CO_2 Adducts of *N*-Heterocyclic Carbenes: Thermal Stability and Catalytic Activity toward the Coupling of CO_2 with Epoxides

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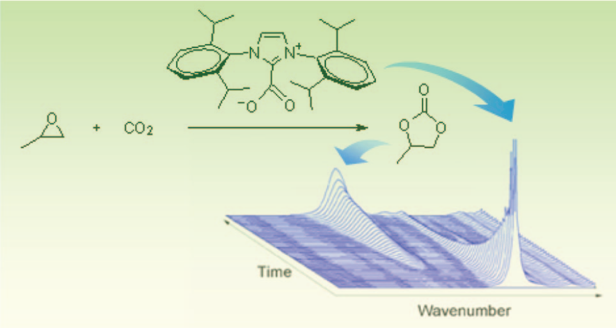

Thermal stability of CO_2 adducts of *N*-heterocyclic carbenes (NHCs) was studied by means of in situ FTIR method with monitoring of the $\nu(CO_2)$ region of the infrared spectra under various conditions. 1,3-Bis(2,6-diisopropylphenyl)imidazolinium-2-carboxylate (SIPr-CO_2) shows higher thermal stability compared with 1,3-bis(2,6-diisopropylphenyl)imidazolium-2-carboxylate (IPr-CO_2). The presence of free CO_2 can significantly inhibit the decomposition of NHC-CO_2 adducts, while the addition of an epoxide such as propylene oxide has a negative effect on stabilizing these adducts. As zwitterionic compounds, NHC-CO_2 adducts were also proved to be effective organic catalysts for the coupling reaction of CO_2 and epoxides to afford cyclic carbonates, for which a possible mechanism was proposed. Among these NHC-CO_2 adducts, the relatively unstable IPr-CO_2 exhibits the highest catalytic activity. The presence of an electrophile such as SalenAlEt could greatly improve the catalytic activity of IPr-CO_2 due to intermolecular cooperative catalysis of the binary components.

Introduction

N-Heterocyclic carbenes (NHCs), first isolated by Arduengo and co-workers in 1991,[1] have become of considerable importance in homogeneous catalysis. They have been extensively employed as versatile ligands for a large variety of organometallic complexes.[2] Furthermore, NHCs have proven to be effective organocatalysts for numerous organic transformations such as benzoin condensation,[3] Stetter reactions,[4] ring-opening polymerization,[5] transesterification reactions,[6] homoenolate formations[7]and other reactions.[8]

NHCs are usually generated by deprotonation of corresponding imidazol(in)ium salts with strong bases. Since free NHCs

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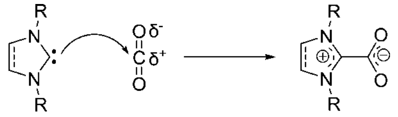
SCHEME 1. Synthesis of *N*,*N*′-Disubstituted Imidazol(in)ium-2-carboxylates



are air- and moisture-sensitive, more stable NHCs adducts such as haloalkane,[9] alcohol,[10] silver,[11] and CO_2 adduct precursors[12] have been developed to thermally liberate NHCs more conveniently. Among these compounds, NHC-CO_2 adducts (for example, *N*,*N*′-disubstituted imidazol(in)ium-2-carboxylates) can efficiently transfer NHCs to transition metal complexes with release of CO_2 under mild conditions.[12] Likewise, Louie and co-workers found that carboxylate groups of *N*,*N*′-disubstituted imidazol(in)ium-2-carboxylates can easily exchange with free CO_2 in solution. Usually, decarboxylation of NHC-CO_2 adducts was thought to be a key step in this transformation. Therefore, the study on stability of NHC-CO_2 adducts appears to be extremely necessary and may offer new opportunity for their further applications.

From a structural point of view, NHC-CO_2 adducts *N*,*N*′-disubstituted imidazol(in)ium-2-carboxylates can be considered to be zwitterionic compounds formed by NHCs nucleophilic attack on the weak electrophilic carbon center of the CO_2 molecule (Scheme 1), just like amidine- or guanidine-CO_2 adducts. It has been reported that sterically hindered strong organic base 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) could catalyze the coupling reaction of CO_2 and epoxides to provide corresponding cyclic carbonates. In this system, CO_2 was thought to be first activated through the formation of a zwitterionic adduct MTBD-CO_2 and thereby adding to the epoxide via nucleophilic attack of carboxylate group.[13] This observation also stimulated us to explore the feasibility of the zwitterionic compounds NHC-CO_2 as organic catalyst for the above-mentioned reaction.

Herein, we report the thermally stability of various NHC-CO_2 adducts *N*,*N*′-disubstituted imidazol(in)ium-2-carboxylates (Figure 1) and their catalytic activities toward the coupling reaction of CO_2 with terminal epoxides.

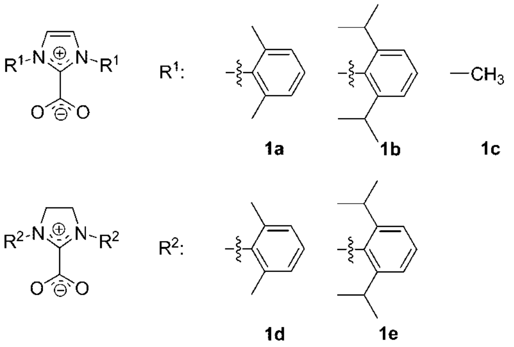


FIGURE 1. Structures of the *N*,*N*′-disubstituted imidazol(in)ium carboxylates.

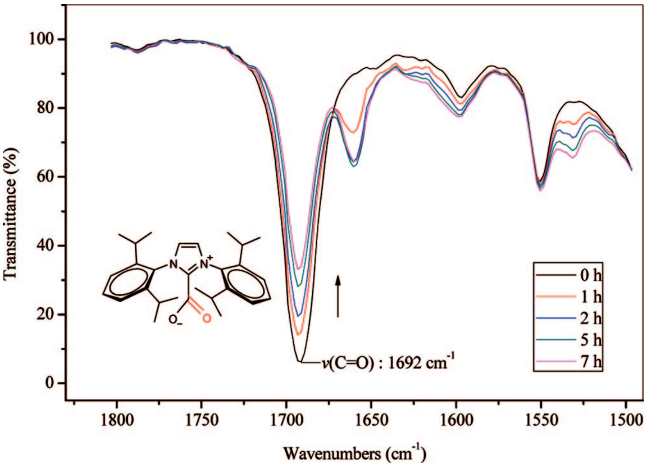


FIGURE 2. FTIR spectra of **1b** (IPr-CO_2) in CH_2Cl_2 at various times at 50 °C.

Results and Discussion

N,*N*′-Disubstituted imidazol(in)ium-2-carboxylates **1a**−**1e** (NHCs-CO_2 adducts) shown in Figure 1 were prepared by reaction of the corresponding NHCs with CO_2 according to the literature procedures.[12] Although they exhibit good stability in solid state at room temperature, these NHCs-CO_2 adducts dissolved in organic solvents were prone to decomposition via decarboxylation, especially at elevated temperature. Because of their higher solubility in CH_2Cl_2 compared with other prepared NHC-CO_2 adducts, thermal stability of 1,3-bis(2,6-diisopropylphenyl)imidazolium-2-carboxylate (IPr-CO_2, **1b**) and 1,3-bis(2,6-diisopropylphenyl)imidazolinium-2-carboxylate (SIPr-CO_2, **1e**) was investigated through in situ monitoring of the $\nu(CO_2)$ region of the infrared spectrum utilizing a temperature-controlled high pressure liquid cell (HPL-TC). Figure 2 displays the decarboxylation profile of **1b** in CH_2Cl_2 with time at 50 °C. The absorption intensity of asymmetric $\nu(CO_2)$ vibrations (1692 cm^{-1}) gradually decreases with prolonging time, which clearly indicates the decarboxylation of NHC-CO_2 adduct **1b**. In comparison to **1b** with an unsaturated imidazolinium ring, **1e** with a saturated counterpart exhibits higher thermal stability (Figure 3).

To assess the effect of temperature on thermal stability of NHC-CO_2 adducts in solution, in situ infrared monitoring of **1b** in CH_2Cl_2 solution was conducted at various temperatures (Figure 4). As anticipation, temperature has a pronounced effect on thermal stability of the NHC-CO_2 adducts. At 12 °C, **1b** is very stable in CH_2Cl_2, and no obvious change in intensity at

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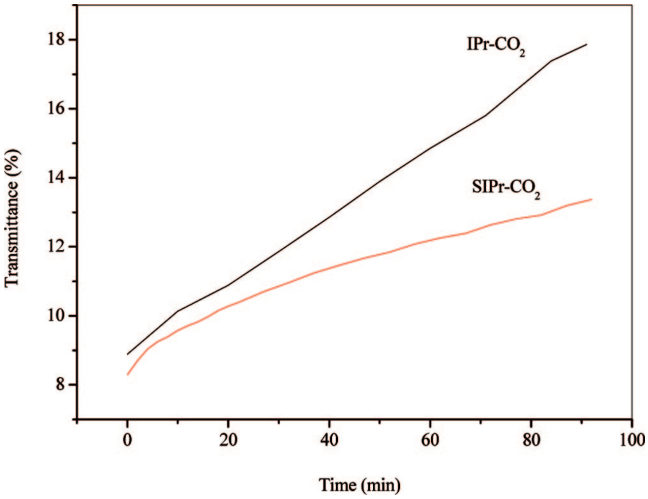

FIGURE 3. Plots of transmittance at 1692 cm^{-1} versus time for decomposition of **1b** (IPr-CO_2) and **1e** (SIPr-CO_2) in CH_2Cl_2 at 50 °C.

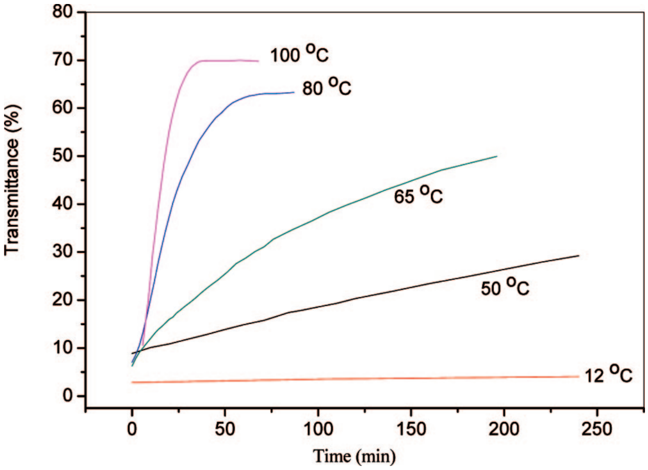

FIGURE 4. Plots of transmittance at 1692 cm^{-1} versus time for the decomposition of **1b** at various temperature.

1692 cm^{-1} was observed in 4 h. On the contrary, most of **1b** decomposed within 1 h at 100 °C.

Interestingly, the presence of free CO_2 can effectively inhibit the decomposition of NHC-CO_2 adducts. For example, when CO_2 pressure of the system was maintained at 2.0 MPa, the decomposition rate of **1b** at 100 °C obviously decreased (Figure 5; a vs c, b vs d). It can be reasonably assumed that a dynamic equilibrium of NHC-CO_2 adducts, free CO_2, and the corresponding NHCs exists in the organic solution of NHC-CO_2 adducts. As a result, excess CO_2 is beneficial to the formation of NHC-CO_2 adduct. In contrast to this result, the presence of an epoxide such as propylene oxide seemed to accelerate the decomposition of NHC-CO_2 adducts (Figure 5; a vs b, c vs d) and simultaneously afforded cyclic carbonate originating from the coupling of CO_2 and epoxide (Figure 6). As clearly shown in Figure 6a, IPr-CO_2 (1692 cm^{-1}) was decomposed gradually and released CO_2 (2342 cm^{-1}) and then reacted with propylene oxide to form propylene carbonate (1803 cm^{-1}). We were interested to note the recent report of Barbarini et al. on the synthesis of cyclic carbonates from CO_2 and epoxides using MTBD (a sterically hindered strong organic base) as catalyst, in which CO_2 was activated through the formation of a zwitterionic adduct MTBD-CO_2 and thereby adding to the epoxide via nucleophilic attack of carboxylate group.[13] The fact stimulated us to explore the feasibility of the zwitterionic NHC-CO_2 adducts as catalyst for the coupling of CO_2 and epoxides.

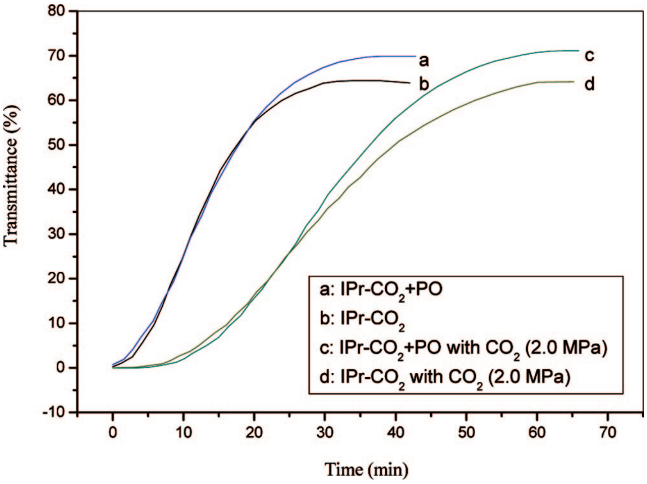

FIGURE 5. Plots of transmittance at 1692 cm^{-1} versus time for the decomposition of **1b** in the presence of propylene oxide and/or free CO_2 (2.0 MPa) at 100 °C.

We gratefully found that NHC-CO_2 adducts alone could catalyze the coupling reaction of CO_2 with propylene oxide to afford propylene carbonate with 100% selectivity. A possible catalysis mechanism (Scheme 2) was proposed on the basis of the study on thermal stability of NHC-CO_2 adducts, as well as the previous papers.[5g,14] The zwitterionic compound NHC-CO_2 could add to the epoxide via nucleophilic attack and generate the new zwitterion, in which the alkoxide can add to the C2 carbon of the azolium, thereby generating a neutral imidazolidine spriocycle. A similar spiro imidazolidine compound has been isolated successfully by the Waymouth group, when NHC reacted with β-butyrolactone.[5g] Then the nucleophilic attacks of the formed alkoxy anion toward the carbon atom of carbonyl group produced cyclic carbonate by intramolecular cyclic elimination. Finally, the produced free NHC quickly reacted with CO_2 to regenerate NHC-CO_2 adduct.

It is noteworthy that **1b** exhibits excellent activity and affords cyclic carbonate with 100% yield at 120 °C for 24 h, whereas much lower yields were observed in some systems of NHC-CO_2 adducts with low solubility in CH_2Cl_2 under the same conditions (Table 1, entries 1−5). Interestingly, unsaturated imidazolium carboxylates (**1a** and **1b**) give higher yield compared with their saturated counterparts (**1d** and **1e**). The result indicates that NHC-CO_2 adduct with higher thermal stability shows lower catalytic activity at the same reaction conditions. This finding can be rationally explained by the mechanism shown in Scheme 2 where cleavage of the C(carbene)−C(carboxylate) bond is more difficult for the intermediate formed by NHC-CO_2 adduct with higher thermal stability.

Once having established that **1b** was an excellent catalyst for the coupling reaction of CO_2 and propylene oxide, capability of **1b** as a catalyst was further investigated using a variety of challenging epoxides substrates to synthesize the corresponding cyclic carbonates. As shown in Table 1 (entries 6−9), IPr-CO_2

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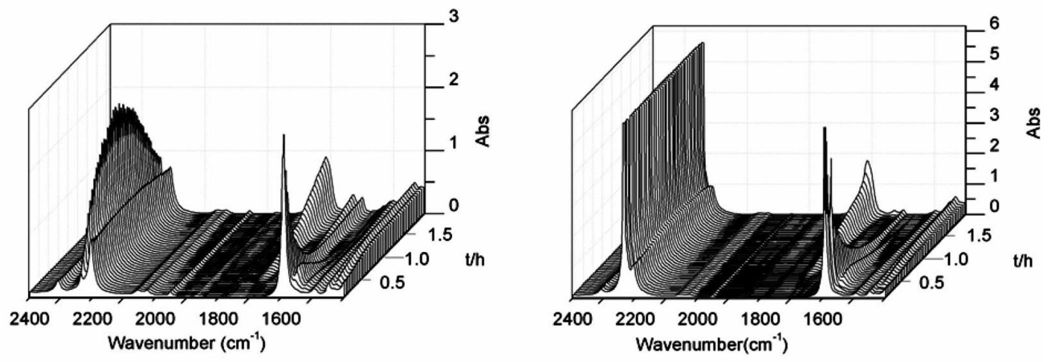


a **b**

FIGURE 6. In situ infrared monitoring of the IPr-CO_2/propylene oxide system in the absence (a) and presence (b, 2.0 MPa) of CO_2 in the $\nu(CO_2)$ region at 100 °C.

SCHEME 2. Possible Mechanism for the Reaction of CO_2 with Epoxides Catalyzed by NHC-CO_2 Adduct Alone

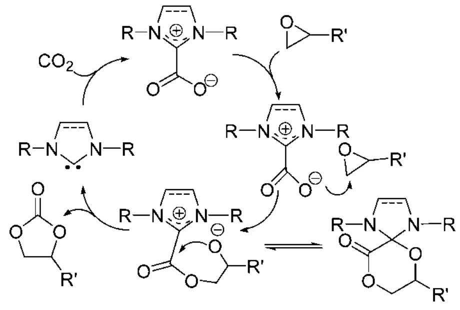
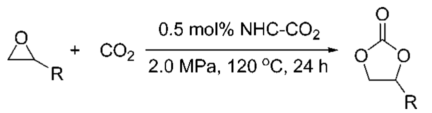


TABLE 1. Reaction of CO_2 with Various Epoxides Catalyzed by NHC-CO_2 Adducts[a]

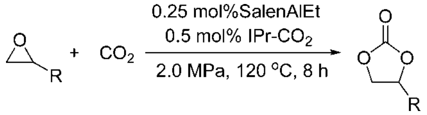


entry	R	NHC-CO_2	yield (%)[b]
1	Me	**1a**	45
2	Me	**1b**	100
3	Me	**1c**	19
4	Me	**1d**	25
5	Me	**1e**	87
6	Et	**1b**	96
7	^{n}Bu	**1b**	91
8	CH_2Cl	**1b**	100
9	Ph	**1b**	97
10	Me[c]	**1b**	100

[a] Reaction condition: 50 mmol epoxides, 0.5 mol % NHC-CO_2, 2 mL CH_2Cl_2. [b] Yield determined by ^{1}H NMR spectroscopy. [c] (*R*)-Propylene oxide.

can effectively catalyze the coupling reaction of monosubstituted terminal epoxides with CO_2 to afford corresponding cyclic carbonates in good to excellent yields with 100% selectivity. The reaction of (*R*)-propylene oxide with CO_2 catalyzed by **1b** affords the corresponding (*R*)-propylene carbonate in 100% yield with retention of stereochemistry (entry 10), which illustrates that the nucleophilic attack of the carboxylate anion exclusively occur at the less sterically hindered carbon atom of the terminal epoxide.

TABLE 2. Reaction of CO_2 with Various Epoxides Catalyzed by a Binary SalenAlEt/IPr-CO_2 System[a]



entry	R	yield (%)[b]
1	Me	100
2	Et	99
3	^{n}Bu	99
4	CH_2Cl	98
5	Ph	96
6[c]	Me	<5

[a] Reaction condition: 50 mmol epoxides, 0.25 mol % SalenAlEt, 0.5 mol % IPr-CO_2, 2 mL CH_2Cl_2. [b] Yield determined by ^{1}H NMR spectroscopy. [c] SalenAlEt alone as catalyst.

In previous papers, we have reported that binary catalyst systems consisting of an electrophile and a nucleophile are more effective in catalyzing the coupling reaction of epoxides with CO_2.[15] As expected, in comparison to the NHC-CO_2 adduct **1b** alone as catalyst, the presence of an electrophile such as SalenAlEt as cocatalyst could remarkably enhance its catalytic activity in the coupling reaction of CO_2 with various epoxdes (Table 2), while SalenAlEt alone did not effectively catalyze this reaction under the same conditions (entry 6). The result demonstrates the existence of an intermolecular cooperative catalysis of the binary components, which significantly increases the reaction rate.

On the basis of our study on the thermal stability of NHC-CO_2 adducts described above, in combination with the earlier reported mechanism for the coupling of CO_2 with epoxide catalyzed by binary catalyst systems,[15−17] we speculate that this reaction catalyzed by IPr-CO_2/SalenAlEt could occur according to the three paths shown in Scheme 3. Shi and co-workers reported that binaphthyldiamino Salen-type Zn, Cu, and Co complexes could catalyzed the coupling of CO_2 with terminal epoxides in the presence of organic bases.[17a] A Lewis acid and

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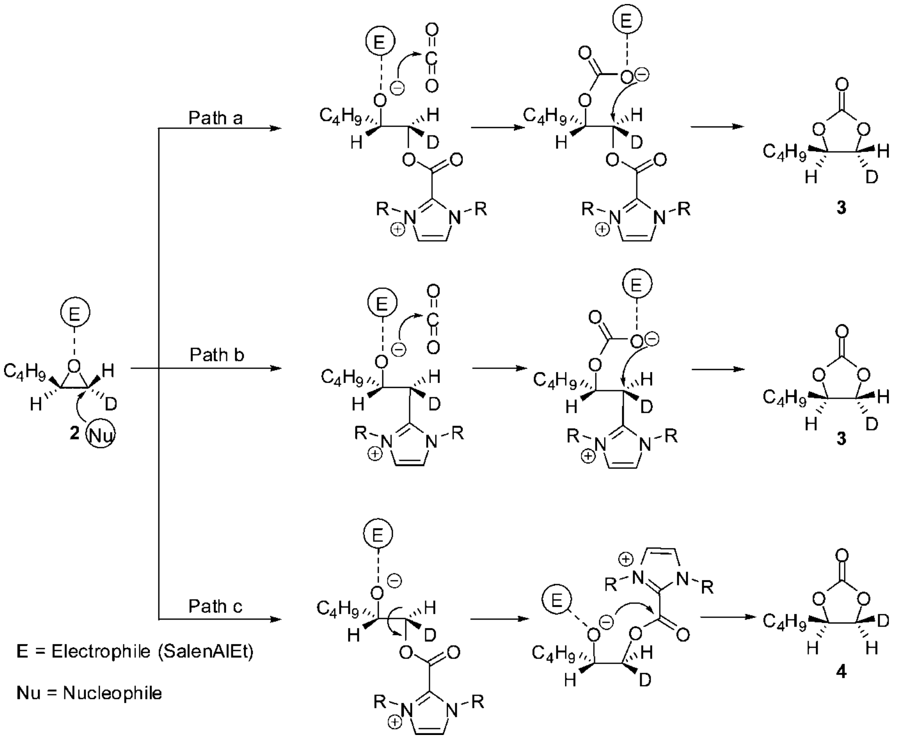
SCHEME 3. Possible Mechanism for Reaction of CO_2 with Epoxide Catalyzed by a Binary SalenAlEt/NHC-CO_2 System



Lewis base cocatalyzed mechanism was proposed on the basis of the reaction of *trans*-deuterioethene oxide with CO_2. For the binary catalyst system of SalenAlEt/NHC-CO_2 adduct, it is clear that the electrophilicity of Al^{3+} in SalenAlEt and the nucleophilicity of the NHC-CO_2 adduct or the decomposed free NHC cooperatively catalyze the coupling reaction of CO_2 and epoxides. In order to clarify the reaction mechanism, we also synthesized *trans*-1-deuterio-1,2-hexene oxide (**2**)[18] and utilized it as the substrate in the reaction with CO_2 catalyzed by SalenAlEt/IPr-CO_2 at 50 °C. If the reaction proceeded via path c, *cis*-deuterated cylcic carbonate (**4**) should be the dominant product. Indeed, we found that *trans*-1-deuterio-1,2-hexene carbonate (**3**) was formed exclusively, with the aid of ^1H NMR analysis (Supporting Information, Figure S1). The result suggests that the formation of cyclic carbonate in our reaction system proceeds via path a or b as show in Scheme 3, in which the epoxide is first activated by its coordination to the central Al^{3+} of SalenAlEt, then is ring-opened by nucleophilc attack of NHC-CO_2 adduct or free NHC at the less substituted C−O bond, and further reacts with CO_2 to afford the corresponding *trans*-deuterated cyclic carbonate. The formation of *trans*-1-deuterio-1,2-hexene carbonate (**3**) can involve both path a or b, but probably only one predominantly plays a significant role, which is dependent on reaction conditions such as temperature and pressure. Usually, high temperature and low CO_2 pressure are in favor of the decomposition of NHC-CO_2 adducts to produce NHC, thereby benefiting the reaction to proceed via path b.

In situ infrared monitoring of the SalenAlEt/IPr-CO_2/propylene oxide system in the $\nu(CO_2)$ region also supports the mechanism that the reaction proceeds via path a or b. A solution of SalenAlEt/IPr-CO_2/propylene oxide (molar ratio 1:2:100) in CH_2Cl_2 was transferred to the HPL-TC and monitored at 80 °C in the absence of CO_2. A time-dependent IR stack plot of the above reaction sequence is shown in Figure 7. The carbonyl peak of IPr-CO_2 at 1692 cm^{-1} gradually shrank, which indicated decomposition of IPr-CO_2. If the reaction proceeds via path c, the $\nu(CO_2)$ vibration of propylene carbonate at 1803 cm^{-1} should be detected simultaneously at the beginning of the decomposition of IPr-CO_2. However, the carbonyl peak was observed after the reaction was carried out for about 1 h. The result demonstrates that part of IPr-CO_2 was first decomposed into IPr and CO_2, and then the epoxide coordinated to the central Al^{3+} of SalenAlEt was ring-opened by nucleophilc attack of nondecomposed IPr-CO_2 adduct or free IPr and further reacted with CO_2 originated from the decomposition of IPr-CO_2 adduct to give cyclic propylene carbonate.

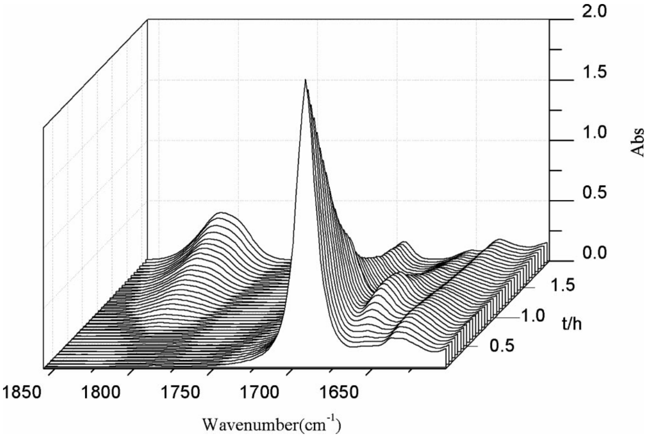


FIGURE 7. In situ infrared monitoring of SalenAlEt/IPr-CO_2/propylene oxide system in the $\nu(CO_2)$ region.

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[18] (a) Ratzenhofer, M.; Kisch, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 317–318. (b) Skell, P. S.; Freeman, P. K. *J. Org. Chem.* **1964**, *29*, 2524–2526. (c) Refrik, M. D.; Froese, R. D. J.; Goddard, J. D.; Pham, H. H.; Pippert, M. F.; Schwan, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 184–192. (d) Schwan, A. L.; Roche, M. R.; Gallagher, J. F.; Fergwson, G. *Can. J. Chem.* **1994**, *72*, 312–324. (e) Paddon-Jones, G. C.; McErlean, C. S. P.; Hayes, P.; Moore, C. J.; Konig, W. A.; Kitching, W. *J. Org. Chem.* **2001**, *66*, 7487–7495.

Conclusion

We have investigated the thermal stability of NHC-CO_2 adducts in organic solvent by means of an in situ FTIR method. Saturated imidazolinium carboxylates exhibit higher thermal stability compared with their unsaturated counterpart. The presence of free CO_2 can effectively inhibit thermal decomposition of NHC-CO_2 adducts, while the addition of an epoxide accelerates their decomposition and simultaneously provides the corresponding cyclic carbonate. Soluble NHC-CO_2 adducts alone are effective organic catalysts for the coupling reaction of CO_2 and epoxides to synthesize cyclic carbonates. Relatively unstable IPr-CO_2 adduct exhibited higher catalytic activity compared with other NHC-CO_2 adducts at the same conditions. The reaction of CO_2 with (*R*)-propylene oxide catalyzed by IPr-CO_2 adduct affords the corresponding (*R*)-propylene carbonate in 100% yield with retention of stereochemistry. The presence of SalenAlEt could greatly improve the catalytic activity of IPr-CO_2 due to intermolecular cooperative catalysis of the binary components.

Experimental Section

Typical Procedure for in Situ Infrared Monitoring of NHC-CO_2 Adducts. The temperature-controlled high pressure liquid cell (HPL-TC) was installed with ZnS windows. A solution of NHC-CO_2 adduct in CH_2Cl_2 was transferred into the HPL-TC under N_2 atmosphere. Then the HPL-TC was installed in the FTIR spectrometer, and data were collected over an appropriate period of time.

Typical Procedure for the Reaction of CO_2 with Epoxides. In a typical procedure, 50 mmol of epoxide and 0.108 g (0.25 mmol) of IPr-CO_2 were dissolved in 2 mL of CH_2Cl_2, the solution was added to the 40 mL autoclave under N_2, and the autoclave was closed and pressurized with 2.0 MPa CO_2. The reaction was carried out at 120 °C for 24 h with continuous stirring. Then, the autoclave was cooled, and the excess CO_2 was vented. The yield of cyclic carbonates was determined by ^{1}H NMR analysis.

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Supporting Information Available: Experimental procedures, characterization data for compounds **1a**−**1e**, *trans*-1-deuterio-1-hexene, *trans*-1-deuterio-1,2-hexene oxide, various cyclic carbonates, and SalenAlEt. This material is available free of charge via the Internet at http://pubs.acs.org.

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