nucleophile by two different Cr-complexes.⁹

In consideration of the Jacobsen bimetallic mechanism, we examined the ring-opening of the activated epoxide with another molecule of (salen)Cr(III)Cl, which acts as a nucleophile. This attempt failed and we were unable to obtain reasonable molecular structures in our geometry optimizations despite significant efforts (see ESI† for details). Although tandem activation of both nucleophile

and electrophile was considered previously in a few cases of epoxide and CO₂ copolymerization,¹⁹ 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, this latter process can be competitively inhibited by coordination of the Lewis-basic 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, the energy barrier for the epoxide ring-opening by DMAP was found to be 27.8 kcal mol⁻¹ at a temperature of 80 °C. Because this energetic requirement can be achieved under the reaction conditions, 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 are not necessary for the purpose of illustrating the overall mechanism.)

Following the epoxide ring-opening by the nucleophilic DMAP, CO₂ is inserted into the resulting Cr-alkoxide bond. The transition state for the intermolecular CO₂ insertion reaction was located at 22.2 kcal mol⁻¹. Salient features of this TS include an elongated Cr–O bond (from 1.96 Å in **2** to 2.12 Å) as well as a bent CO₂ molecule (OCO angle is 146.7°) (Fig. 3). Our calculations reveal that no prior activation of CO₂ by coordination to the Lewis acidic Cr(III) center is required. The lack of CO₂ coordination and subsequent activation is easy to understand given the coordinatively saturated nature of the Cr-center. As a result, the new O–C and Cr–O bonds (from CO₂ insertion) form synchronously (**2** → **3**). Luinstra *et al.* proposed salen-ligand detachment to create a free coordination site before CO₂ insertion based on computational results.²⁰ However, our attempts toward creating unsaturation at the Cr(III) center – by either loss of the chloride or detachment of oxygen/nitrogen ligation of the salen backbone – resulted in significant energy penalties, leading to the conclusion that such a step is not possible in this case. We note that CO₂ insertion into 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 play an important role in reaction 1, activating CO₂ by reduction; the resulting Cr-bound η¹-carbonate species may then be attacked by the epoxide ring at the less sterically less-hindered position.⁷

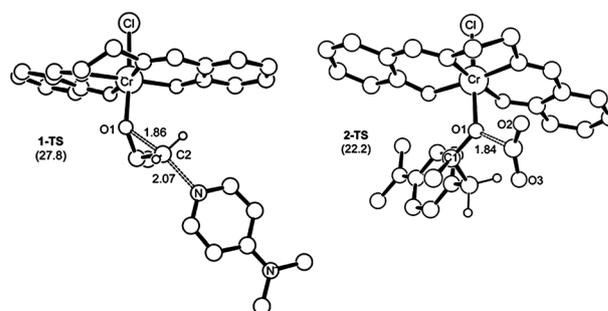


Fig. 3 Calculated structures of transition states **1-TS** and **2-TS**. Hydrogens are omitted for clarity except for those bound to C2.

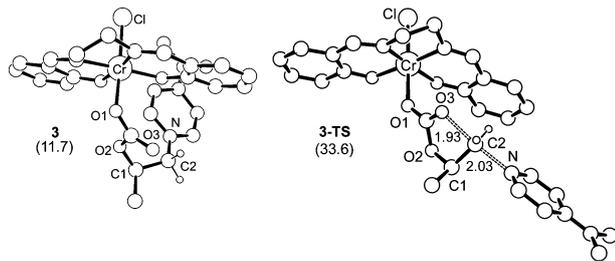


Fig. 4 Calculated structures of the intermediate **3** and transition state **3-TS**. Hydrogens are omitted for clarity except for those bound to C2.

Our calculations suggest that the Cr-bound carbonate species is very high in energy. The considerably higher energy penalty in reducing CO₂ can be understood considering the difficulty involved in effecting a two-electron oxidation of the Cr(III)-center. Overall, the nucleophilic chromium-bound carbonate species is not predicted to form under the experimental conditions.

The CO₂-inserted intermediate **3** exposes two nucleophilic sites, one at the alkoxide oxygen bound to metal center (labeled O1 in Fig. 4) and the other at the carbonyl oxygen (labeled O3 in Fig. 4), both of which can engage in nucleophilic attack at the carbon atom bound to the cocatalyst moiety (**3** → **4**). The electronic energy barrier for the alkoxide attack is 25.8 kcal mol⁻¹, smaller than the 31.7 kcal mol⁻¹ barrier for the carbonyl-mediated attack (see ESI,† Fig. S1). We surmise that the latter process would require significant rearrangement and rehybridization of the carbonyl oxygen, 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 nucleophilic 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 Fig. 4. The carbon atom adopts a trigonal bipyramidal structure, as expected for a S_N2 transition state. The computed energy barrier for formation of 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 °C. Overall, the reaction is thermoneutral with a free energy of 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 CO₂.

In summary, this computational work provides convincing evidence for the role of the (salen)Cr^{III}Cl complex in reaction 1 as a dedicated Lewis acid that 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 CO₂, as have been previously speculated.

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Notes and references

- M. Mikkelsen, M. Jorgensen and F. C. Krebs, *Energy Environ. Sci.*, 2010, **3**, 43–81.
- E. E. Benson, C. P. Kubiak, A. J. Sathrum and J. M. Smieja, *Chem. Soc. Rev.*, 2009, **38**, 89–99.
- D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388–2410.
- D. J. Darensbourg, *Inorg. Chem.*, 2010, **49**, 10765–10780.
- D. J. Darensbourg and S. J. Wilson, *Green Chem.*, 2012, **14**, 2665–2671.
- A. Decortes, A. M. Castilla and A. W. Kleij, *Angew. Chem., Int. Ed.*, 2010, **49**, 9822–9837.
- R. L. Paddock and S. T. Nguyen, *J. Am. Chem. Soc.*, 2001, **123**, 11498–11499.
- R. L. Paddock, PhD thesis in Chemistry, Northwestern University, 2004.
- R. G. Konsler, J. Karl and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1998, **120**, 10780–10781.
- K. B. Hansen, J. L. Leighton and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1996, **118**, 10924–10925.
- K. Nakano, S. Hashimoto and K. Nozaki, *Chem. Sci.*, 2010, **1**, 369–373.
- E. N. Jacobsen, *Acc. Chem. Res.*, 2000, **33**, 421–431.
- J. Meléndez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, 3323–3326.
- D. J. Darensbourg, J. C. Yarbrough, C. Ortiz and C. C. Fang, *J. Am. Chem. Soc.*, 2003, **125**, 7586–7591.
- X.-B. Lu, Y.-J. Zhang, K. Jin, L.-M. Luo and H. Wang, *J. Catal.*, 2004, **227**, 537–541.
- X.-B. Lu, Y.-J. Zhang, B. Liang, X. Li and H. Wang, *J. Mol. Catal. A: Chem.*, 2004, **210**, 31–34.
- X.-B. Lu, W.-M. Ren and G.-P. Wu, *Acc. Chem. Res.*, 2012, **45**, 1721–1735.
- G.-P. Wu, D. J. Darensbourg and X.-B. Lu, *J. Am. Chem. Soc.*, 2012, **134**, 17739–17745.
- D. J. Darensbourg and R. M. Mackiewicz, *J. Am. Chem. Soc.*, 2005, **127**, 14026–14038.
- G. A. Luinstra, G. R. Haas, F. Molnar, V. Bernhart, R. Eberhardt and B. Rieger, *Chem.–Eur. J.*, 2005, **11**, 6298–6314.
- R. D. Simpson and R. G. Bergman, *Angew. Chem., Int. Ed.*, 1992, **31**, 220–223.
- D. J. Darensbourg, B. L. Mueller, C. J. Bischoff and J. H. Reibenspies, *Inorg. Chem.*, 1990, **29**, 1789–1791.
- D. J. Darensbourg, M. W. Holtcamp, G. E. Struck, M. S. Zimmer, S. A. Niezgodá, P. Rainey, J. B. Robertson, J. D. Draper and J. H. Reibenspies, *J. Am. Chem. Soc.*, 1998, **121**, 107–116.