Chemical fixation of CO_2 using metalloporphyrins as catalysts for the production of cyclic carbonates

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ABSTRACT

Rising CO_2 levels and continued reliance on fossil fuels have driven research into catalytic CO_2 conversion. Projections suggest that CO_2 concentrations could reach 970 ppm within the next century. Although CO_2 has various industrial applications, its use in fine chemical production remains limited. Recent advances have focused on converting CO_2 into valuable products such as organic carbonates, contributing to sustainability by replacing phosgene in certain processes. Metalloporphyrin catalysts, as zinc, manganese, and copper complexes, have demonstrated high efficiency in the chemical fixation of CO_2 into epoxides, with an activation energy of 39.76 kJ mol^{-1} using the ZnTCPP/TBAB system and a conversion rate of 92% to cyclic carbonates.

Keywords: Carbon dioxide; Cyclic carbonate; Catalysis; Metalloporphyrin complexes; Sustainability.

INTRODUCTION

The increase in CO_2 emissions, primarily due to the combustion of fossil fuels, has intensified the greenhouse effect and global warming. Projections indicate that CO_2 levels could reach 970 ppm in the next century, driving research into its catalytic conversion into higher-value products. Although the use of CO_2 in the chemical industry remains limited, new technologies show potential for creating valuable organic compounds such as alcohols and carbonates[1]. CO_2 is a promising C1 building block for synthesizing other molecules, and replacing phosgene with CO_2 in the synthesis of organic carbonates represents a significant environmental and economic advancement[2].

In this study, six metalloporphyrin complexes based on 5,10,15,20-tetrakis(4-

carboxyphenyl)porphyrin (H_2T4CPP) and 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H_2T4SPP), coordinated with Zn(II), Mn(III), and Cu(II) metal cations, were synthesized to evaluate their efficiency as catalysts in the reaction between CO_2 and epoxides to produce cyclic carbonates (**Fig. 1**). The catalysts obtained proved to be highly effective, operating under mild temperature and pressure conditions, which is crucial for the industrial viability of this process.

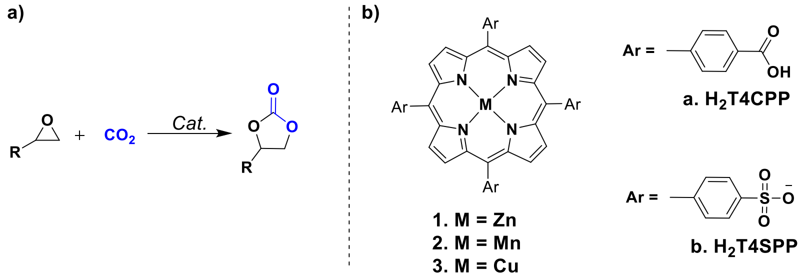

Figure 1. a) Reaction between CO_2 and epoxides. b) Metalloporphyrins (1-3a) $[M(T4CPP)]^{n+}$ and (1-3b) $[M(T4SPP)]^{n+}$ used as catalysts.

MATERIALS AND METHODS

Synthesis of Metalloporphyrins

The porphyrins H_2T4CPP and H_2T4SPP, used as precursors for the preparation of zinc(II), copper(II) and manganese(III) metalloporphyrins, were obtained commercially from Aldrich and used without prior purification. The metalloporphyrins were synthesized from H_2T4CPP and H_2T4SPP with the respective metal ions. This process involved dissolving the porphyrins in N,N-dimethylformamide (DMF) and refluxing the solution under stirring in the presence of the metal ion. A DMF solution of zinc, copper or manganese acetate salts was added, and the mixture was heated (~100 °C) with continuous stirring for 4 h. The progress of the reaction was monitored by UV-Vis spectroscopy, focusing on the changes in the Soret and Q bands to confirm the formation of the metalloporphyrin.

Catalytic Synthesis

In a standard procedure, in a 10 mL round bottom flask was charged with the 0,1 mol% catalyst (MTCPP or MTSPP), cocatalyst 2 mol% (TBAX, where X = Cl, Br, or I), and styrene oxide 3 mmol (SO). The system was then connected to a gas flask containing carbon dioxide at 1 atm, and the reaction was carried out at 70 °C for either 8 and 24 hours. After the reaction time elapsed, the reaction was quenched, cooled to room temperature, and a sample of the crude mixture was collected and dissolved in $CDCl_3$ for analysis by hydrogen nuclear magnetic resonance spectroscopy (^1H NMR). The conversion was determined based on the ^1H NMR spectra of the crude reaction mixture.

kinetic study

The kinetic study of the cycloaddition reaction between CO_2 and styrene oxide, using [Zn(T4CPP)] as the catalyst and TBAB as the cocatalyst, involved analyzing the formation of styrene carbonate over time at different temperatures (40 °C, 50 °C, 60 °C, 70 °C, and 80 °C), with the conversion determined by NMR. Reagent concentrations were kept constant, and samples were taken hourly. The activation energy (Ea) was determined by fitting the experimental data to the Arrhenius equation, while thermodynamic parameters, such as enthalpy ($\Delta H^{\neq}$), entropy ($\Delta S^{\neq}$), and Gibbs free energy ($\Delta G^{\neq}$), were obtained using the Eyring equation.

RESULTS AND DISCUSSION

The catalytic tests for the chemical fixation of CO_2 into epoxides were initially performed as control experiments using tetrabutylammonium bromide (TBAB, 2 mol%) as the sole cocatalyst, which resulted in low catalytic activity, with conversions of 2% and 15% after 1 and 8 hours, respectively. The introduction of porphyrin H_2T4CPP (0,1 mol%) as a catalyst improved the process. The carboxyl groups of the macrocycle facilitated the epoxy ring opening through hydrogen bonding. However, the conversion to cyclic carbonate was limited to 44%, highlighting the necessity of incorporating a metal center. Under standard reaction conditions using styrene oxide (SO) as the epoxide, with a reaction time of 8 hours, at 70 °C, 1 bar CO_2, 0.1 mol% catalyst (MTCPP and MTSPP), and 2 mol% cocatalyst (TBAB), the use of metalloporphyrin complexes provided Lewis acidity at the metal center, thus enhancing catalytic efficiency. The best results were obtained with Zn^{2+}, Mn^{3+}, and Cu^{2+} ions after 8 hours of reaction, with conversions of 92% for ZnTCPP, 95% for MnTSPP, and 33% for CuTCPP. Among them, the metalloporphyrin [Zn(T4CPP)] demonstrated the best cost-performance ratio, offering an excellent balance between structure and acidity, achieving a conversion rate of 92% after 8 hours.

To assess the versatility of the [Zn(T4CPP)]/TBAB catalytic system, the CO_2 addition reaction with styrene oxide was tested with 10 other substrates with different substituent groups under optimized conditions. All epoxides were successfully converted into their corresponding cyclic carbonates with excellent yields. Syntheses were carried out using [Zn(T4CPP)] (0.003 mmol; 0.1 mol%) and TBAB (0.06 mmol; 2.0 mol%) with 3 mmol of epoxide under a CO_2 pressure of 1 bar at 70 °C for 8 h or 24 h. Conversion was evaluated by ^1H NMR, and yield was calculated by mass obtained after column chromatography. The products were isolated by chromatography and characterized by ^1H and ^{13}C NMR, as well as ESI mass spectrometry, providing a detailed analysis of the molecular structures.

The combination of [Zn(T4CPP)] and TBAB significantly lowered the activation energy for the CO_2 and styrene oxide cycloaddition to 39.76 kJ mol^{-1}, indicating high efficiency[3]. In contrast, TBAB alone had an activation energy of 51.98 kJ mol^{-1}. TBAB excelled among other catalysts for its balance between nucleophilicity and leaving group capacity, while TBAC and TBAI exhibited higher activation energies and lower efficiencies (**Table 1**). The [Zn(T4CPP)]/TBAB system also showed a lower enthalpy variation (42.52 kJ mol^{-1}) compared to the TBAB-only system (54.75 kJ mol^{-1}), suggesting better stability of intermediates with [Zn(T4CPP)]. Additionally, the [Zn(T4CPP)]/TBAB system had a more pronounced entropy variation (-103.92 J K^{-1} mol^{-1}), indicating greater molecular organization of intermediates compared to the other systems.

Table 1. Activation parameters for the formation of styrene carbonate (SC) using the binary system [Zn(T4CPP)]/TBAB and with TBAB alone or TBAC or TBAI.

Catalyst	E_a (kJ mol^{-1})	$\Delta G^‡$ (kJ mol^{-1})	$\Delta H^‡$ (kJ mol^{-1})	$\Delta S^‡$ (J K^{-1} mol^{-1})
[Zn(T4CPP)]/TBAB	39,76	81,28	42,52	-103,92
TBAB	51,98	87,30	54,75	-87,29
TBAI	56,14	86,09	58,90	-72,91
TBAC	79,51	82,99	82,28	-1,92

$\Delta G^‡ = \Delta H^‡ - T\Delta S^‡$; T = 373 K.

Based on recent studies, the proposed mechanism for the catalytic system is as follows: The reaction initiates with the catalyst functioning as a Lewis acid, coordinating with two epoxides simultaneously at the metal center (an intermediate detected by mass spectrometry). The cocatalyst (TBAB) supplies the nucleophile required for epoxide ring opening, leading to the formation of an alkoxide intermediate, which then reacts with carbon dioxide. For an intramolecular reaction to occur, the nucleophile must be an effective leaving group, facilitating ring closure in the final step. This process results in the formation of a five-membered cyclic carbonate while simultaneously regenerating the catalyst and cocatalyst.

CONCLUSION

In this study, six metalloporphyrins derived from H_2T4CPP and H_2T4SPP with zinc(II), manganese(II), and copper(II) metal ions were synthesized and characterized. These metalloporphyrins were employed as catalysts in reactions between CO_2 and epoxides, resulting in conversions exceeding 92% and yields above 85% in the production of cyclic carbonates. The most effective catalyst was identified as [Zn(T4CPP)] combined with TBAB. Kinetic studies revealed a significant reduction in activation energy and improved molecular organization, indicating high catalytic efficiency. High-resolution mass spectrometry was utilized to investigate the reaction mechanisms, revealing intermediate complexes and suggesting direct passage through transition states. These findings demonstrate the potential of the developed catalytic system for the efficient and selective synthesis of cyclic carbonates from CO_2.

ACKNOWLEDGMENT

CNPq; CAPES; FAPEG.

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