The Effect of Oxygen to Salen-Co Complexes for the Copolymerization of PO/CO₂

Ran-Long Duan, Yan-Chuan Zhou, Zhi-Qiang Sun, Yue-Zhou Huang, Xuan Pang, Yan-Chuan Zhou, Zhi-Qiang Sun, and Xue-Si Chen

Abstract
A series of Salen-Co(II) complexes were synthesized to study the effect of O₂ on the catalytic performance of Salen-Co complexes for the copolymerization of PO/CO₂. The Salen-Co(II) complexes showed low activity on the cyclo-addition of CO₂ to PO with the aid of a cocatalyst such as PPNCl. Unexpectedly, with the addition of O₂, the activity of Salen-Co(II) complexes was obviously increased and 100% cyclic carbonate was obtained. As the pressure of O₂ increased, the activity of the complex also increased. With the existence of O₂, the activity of the complexes was influenced by their structures and the pressure of O₂, and the complexes with the conjugated structure showed higher activity. The structures of cocatalyst also played a crucial role as for the change of the activity. By altering the electrophilicity of Salen-Co(III), O₂ can also be used as cocatalyst for the copolymerization of PO/CO₂.

Keywords
Salen-cobalt; Epoxides; Carbon dioxide; Copolymerization

INTRODUCTION
As a kind of greenhouse gas, CO₂ is considered as one of the prime reasons for the climate change and global warming. Reduction of the emissions and the concentration of CO₂ in the environment has become a globe issue that could affect the sustainable development of human society. Therefore, the application of CO₂ has received widespread attention. As a source of nontoxic, abundant, inexpensive, and sustainable C1 feedstock, CO₂ has been used in the chemical industry for the production of urea, carboxylic acids, methanol, cyclic carbonates, and polycarbonates. Cyclic carbonates can be prepared by cyclo-addition of CO₂ to epoxides and have been widely used as electrolytes for batteries, aprotic solvents, monomers for polymerizations, and intermediates of chemical syntheses while polycarbonates can be prepared by copolymerization of CO₂ with epoxides and show potential applications as packaging materials, coatings, adhesives, and in many other fields. Due to the high stability and low reactivity of CO₂, a large number of catalytic systems such as organocatalysts and metal-based catalysts such as K, Mg, Ca, Fe, Cr, Zn, Al, and rare earth metals have been explored to couple epoxides with CO₂ in the past decades.

In previous researches, North and coworkers reported a series of uncomplexed salophen ligands that could activate the reaction as Brønsted acid catalysts and exhibited activity in the cyclo-addition of CO₂ to epoxides. Repo and coworkers also proposed. Unexpectedly, Salen-Co(II) complexes composed of Salen ligands and Co(II) salts showed lower activity in the cyclo-addition reaction of CO₂ to epoxides while the Salen-Co(III) complex systems showed better performance in the copolymerization of epoxides and CO₂ to produce polycarbonates. There were still many complexes showing activity and specific selectivity of cyclic carbonate in the cyclo-addition reaction. The simultaneous formation of cyclic carbonates and polycarbonates in the coupling of epoxides and CO₂ would cause difficulties in product separation. Therefore, it is necessary to develop catalyst systems with high activity and specific selectivity for the copolymerization of epoxides and CO₂.

Lu and coworkers reported the mechanism of valence change of Salen-Co(III), which indicated that Salen-Co(III) complexes might undergo redox reaction under the combined action of epoxides and water to achieve the conver-
The synthesis of all complexes was carried out by the method reported in our previous article. [59] PO was purified by distillation after refluxing with CaH₂ for three days under nitrogen atmosphere. The 25 mL steel autoclaves were used as the vessel in all copolymerization. The autoclaves were dried by heating to 120 °C for 24 h, and then cooled to ambient temperature prior to use under dry nitrogen atmosphere. In a typical copolymerization procedure, complexes, co-catalyst, and epoxides in designed ratio were added into an autoclave with a magnetic bar. O₂ and CO₂ were introduced into the autoclave before sealing and then heated to the designed temperature. After the ordered copolymerization time, the autoclave was cooled to ambient temperature and the pressure of autoclaves was reduced slowly and a small amount of the crude product was taken out to produce cyclic carbonate with very low activity (Table 1, entries 1, 14, and Figs. S1 and S2 in the electronic supplementary information, ESI). Using bis(triphenylphosphine) iminium chloride (PPNCl) as cocatalyst, complex 1 could catalyze the cyclo-addition of CO₂ to PO to produce cyclic carbonate with very low activity (Table 1, entries 3, 7, and 16, and Figs. S1 and S2 in ESI). As shown in Figs. 1 and 2, the addition of O₂ showed very interesting performance in the reaction. Due to the participation of O₂, the activity of complex 1 was more than 30 times higher (TOF from 10 h⁻¹ to 310 h⁻¹, Table 1, entries 3 and 5 and Fig. S1 in ESI) and that of complex 2 was more than 60 times higher on the cyclo-addition of CO₂ to PO by using complexes 1 and 2.

### RESULTS AND DISCUSSION

In general, most of organometallic catalysts are sensitive to water and oxygen and would lose activity under water or oxygen, while the operation to remove water and oxygen increases the difficulty in practical application. Among metal-based complexes, Salen-Co complexes have relatively high stability. A trace concentration of water could not retard their activity but even have a positive effect on the results of copolymerization, occasionally. [53,56] There have been a few researches about the effect of O₂ on the performance of Salen-Co(III) complex during the copolymerization of PO and CO₂. As described in the report of Wang and coworkers, O₂ worked as a trigger in the ternary copolymerization of epoxide, CO₂, and vinyl monomer. The CO₂-based block copolymers had been synthesized by a one-pot procedure. [57] This result indicated that the Salen-Co(III) complex could maintain activity for copolymerization of PO and CO₂ in the presence of O₂. Herein, the effect of O₂ on the performance of Salen-Co complexes in copolymerization of PO/CO₂ was studied.

Based on the previous studies, the effect of O₂ on Salen-Co(II) complexes in the cyclo-addition of CO₂ to PO was investigated by complexes 1 and 2. As shown in Table 1, the cyclo-addition reaction could not occur without the presence of cocatalyst, regardless of whether O₂ was added for both complexes (Table 1, entries 1, 2, 14, and 15, and Figs. S1 and S2 in the electronic supplementary information, ESI). Using bis(triphenylphosphine) iminium chloride (PPNCl) as cocatalyst, complex 1 could catalyze the cyclo-addition of CO₂ to PO to produce cyclic carbonate with very low activity (Table 1, entries 3, 7, and 16, and Figs. S1 and S2 in ESI). As shown in Figs. 1 and 2, the addition of O₂ showed very interesting performance in the reaction. Due to the participation of O₂, the activity of complex 1 was more than 30 times higher (TOF from 10 h⁻¹ to 310 h⁻¹, Table 1, entries 3 and 5 and Fig. S1 in ESI) and that of complex 2 was more than 60 times higher on the cyclo-addition of CO₂ to PO by using complexes 1 and 2.

| Entry | Complex | Temp. (°C) | [Cocat]/[Cat] | O₂ (MPa) | Conv. (%) | TOF | cPC |
|-------|---------|-----------|--------------|----------|-----------|----|-----|
| 1     | 1       | 80        | 0            | 0.2      | 0         | 0  | -   |
| 2     | 1       | 80        | 0            | 0.2      | 0         | 0  | -   |
| 3     | 1       | 60        | 1            | 1        | 10        | 100| 100 |
| 4     | 1       | 60        | 1            | 0.05     | 11        | 100| 100 |
| 5     | 1       | 60        | 1            | 0.2      | 31        | 100| 100 |
| 6     | 1       | 60        | 2            | 0.05     | 25        | 250| 100 |
| 7     | 1       | 80        | 1            | 0        | 3         | 30 | 100 |
| 8     | 1       | 80        | 1            | 0.05     | 71        | 710| 100 |
| 9     | 1       | 80        | 1            | 0.2      | 86        | 860| 100 |
| 10    | 1       | 80        | 2            | 0.05     | 77        | 770| 100 |
| 11    | 1       | 80        | 1            | 0.2      | 24        | 480| 100 |
| 12    | 1       | 100       | 1            | 0.2      | 77        | 1440| 100 |
| 13    | 1       | 120       | 1            | 0.05     | 91        | 1820| 100 |
| 14    | 2       | 60        | 0            | 0        | 0         | 0  | -   |
| 15    | 2       | 60        | 0            | 0.2      | 0         | 0  | -   |
| 16    | 2       | 60        | 1            | 0        | 0.5       | 5  | 100 |
| 17    | 2       | 60        | 1            | 0.2      | 30        | 300| 100 |
| 18    | 2       | 60        | 1            | 0.2      | 43        | 430| 100 |
| 19    | 2       | 60        | 3            | 0        | 50        | 500| 100 |
| 20    | 2       | 80        | 1            | 0.05     | 22        | 220| 100 |
| 21    | 2       | 80        | 1            | 0.2      | 45        | 450| 100 |
| 22    | 2       | 100       | 1            | 0.3      | 61        | 610| 100 |

* The different amounts of complexes and cocatalysts were dissolved in 2 mL of PO and carefully added into a 25 mL autoclave. Using complexes 1 and 2 at molar ratio (PO)/[complex] = 1000/1. The autoclave was heated up to desired temperature and the copolymerization was suspended after 1 h. No detectable polyether units were observed by ¹H-NMR analysis. [53] Molar ratio: The autoclave was filled with 0.05 or 0.2 MPa of oxygen and then pressurized with CO₂ to 3.0 MPa. [54] The results were determined by the conversion of PO in the crude copolymerization mixture by ¹H-NMR analysis. * Turn over frequency (TOF) = moles of product/mole of complex per hour. + Selectivity for cPC over PPO, determined by ¹H-NMR analysis. [55] Using complexes 1 or 2 ([PO]/[complex] = 2000/1).

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In order to study the mechanism of the activity change in the cyclo-addition reaction with the existence of O₂, the effect of cocatalyst was investigated firstly. As shown in Fig. 4 and Table 2, with DMAP as cocatalyst, the Salen-Co(II) complex 1 showed no catalytic activity to the cyclo-addition of CO₂ to PO regardless of whether O₂ was added or not (Table 2, entries 5 and 6). Using tetrabutylammonium bromide (TBAB) as cocatalyst, the addition of O₂ could obviously improve the activity of complex 1 (Table 2, entries 7 and 8). By using the mixture of TBAB and DMAP as cocatalyst, only a few amount of PO was converted to cyclic carbonate while the decrease of activity was observed with the addition of O₂ (Table 2, entries 9 and 10).

As shown in Fig. 5 and Table 2, different from complex 1, with DMAP as cocatalyst, complex 2 showed very low activity to the cyclo-addition of CO₂ to PO and the activity was improved obviously when O₂ was added (Table 2, entries 11 and 12). The TOF value up to 250 h⁻¹ was observed when employing 2 equivalents of PPNCl ([Cat]/[PPNCl] = 1/1, O₂ = 0.2 MPa; CO₂ = 3 MPa; 1 h). The TOF increased obviously in the presence of O₂ (Fig. 5, Table 2, entries 13 and 14).

Investigation concerning the concentration of cocatalyst showed that the increasing amount of cocatalyst resulted in the improved activity of complex 1. The TOF value up to 250 h⁻¹ was observed when employing 2 equivalents of PPNCl (Table 1, entries 4 and 6). Same conclusion can be drawn with complex 2 (Table 1, entries 17, 18, and 19).

As shown in Fig. 1 and Table 1, with TBAB as cocatalyst, complex 1 and 2 showed higher activity in the presence of O₂ than that of complex 1 under the same conditions; this result could be attributed to the conjugated structure of complex 1 compared with that of complex 2. The conjugated structure played a crucial role in the change of the electrophilicity of the metal center, and this role made complex 1 show higher activity in the cyclo-addition of CO₂ to PO.[55]
Table 2  Influence of the cocatalyst on the cyclo-addition of CO2 to PO by using complexes 1 and 2 with O2. a

| Entry | Complex PPNCl b | DMAP b | PO (MPa) | Conv. d | TOF e | cPC f |
|-------|-----------------|--------|----------|---------|-------|-------|
| 1     | 1 0 0 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 2     | 1 0 0 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 3     | 1 0 0 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 4     | 1 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 5     | 1 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 6     | 1 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 7     | 1 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 8     | 1 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 9     | 1 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 10    | 1 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 11    | 1 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 12    | 1 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 13    | 2 0 0 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 14    | 2 0 0 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 15    | 2 1 0 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 16    | 2 1 0 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 17    | 2 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 18    | 2 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 19    | 2 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |
| 20    | 2 0 1 0 0 0 0   | 0 0 0 0 0 | 0 0 0 0 0 | −      |

a The different amounts of complexes and cocatalyst were dissolved in 2 mL of PO and carefully added into a 25 mL autoclave. Using complex 1 and 2 at molar ratio (PO)/complex) = 1000:1. The autoclave was heated up to 80 °C and the copolymerization was suspended after 1 h. No detectable polyether units were observed by 1H-NMR analysis. b Molar ratio. c The autoclave was filled with 0.2 MPa of oxygen and then pressurized with CO2 to 3.0 MPa. d The results were determined by the conversion of PO in the crude copolymerization mixture by 1H-NMR analysis. e Turn over frequency (TOF) = moles of product/mole of complex per hour. f Selectivity for cPC over PPC, determined by 1H-NMR analysis. g The 1 equivalent of 2,4-dinitrophenol to the catalyst was added to copolymerization.

18). This result might be attributed to the intermediates formed by binding with conjugated complex 1 and DMAP. The stabler intermediates were difficult to activate the cyclo- addition reaction. Same as complex 1, when cocatalyst was alternated to TBAB, the addition of O2 could increase the activity of complex 2 (Table 2, entries 19 and 20). This indicated that TBAB and PPNCl played identical role in the cyclo- addition of CO2 to PO using complexes 1 and 2. Compared with DMAP, both PPNCl and TBAB had a stabilizing anion group. Therefore, the cocatalyst with a stabilizing anion is considered more active for the initiation of PO in the coupling reaction with CO2. 100% Cyclic carbonate was obtained when 2,4-dinitrophenol and PPNCl were used as cocatalysts (Table 2, entry 11). These results indicated that there was no formation of new Salen-Co(III) complex which was supposed to generate polycarbonate. The existence of O2 could not reduce the selectivity of cyclic carbonate by in situ oxidation of Salen-Co(II) complex.

On the basis of the above investigation, we hypothesized the mechanism of cyclo-addition of CO2 to PO with the presence of O2 (Fig. 6). PO was activated by Salen-Co(II) complexes at first; then, the cocatalyst as nucleophile ring-opened the activated PO to generate an alkoxide intermediate. With the insertion of CO2 and elimination of nucleophiles, the cyclic carbonate was obtained. Through this cyclic process, Salen-Co(II) could continuously catalyze the cyclo-addition of
CO₂ to PO. With the existence of O₂, the electrophilicity of metal Co(II) was improved by oxidation reaction. The improvement of the electrophilicity accelerated the cyclic process of the activation of PO, the insertion of CO₂, and the elimination of nucleophiles.

Previous studies had found that the Salen-Co(II) complex can catalyze copolymerization of PO and CO₂ in the absence of nucleophilic cocatalyst by altering the electrophilicity of the Co(III).[53] Based on the above experiments, the electrophilicity of Salen-Co(III) was improved with the existence of O₂. Therefore, the effect of O₂ on Salen-Co(III) complex in copolymerization of PO and CO₂ was studied. As shown in Table 3, the Salen-Co(III) complex showed very low activity and selectivity in the absence of nucleophilic cocatalyst, but with the addition of O₂, the activity and selectivity of complexes 3 were improved (Table 3 entries 1 and 2). This result indicates that the existence of O₂ in the copolymerization could improve the electrophilicity of the Salen-Co(III) complexes and O₂ could be used as a cocatalyst in copolymerization. In the copolymerization using PPNCl as cocatalyst, the existence of O₂ improved the activity of copolymerization slightly (Table 3 entries 3, 4, 5, and 6). This result could be attributed to the existence of O₂ that increased the amount of cocatalyst which could improve the activity.[53] Using complexes 1 and 3 together as catalysts, the selectivity of the mixture decreased (Table 3, entries 7 and 8). This result indicated that the effect of oxygen on the catalytic performance of Salen-Co(II) was more obvious. Based on these studies, it can be concluded that the addition of O₂ improved the activity and selectivity of the complexes 3 in the absence of nucleophilic cocatalyst and simultaneously it had no negative effect on the copolymerization using nucleophilic cocatalyst.

CONCLUSIONS

Salen-Co(II) has been investigated with the addition of O₂ in coupling reaction of PO/CO₂. Salen-Co(II) complexes showed very low activity in the cyclo-addition of CO₂ to PO. With the existence of O₂, the activity of Salen-Co(III) complexes was significantly increased and 100% cyclic carbonate was formed.

The catalytic performance of the complexes was influenced by the structure, and the complexes with the conjugated structure showed higher activity. The cocatalysts played an important role in the copolymerization, and cocatalysts with a stabilizing anionic group showed higher activity than organic bases cocatalyst. Through the study of cocatalysts, possible reaction mechanisms were proposed. Salen-Co(III) was investigated with the addition of O₂ in copolymerization of PO/CO₂. By altering the electrophilicity of Salen-Co(III), O₂ could also improve the activity of complex as cocatalyst. Overall, the addition of O₂ had a positive effect on the performance of Salen-Co complexes in the copolymerization of PO and CO₂.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-020-2451-5.

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