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Cooperative Catalysis of Ru(III)-Porphyrin in CO_2-Involved Synthesis of Oxazolidinones

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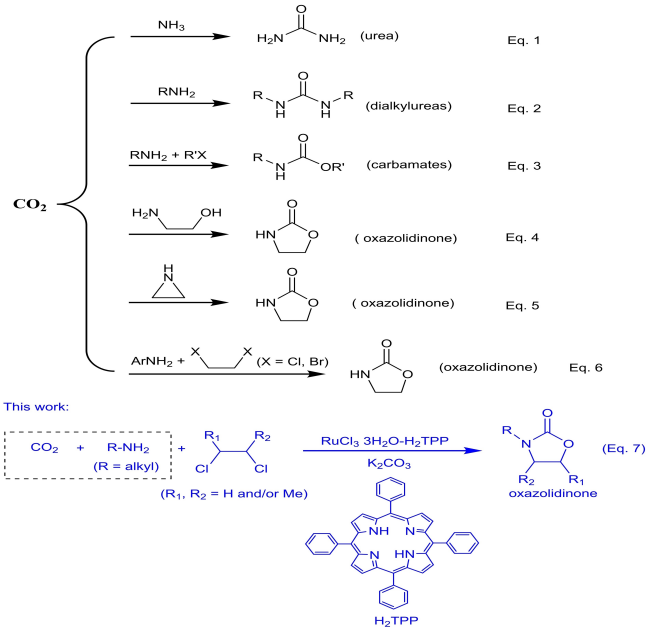
Dedicated to Prof. T. S. Andy Hor for his 65th birthday.

Abstract: CO_2-transformations into high value-added products have become a fascinating area in green chemistry. Herein, a Ru(III)-porphyrin catalyst ($RuCl_3 \cdot 3H_2O$–H_2TPP) was found highly efficient in the three-component reaction of CO_2, aliphatic amines and dichloroethane (or its derivative) for synthesis of oxazolidinones in the yields of 71~91%. It was indicated by means of the control experiments and UV-vis spectra that CO_2 was stoichiometrically activated by the involved aliphatic amine substrates to form a stable carbamate salt while 1,2-dichloroethane (or its derivative) was independently activated by the involved Ru(III)-porphyrin catalyst. The combination of CO_2-activation by aliphatic amines with 1,2-dichloroethane activation by Ru(III)-porphyrin catalyst cooperatively contributed to this successful transformation.

Introduction

Conversion of CO_2 into high value-added products has fascinated chemists ever since the advent of the area of green and sustainable chemistry.[1–5] CO_2, one of the major man-made greenhouse gases, is a nontoxic, nonflammable, and inexpensive molecule. It has a large atmospheric abundance of about 2.3×10^{12} t, which makes it a renewable alternative to other C1-substances that are being depleted.[6] At present, CO_2 is usually reduced as C1 compounds such as CO, formic acid, methanol, or urea in industrial scale as potential sustainable fuels or synthetic building blocks.[4,7–10] However, the transformation of CO_2 to organic compounds containing three or more than three carbon atoms are rarely established in large scale.[11,12]

It has been well known that the reactions of CO_2 with different amino compounds can produce various organic chemicals, such as urea,[13,14] bis-substituted urea,[15] carbamates[16–18] (Scheme 1, Eq. 1–3) and oxazolidinones (i.e., cyclic urethanes),[19–25] revealing that the activation of CO_2 by alkaline amino-compounds in cooperative combination of a suitable catalyst is of fundamental importance in CO_2-involved synthesis protocols. As for the synthesis of oxazolidinones via CO_2-fixation using high-energy N-containing compounds (such as ethanolamines, aziridines or ethylene epoxide) featured with strict structural limitation (Scheme 1, Eq. 4,5),[19–21] the application of simple amines was advantageous with structural variety, low-cost, and facile manipulation (Scheme 1). Encouragingly,



Scheme 1. Transformation of CO_2 with amino-compounds for the synthesis of various organic compounds.

the three-component reaction of CO_2, aromatic amines and 1,2-dihaloethane have been reported with the presence of carefully selected organocatalyst,[22,23] wherein the nucleophilic substitution of the involved aromatic amines with haloalkanes was the rate-determining step (Scheme 1, Eq. 6). However, these developed methods were not applicable to the stronger basic (primary/secondary) aliphatic amine-participated processes. Herein, highlighted by the strategy of activation of CO_2 by alkaline amino-compounds in cooperative combination of a suitable catalyst in CO_2-involved synthesis, the three-component reaction of CO_2, aliphatic amines and 1,2-dihaloethane (or its derivative) for the synthesis of oxazolidinones was investigated for the first time, wherein CO_2 was activated stoichio-

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metrically by the involved amine substrate and 1,2-dihaloethane was activated catalytically by the Ru(III)-porphyrin catalyst [$RuCl_3 \cdot 3H_2O$–H_2TPP] (Scheme 1). The control experiments demonstrated that the carbamate salt as a white solid was formed immediately at RT while CO_2 was charged into the aliphatic amine (like cyclohexylamine). The UV-vis spectroscopic analyses convinced that Ru(III)-porphyrin catalyst was able to efficiently activate 1,2-dichloroethane via utilizing 1,2-dichloroethane as the axial ligand.

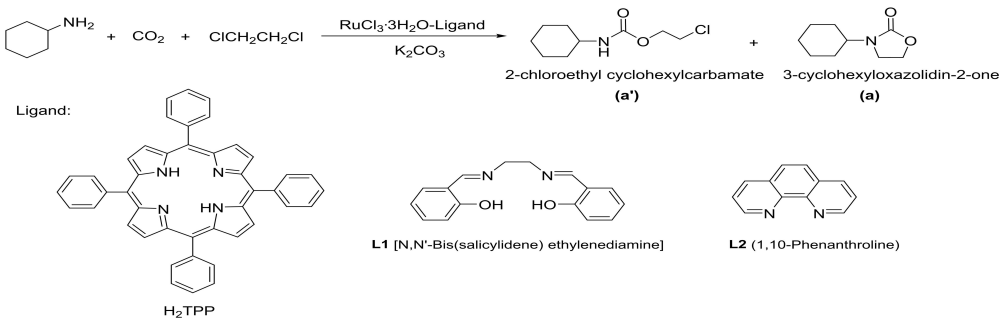
Results and Discussion

The three-component reaction of CO_2, cyclohexylamine and 1,2-dichloroethane for the synthesis of 3-cyclohexyloxazolidin-2-one was investigated as a model reaction (Table 1). Under the optimal conditions (100 °C, 9 h, 1.0 MPa CO_2, 1 mol% $RuCl_3 \cdot 3H_2O$–H_2TPP, and K_2CO_3 as a base), 3-cyclohexyloxazolidin-2-one (**a**) was obtained with yield of 90% (Entry 2). Evidently, without the presence of $RuCl_3 \cdot 3H_2O$–H_2TPP catalyst, the much lower yield of 52% was obtained for the desired product (Entry 1). The decrease in Ru-catalyst concentration or temperature decelerated the reaction rate to some extent (Entries 3 and 4 *vs* 2). The increase of CO_2-pressure (from 1.0 MPa up to 2.0 MPa) had negligible effect on the reaction rate (Entry 5 *vs* 2), implying that the activation of CO_2 was not involved in the rate-determining step in this three-component reaction. The as-synthesized Ru^{III}(TPP)Cl complex exhibited the same activity as the one in situ formed upon mixing $RuCl_3 \cdot 3H_2O$ and H_2TPP at molar ratio 1/1 (Entries 6 *vs* 2). Emphatically, the use of K_2CO_3 or DBU exhibited no difference for the *in situ* formation of Ru^{III}(TPP)Cl as indicated in Figure S2 of ESI. While H_2TPP was replace by the phosphorous-free ligands like **L1** and **L2** respectively, **L1** as a kind of typical Salen-ligands corresponded to the relatively lower yield of 62% for **a** (Entry 7) while the bidental ligand of **L2** (1,10-phenanthroline) just to 45% (Entry 8). Unfortunately, the replacement of cyclohexylamine by aniline corresponded to no reaction at all (Entry 9). It was noted that when sterically bulky DBU was applied in place of K_2CO_3 as an acid scavenger, a large amount of 2-chloroethyl cyclohexylcarbamate (**a'**) as side-product was formed in the yield of 36% (Entry 10 *vs* 2).

The evolving profiles for cyclohexylamine conversion and product selectivity *vs* reaction time (Figure 1) indicated that the target oxazolidinone (**a**) was prevailingly formed with selectivity up to 94% at any time along with the carbamate (**a'**) as a minor side-product, and then the formed **a'** could completely convert to **a** when the reaction time was prolonged.

It was found that once CO_2 was introduced into the cyclohexylamine, a white solid was precipitated [Scheme 2-(1)], which was proved to be the stable carbamate salt (**C**, cyclohexyl-ammonium cyclohexylcarbamate) by $^1H/^{13}C$ NMR spectroscopic characterizations (see Figure S1 in ESI). The similar phenomena have also been observed in previous work.[26] In the control experiment, the reaction of as-synthesized **C** with 1,2-dichloroethane over $RuCl_3 \cdot 3H_2O$–H_2TPP catalytic system led to the generation of 3-cyclohexyl-2-oxazolidinone (**a**) in the yield of 87% whereas the yield of product was just 21% without the presence of $RuCl_3 \cdot 3H_2O$–H_2TPP [Scheme 2-(2) *vs* Scheme 2-(3)]. Under the same conditions, the

Table 1. The three-component reaction of CO_2, aniline and 1,2-dichloroethane for the synthesis of 3-phenyl-2-oxazolidinone under different conditions.[a]



Entry	Precursor [mol%]	Ligand [mol%]	Base	Temp. [°C]	Conv. [%][b]	Sel. [%][c]		Yield of **a** [%]
						a'	**a**	
1	$RuCl_3 \cdot 3H_2O$ (1.0)	–	K_2CO_3	100	44	3	97	42
2	$RuCl_3 \cdot 3H_2O$ (1.0)	H_2TPP	K_2CO_3	100	90	0	100	90
3	$RuCl_3 \cdot 3H_2O$ (1.0)	H_2TPP	K_2CO_3	80	79	3	97	77
4	$RuCl_3 \cdot 3H_2O$ (0.75)	H_2TPP	K_2CO_3	100	71	4	96	68
5[d]	$RuCl_3 \cdot 3H_2O$ (1.0)	H_2TPP	K_2CO_3	100	91	0	100	91
6[e]	Ru^{III}(TPP)Cl (1.0)	–	K_2CO_3	100	91	0	100	91
7	$RuCl_3 \cdot 3H_2O$ (1.0)	**L1**	K_2CO_3	100	63	2	98	62
8[f]	$RuCl_3 \cdot 3H_2O$ (1.0)	**L2**	K_2CO_3	100	46	2	98	45
9[g]	$RuCl_3 \cdot 3H_2O$ (1.0)	H_2TPP	K_2CO_3	100	–	–	–	–
10	$RuCl_3 \cdot 3H_2O$ (1.0)	H_2TPP	DBU	100	89	40	60	53

[a] Cyclohexylamine 2.0 mmol, $RuCl_3 \cdot 3H_2O/H_2TPP = 1/1$ molar ratio, CO_2 1.0 MPa, time 9 h, 1,2-dichloroethane 3.0 mL (dually as solvent), K_2CO_3 2.0 mmol (DBU 4.0 mmol) ; [b] Determined by GC with n-dodecane as the internal standard; [c] Determined by GC with normalization method which was calibrated by the authentic sample of 3-cyclohexyl-2-oxazolidinone (**a**); [d] CO_2 2.0 MPa; [e] The as-synthesized Ru^{III}(TPP)Cl (2.0 mmol) was used instead of the mixture of $RuCl_3 \cdot 3H_2O$ (2.0 mmol) and H_2TPP; [f] $RuCl_3 \cdot 3H_2O$/**L2** = 1/2 molar ratio; [g] Aniline was used instead of cyclohexylamine.

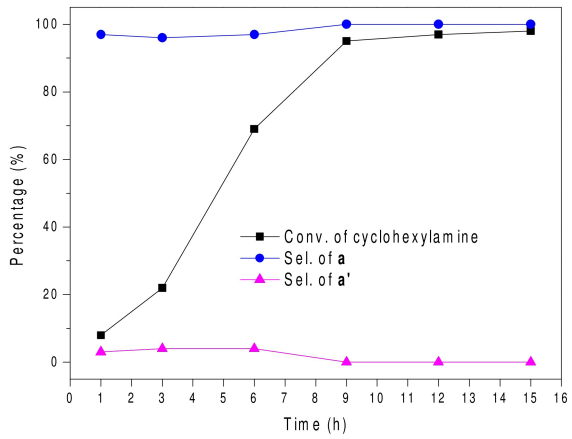
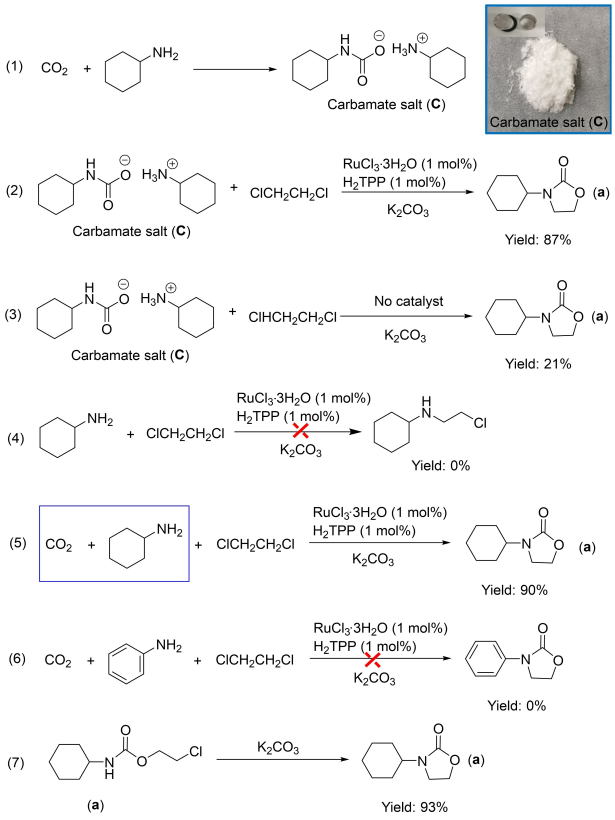


Figure 1. The evolving profiles for cyclohexylamine conversion and product selectivity *vs* reaction time under the optimal reaction conditions (cyclohexylamine 2.0 mmol, $RuCl_3 \cdot 3H_2O$ 0.02 mmol, H_2TPP 0.02 mmol, CO_2 1.0 MPa, 1,2-dichloroethane 3.0 mL, K_2CO_3 2 mmol, temp. 100 °C).



Scheme 2. The control experiments of CO_2-invovled synthesis under different conditions [K_2CO_3 2.0 mmol, time 9 h, temperature 100 °C cyclohexylamine or aniline 2.0 mmol and CO_2 1.0 MPa if required in (1), (5) and (6), 1,2-dichloroethane 3.0 mL if required; The applied substrate of 2-chloroethyl cyclohexylcarbamate (**a'**, 2 mmol) in (7) was isolated from the reaction mixture of Entry 10 in Table 1].

nucleophilic substitution of 1,2-dichloroethane with cyclohexylamine completely failed [Scheme 2-(4)]. The control experiments in Scheme 2-(1)~(4) revealed that the nucleophilic addition of cyclohexylamine towards one carbonyl group of CO_2 to form the corresponding carbamate salt of **C** was the initial-step for this three-component reaction whereas the nucleophilic substitution of 1,2-dichloroethane with cyclohexylamine didn't happen during the course. Then the available **C** was attacked by 1,2-dichloroethane activated by $RuCl_3 \cdot 3H_2O$–H_2TPP catalyst to accomplish the subsequent cyclization with the involvement of an acid-scavenger (K_2CO_3) [Scheme 2-(5)]. In contrast, the reaction of CO_2 with aniline couldn't form any carbamate salt. As a result, no target product of **a** was found under the same applied conditions [Scheme 2-(6)], but the substituted products were obtained prevailingly upon the nucleophilic substitution of 1,2-dichloroethane with aniline. On the other hand, when the side-product of cyclohexylcarbamate (**a'**) isolated from the reaction mixture of Entry 10 in Table 1 was treated with K_2CO_3 at 100 °C without any catalyst, the target 3-cyclohexyloxazolidin-2-one (**a**) was obtained with yield of 93% in 9 h, which further indicated that **a'** could smoothly convert into a upon effective HCl-scavenging by a base.

The activation of 1,2-dichloroethane by $RuCl_3 \cdot 3H_2O$–H_2TPP catalyst was confirmed by the UV-Vis spectroscopic analysis. As shown in the evolving UV-Vis spectroscopic profiles in Figure 2, at 100 °C as the reaction time increased from 3 to 9 h, a new absorption at ca. 248 nm along with the strong Soret band ascribed to Ru-porphyrin structure (412 nm) appeared due to the formation of an active intermediate complex (denoted as **A**) derived from the effective interaction of 1,2-dichloroethane with the Ru(III)-porphyrin catalyst.

Accordingly, the reaction mechanism of three-component reaction of CO_2, aliphatic amines and 1,2-dichloroethane over $RuCl_3 \cdot 3H_2O$–H_2TPP catalyst was proposed as presented in Scheme 3, wherein the reaction of CO_2 with aliphatic amines to form the carbamate salt as well as the independent activation of 1,2-dichloroethane by Ru(III)-porphyrin catalyst cooperatively contributes to this successful transformation. Firstly, a primary aliphatic amine reacts with CO_2 rapidly to afford the relatively stable carbamate salt intermediate (**C**-analogue). Simultane-

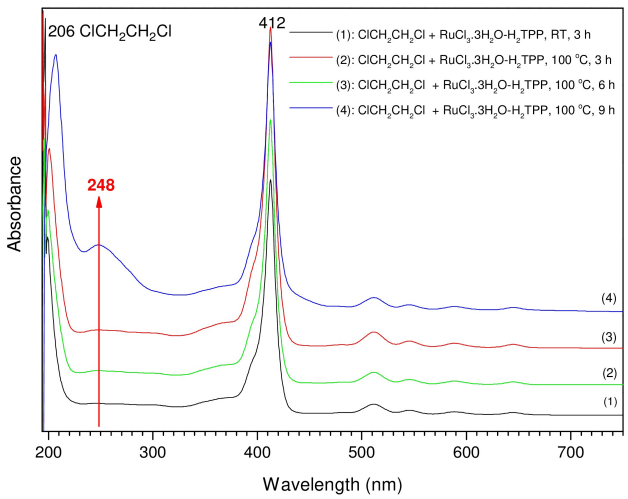
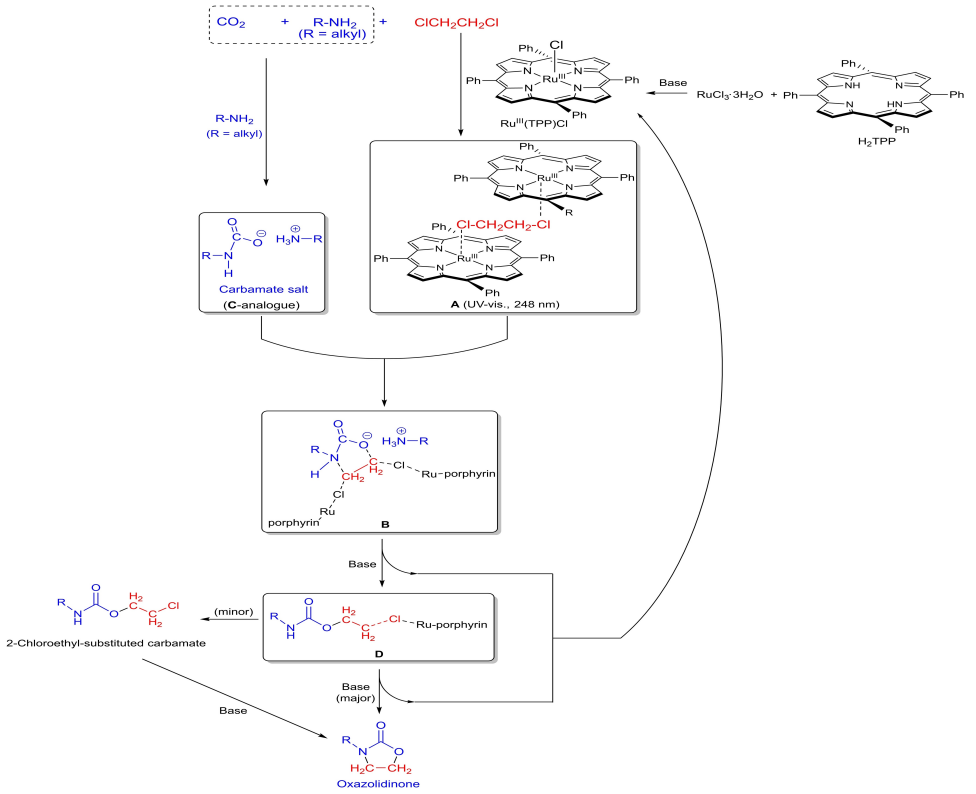


Figure 2. The evolving profiles of the UV-vis spectra for the mixture of 1,2-dichloroethane and $RuCl_3 \cdot 3H_2O$–H_2TPP (1 mol%) in $CDCl_3$ recorded upon treating at 100 °C for different time (CH_3OH as the reference sample).

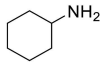
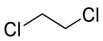
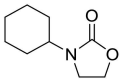
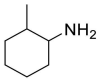
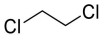
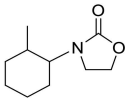
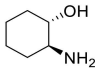
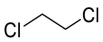
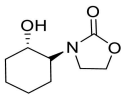
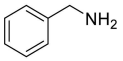
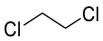
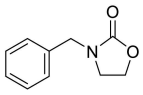
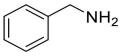
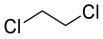
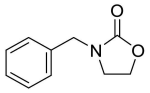
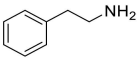
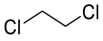
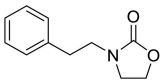
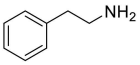
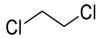
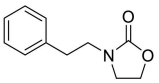
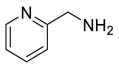
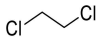
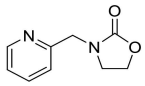
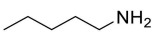
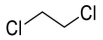
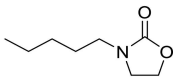
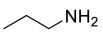
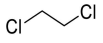
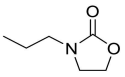
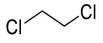
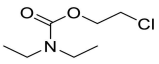
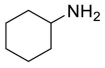
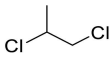
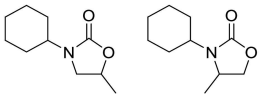
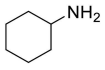
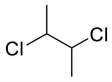
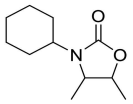
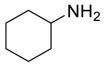


Scheme 3. Reaction mechanism for synthesis of oxazolidinone by three-component reaction of CO_2, cyclohexylamine and 1,2-dichloroethane over $RuCl_3 \cdot 3H_2O$–H_2TPP catalytic system.

ously, the axial-ligand exchange in Ru^{III}(TPP)Cl complex by 1,2-dichloroethane leads to the formation of 1,2-dichloroethane-bridged Ru(III)-porphyrin intermediate of **A**, with satisfied energy level because of the universally available π-π stacking interaction between porphyrin-rings.[27–31] Reasonably, when dichloroethane is activated by Ru-porphyrin complex via serving as the bridge axial ligand, the two Cl–C bonds should be equally weakened without discrimination to form intermediate **B** upon the attack by **C**-analogue intermediate. The latter then undergoes successive substitutions with aid of a base to afford the target oxazolidinone as major product. Alternatively, the first-step substitution from intermediate **B** towards **D** also can lead to the formation of 2-chloroethyl-substituted carbamate occasionally, which will transform into the target oxazolidinone via subsequent intramolecular cyclization (as observed in Scheme 2-(3) and Scheme 2-(7)). When DBU is applied instead of K_2CO_3, the second-step substitution from intermediate **D** to oxazolidinone for intramolecular cyclization is depressed due to the bulky steric hindrance of DBU, giving way to the formation of 2-chloroethyl-substituted carbamate as observed in Entry 10 of Table 1 (*vs* Entry 2).

The scope of the substrates for this three-component reaction with the presence of $RuCl_3 \cdot 3H_2O$–H_2TPP catalytic system were investigated in Table 2. In general, the reaction of CO_2 and 1,2-dichloroethane with different primary aliphatic amines performed smoothly, affording the N-substituted oxazolidinones in the yields of 71–91% (Entries 1–10). As for benzylamine and phenethylamine tailed with bulky substituents, the prolonged reaction time from 9 h to 15 h was required to give 83% and 81% yields of the target products respectively (Entries 5 and 7 *vs* Entries 4 and 6). In Entry 3, when (1R,2R)-*trans*-2-aminocyclohexanol was applied as the starting material, the corresponding oxazolidinone showed retention of configuration as confirmed by $^1H/^{13}C$ NMR spectra provided in Figure S4 of ESI. Reasonably, as for a secondary aliphatic amine such as diethylamine, only the corresponding 2-chloroethyl diethyl-carbamate was obtained in the yield of 64% (Entry 11). When 1,2-dichloropropane or 2,3-dichlorobutane was used instead of 1,2-dichloroethane, the relatively lower yield of target oxazolidinone (78% or 83%) was obtained in comparison to 90% in case of 1,2-dichloroethane (Entry 12 or 13 *vs* 1). However, when 1,2-dicholobenzene was applied in place of 1,2-dichloroethane to repeat the reaction, no any product was obtained (Entry 14). Interestingly, the use of 1,2-dibromoethane (or 1,2-diiodioethane) instead of 1,2-dichloroethane to repeat the reaction just led to the formation of the N-alkylated cyclohexylamine derivatives (Entry 15 and 16) due to the prevailing substitution reaction of 1,2-dihaloethane (halo = Br or I) with cyclohexylamine rather than the nucleophilic addition of CO_2 with cyclohexylamine to form the carbamate salts. In accordance with the proposed mechanism in Scheme 3, the role of $RuCl_3 \cdot 3H_2O$–H_2TPP catalyst is to activate 1,2-dichloroethane (or its derivative like 1,2-dichloropropane or 1,2-dichlorobutane) but not to activate CO_2. Once 1,2-dichloroethane reacted with cyclohexylamine as a matter of priority to form the N-substituted cyclohexylamine derivatives as shown in

Table 2. The substrate scope of three-component reaction of CO_2, amine and dihalogenated hydrocarbon catalyzed by $RuCl_3 \cdot 3H_2O$–H_2TPP system.[a]

Entry	Amine	Dihalogenated hydrocarbon	Product	Conv. of amine [%][b]	Sel. of oxazolidinone [%]	Yield [%][b]
1				90	100	90
2				87	100	87
3[c]				71	100	71
4				63	100	63
5[d]				83	100	83
6				51	100	51
7[d]				81	100	81
8				77	100	77
9[d]				86	100	86
10[d]				91	100	91
11[d]				64	100	64
12				83	100	78 (1:1)
13[e]				83	100	83
14			–	–	–	–
15[e]				47	0	0
16[f]				61	0	0
17			–	–	–	–

[a] $RuCl_3 \cdot 3H_2O$ 0.02 mmol (1 mol%,), H_2TPP 0.02 mmol (1 mol%), amines 2.0 mmol, CO_2 1.0 MPa, dihalogenated hydrocarbon 3.0 mL, K_2CO_3 2 mmol, time 9 h, temp. 100 °C; [b] Determined by GC and GC-MS with n-dodecane as internal standard. The $^1H/^{13}C$ NMR spectra of the isolated oxazolidinones were provided in ESI; [c] The target oxazolidinone with retention of configuration was confirmed by the $^1H/^{13}C$ NMR spectra (provided in ESI) when (1R,2R)-*trans*-2-aminocyclohexanol (CAS No: 931-16-8) was used as the starting material; [d] Reaction time 15 h; [e] 2,3-Dichlorobutane is a mixture of R/S- and meso-compounds; [f] No oxazolidinone was obtained instead of the prevailing N-substituted product with the structure as indicated.

Entries 15 and 16, the required activation of 1,2-dichloroethane by Ru(III)-porphyrin catalyst didn't take place. Similarly, as for aniline with weak basicity (nucleophilicity), the three-component reaction didn't happen due to lack of the required

carbamate salt (Entry 17), which was convinced by the *in situ* high-pressure FT-IR spectroscopic analysis (See Figure S3 in ESI). Herein, even the substitution reaction of 1,2-dichloroethane with aniline was not ensued.

Conclusion

The three-component reaction of primary aliphatic amine, CO_2 and 1,2-dichloroethane (or its derivative) was accomplished over $RuCl_3 \cdot 3H_2O$–H_2TPP catalytic system for the synthesis of N-substituted-2-oxazolidinones in the yields of 71~91% ([Ru] = 1 mol%, 2 equiv. K_2CO_3 as base, 100 °C, 9~15 h). In this synthesis protocol, the combination of stoichiometric activation of CO_2 by the involved aliphatic amine with the Ru(III)-porphyrin catalysis towards 1,2-dichloroethane (or its analogue) cooperatively contributes to this successful three-component reaction, which proves to be a novel strategy for CO_2-utilization. The UV-vis spectroscopic analysis convinced that the Ru(III)-porphyrin catalyst was able to efficiently activate 1,2-dichloroethane into an active electrophilic intermediate (**A**) via utilizing 1,2-dichloroethane as the axial ligand of Ru(III)-porphyrin.

Experimental Section

Reagents and analysis: The chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. and Alfa Aesar China, and used as received. The ^1H and ^{13}C NMR were recorded on a Bruker Avance 500 spectrometer. Gas chromatography (GC) was performed on a SHIMADZU-2014 equipped with a DM-Wax capillary column (30 m × 0.25 mm × 0.25 μm). GC-mass spectrometry (GC-MS) which equipped with a DB-Wax capillary column (30 m × 0.25 mm × 0.25 μm) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector. The UV-vis spectra were recorded by the Shimadzu UV-2700 spectrometer. The FT-IR spectra were recorded on using a Nicolet NEXUS 670 spectrometer.

General procedures for three-component reaction of CO_2, aliphatic amine and 1,2-dihaloethane: In a typical experiment, $RuCl_3 \cdot 3H_2O$ (0.02 mmol), ligands (0.02 mmol) and K_2CO_3 (2.0 mmol) were added into 1,2-dichloroethane (3.0 mL) and the amine (2.0 mmol). The obtained mixture in a 50 mL Teflon-lined stainless-steel autoclave was sealed and pressured by CO_2 (1.0 MPa). Then the reaction mixture was stirred vigorously at 100 °C for 9 h. Upon completion, the autoclave was cooled down to room temperature and slowly depressurized. The solution was analyzed by GC to determine the conversion (n-dodecane as internal standard) and the selectivity (normalization method), and the products were further identified by GC-MS and 1H/13C NMR spectrometers.

Pseudo in situ UV-vis absorption spectroscopic characterization: The UV-vis spectra were recorded by the Shimadzu UV-2700 spectrometer. The same samples used in ^1H NMR spectroscopic characterization were also applied herein. The reaction mixture upon treating at 100 °C for different time (3 h, 6 h, or 9 h) respectively in the autoclave were diluted by 1,2-dichloroethane required for the UV-vis detection (MeOH as reference).

Preparation of Ru^{III}(TPP)Cl complex: H_2TPP [307.5 mg, 0.5 mmol, 421 nm (Soret band)] dissolved in CH_3OH (30 mL) was added with $RuCl_3 \cdot 3H_2O$ (103.7 mg, 0.5 mmol) and K_2CO_3 (69.1 mg, 0.5 mmol). The obtained mixture was stirred at 100 °C for 30 min. Then the cooled solution was concentrated under vacuum to give the crude product after washing by Et_2O. The obtained crude product was dissolved in CH_2Cl_2 (10 mL), and crystallized by the addition of Et_2O (20 mL), yielding the complex of Ru^{III}(TPP)Cl [332.8 mg, 90%, 412 nm (Soret band)] as a dark solid. By following the similar procedures, when DBU was applied instead of K_2CO_3, the same Ru^{III}(TPP)Cl complex was obtained (The UV-vis spectra of the obtained Ru^{III}(TPP)Cl was provided in Figure S2 of ESI).

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Carbamate salt · Cooperative catalysis · Oxazolidinones · Ru(III)-porphyrin catalyst · Transformation of CO_2

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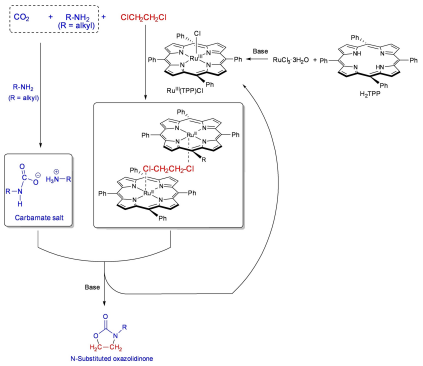
FULL PAPER

In the three-component reaction of CO_2, aliphatic amines and dichloroethane (or its derivative) for synthesis of oxazolidinones with yields of 71 ~ 91%, CO_2 was stoichiometrically activated by the involved aliphatic amine substrates to form a stable carbamate salt while 1,2-dichloroethane (or its derivative) was independently activated by the involved Ru(III)-porphyrin catalyst.



*Dr. X.-C. Chen, Y.-Q. Yao, K.-C. Zhao, Dr. L. Liu, Prof. Y. Lu, Prof. Y. Liu**

Cooperative Catalysis of Ru(III)-Porphyrin in CO_2-Involved Synthesis of Oxazolidinones

Special Collection