



Intricacies of Cation–Anion Combinations in Imidazolium Salt-Catalyzed Cycloaddition of CO₂ Into Epoxides

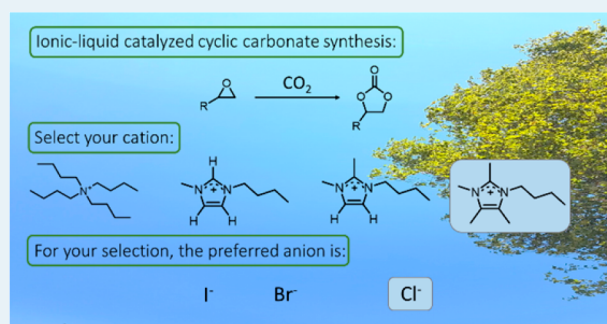
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S Supporting Information

ABSTRACT: The cycloaddition of CO₂ into epoxides catalyzed by imidazolium and related salts continues to attract attention due to the industrial importance of the cyclic carbonate products. The mechanism of the imidazolium-catalyzed transformation has been proposed to require the participation of the acidic C2 proton. However, other simple salts without acidic protons, such as *N,N,N,N*-tetrabutylammonium chloride, are also efficient catalysts for the reaction. Hence, we decided to investigate the role of the ring protons of imidazolium salts in this reaction. To this end, we systematically studied the catalytic activity of a series of methyl-substituted imidazolium cations, in the presence of various halide anions, both by experiment and in silico. Our results demonstrate that, while stabilization of intermediates by C2, C4, or C5 protons in imidazolium salts takes place, it is the nucleophilicity of the anion that governs the overall activity, which is intimately related to the strength of the interactions between the cation and anion. Consequently, the reactivity of the halide anion strongly depends on the nature of the cation and cosolvents. This study completes the (known) mechanism and should facilitate the development of highly efficient catalysts.

KEYWORDS: catalysis, sustainable chemistry, ionic liquids, imidazolium salts, carbon dioxide, cyclic carbonates



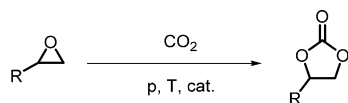
INTRODUCTION

Anthropogenic emissions of CO₂ have led to ever-increasing concentrations of CO₂ in the atmosphere, resulting in global warming.¹ With the increasing abundance of this waste gas, in combination with its low cost and toxicity, CO₂ is increasingly being regarded as a useful C1 source. In this respect, CO₂ transformations into various compounds has been proposed.² Notable examples of such transformations include direct reduction of CO₂ into potential fuels such as CH₄,³ CH₃OH,^{4,5} and formic acid⁶ and in the synthesis of ureas,² quinazoline-2,4-(1*H*,3*H*)-diones,⁷ lactams,⁸ cyclic carbonates,⁹ and others. The preparation of cyclic carbonates from CO₂ and epoxides (the CCE reaction; Scheme 1) has attracted considerable attention due to the importance of the target products.^{10,11} The CCE reaction is 100% atom efficient and is often conducted under solvent-free conditions, further high-

lighting its green metrics.^{12,13} For all these reasons, numerous classes of catalysts have been designed and evaluated.^{14–21}

A potent class of organocatalysts for the CCE reaction comprises organic salts with a halide anion.^{22–24} Various cations have been successfully employed, with tetraalkylammonium salts and imidazolium salts predominant.^{25,26} In the case of imidazolium salts, the transformation was proposed to take place in three steps: (i) ring opening of the epoxide by the nucleophilic anion of the salt, (ii) insertion of CO₂ into the C2-proton-stabilized alkoxide, and (iii) release of the anion via an intramolecular S_N2 reaction (Scheme 2).²⁷ The C2 proton of the imidazolium ring is considered key due to favorable H-bonding interactions with the substrate as well as the alkoxide transition state,²⁸ and both DFT and experimental data have been used to highlight its importance.^{27,29} For example, it was shown that H-bonding could activate the epoxide and decrease the energy barrier of the ring-opening step.²⁷ Most studies, however, overlook the acidity of the C4 and C5 protons of the imidazolium ring, despite their acidity being comparable to that of the C2 proton.³⁰ Furthermore, when the C2 position is

Scheme 1. Cycloaddition of CO₂ into Epoxides To Afford Cyclic Carbonates

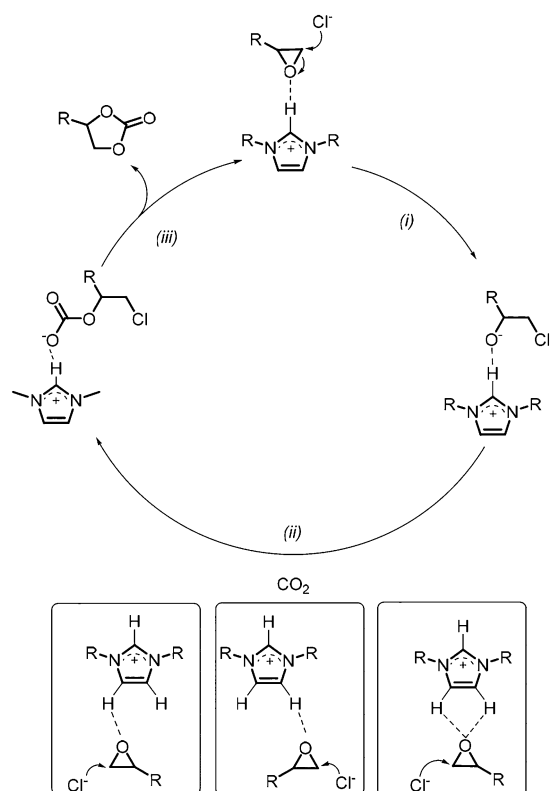


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Scheme 2. Accepted Mechanism of the CCE Reaction (Top) And Additional Possible H Bonds between the Epoxide and the Acidic Protons on the Imidazolium Ring (Bottom)



blocked, the halide strongly interacts with the C4 proton in the solid state,³¹ which could affect the ability of the anion to open the epoxide ring. Moreover, tetraalkylammonium, phosphonium, and pyrrolidinium salts do not possess acidic protons capable of forming pronounced H bonds with the epoxide substrate or the alkoxide transition state, and yet they are potent catalysts for the transformation.²⁵ Unfortunately, direct comparison between catalysts is hindered by the lack of benchmark conditions³² and, since almost every study is “unique”, it is difficult to assess whether true progress has been made. Catalyst development is then frequently dependent on quantum calculations, which are often difficult to verify experimentally due to the poor solubility of many of these salts, leading to pseudoheterogeneous conditions.³³

Hence, we decided to systematically investigate and clarify the role of the acidic C2, C4, and C5 protons of the imidazolium ring, evaluate the influence of the cation on the counteranion, and establish the key differences between the imidazolium- and ammonium-catalyzed reactions under homogeneous (standardized) reaction conditions. For this purpose, we prepared a series of imidazolium salts with varying numbers of ring substituents and different halide counterions and evaluated them in the CCE reaction using epichlorohydrin as the substrate (Figure 1 and Table S1). The activity of these catalysts was compared to that of tetra-*n*-butylammonium halides, and key aspects of the transformation were elucidated with the aid of DFT calculations.

RESULTS AND DISCUSSION

The salt catalysts, 1X–4X (Figure 1) were evaluated under a kinetic regime (i.e., to allow a comparison of the yields at

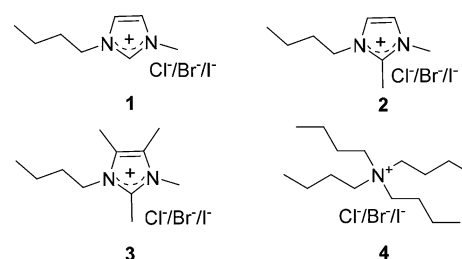


Figure 1. Salt-based catalysts 1X–4X (where X = Cl⁻, Br⁻, I⁻) studied in this work.

moderate conversions) in the cycloaddition reaction between epichlorohydrin and CO₂ at atmospheric pressure without a cosolvent (Table 1). Note that a similar analysis is not possible

Table 1. Influence of the Cation and Anion on the CCE Reaction in the Synthesis of Epichlorohydrin Carbonate^a

entry	catalyst	yield (%)
1	1Cl	52
2	2Cl	49
3	3Cl	51
4	4Cl	56
5	1Br	53
6	2Br	46
7	3Br	60
8	4Br	45
9	1I	62
10	2I	50
11	3I	53
12	4I	36

^aReaction conditions: epichlorohydrin (1 g, 10.8 mmol), catalyst (5 mol %), CO₂ (1 bar), 50 °C, 3 h, average yield from three runs. See the Supporting Information for full experimental details.

with propylene oxide (the most widely used epoxide) at atmospheric pressure, as the catalysts are not completely soluble in the substrate, which appears to be frequently overlooked in the literature. Under these standardized reaction conditions, the most common imidazolium salt, [BMIm]Cl (1Cl), gave the product in a 52% yield (Table 1, entry 1). Methylation of the C2 position, i.e. catalyst 2Cl, resulted in a slightly lower yield of 49% (Table 1, entry 2) in comparison to that obtained with 1Cl as previously reported,³⁴ indicating that the H-bonding between the epoxide ring or the reaction intermediates with the C2 proton could play a role in the reaction. The relatively small difference between 1Cl and 2Cl could possibly be attributed to the H-bonding ability of 2Cl via its C4 and C5 protons. However, the fully substituted imidazolium salt 3Cl, which cannot form strong H bonds at any position, resulted in a yield comparable to that of 1Cl of 51% (Table 1, entry 3). In addition, *N,N,N,N*-tetrabutylammonium chloride (4Cl) is even more active than 1Cl, giving the product in 56% yield (Table 1, entry 4). These results rule out the possibility that a carbene, formed via the deprotonation of the C2 proton or the more rare C4 or C5³⁵ position of the imidazolium ring by the alkoxide intermediate (Scheme 2, step i), is the key active catalytic species.^{28,34} In addition, H-bonding

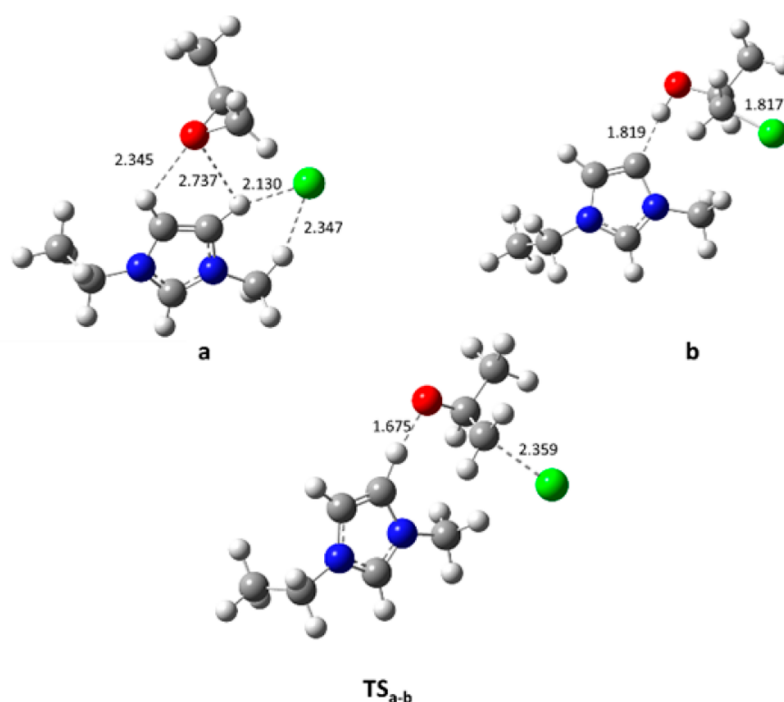


Figure 2. Optimized geometries for the intermediates and transition states for C4–H-assisted ring opening of the epoxide computed at the B3PW91-D3/6-31G** level.

does not appear to be crucial for the catalysis either, as the yields are comparable for all of the imidazolium salts and the tetrabutylammonium catalyst (52%, 49%, 51%, and 56% for 1Cl–4Cl, respectively), irrespective of whether they can form H bonds or not.

Although the experimental results suggests that H-bonding via the ring protons does not play a vital role in the reaction, the substantial computational evidence that suggests otherwise cannot be disregarded, especially with respect to the rate-limiting epoxide ring opening step (Scheme 2, step *i*).^{29,36} Note that, when additional or external H bond donors are present, computational findings suggest that the rate-determining step can be, but is not limited to, epoxide ring opening.^{37,38} Hence, we decided to perform calculations on the energy barrier for the epoxide ring opening with the three imidazolium catalysts 1Cl–3Cl. In addition, we expanded these calculations to include the possibility of the epoxide ring opening via participation of the C4 and C5 protons, which were previously not considered.^{27,29,34,39,40} The strengths of C2H···O, C4H···O, and C5H···O H bonds in imidazolium IIs are quite similar,³⁰ and our DFT computations on the stabilization of the alkoxide show that an energy barrier for the ring-opening step via participation of the C4 proton (27.3 kcal mol⁻¹, Figure 2) is only marginally higher than the barrier for that of the C2 proton participation (25.9 kcal mol⁻¹, Figure S1). The calculations for the ring-opening step with the fully substituted imidazolium cation 3Cl, which does not contain a strong H-bonding donor, give an energy barrier of 23.0 kcal mol⁻¹, even lower than that of 1Cl or 2Cl (Figure S2). Moreover, the enthalpies ($-\Delta H_{\text{HB}}$) of nonconventional CH···O H bonds with the epoxide, estimated using literature approaches,³⁰ are quite small relative to typical conventional OH···O H bonds: compare $-\Delta H_{\text{HB}}(\text{C5H}\cdots\text{O}) \approx 1.2$ kcal mol⁻¹ for structure a (Figure 2) vs $-\Delta H_{\text{HB}}(\text{OH}\cdots\text{O}) \approx 4.2$ kcal mol⁻¹ for the gas-phase H-bonded complex of the epoxide with methanol. These results indicate that even if H bonds are able to activate

epoxides toward ring opening, they do not play a key role in the ring opening of the epoxide, and that another underlying feature or a combination of features of the catalyst must control the observed reaction rate. Note that an ethyl group was used for the calculations instead of a butyl group (Figure 2, 3Cl), as it was previously demonstrated that the side chain does not affect the computational results in the gas phase.²⁷ However, experimentally smaller alkyl chains reduce the solubility of the catalyst in the epoxide, leading to lower yields.⁴¹

The role of the imidazolium ring protons has only been associated with the activation of the epoxide via H-bonding. However, they may also interact with the anion of the salt, leading to a reduction in the nucleophilicity of the anion and its ability to open the epoxide ring. To understand the relationship between cation–anion interactions in the CCE reaction, the effect of the halide anion was also investigated using the salts 1X, 2X, 3X, and 4X (where X = Cl⁻, Br⁻, I⁻). Numerous studies have confirmed the importance of the halide on the catalytic activity with the trend for imidazolium cations usually being I⁻ > Br⁻ > Cl⁻, which is attributed to the nucleophilic character of the anion under the catalytic conditions. Interestingly, for 1X, containing three acidic protons, the order is I⁻ > Br⁻ \approx Cl⁻ (62, 53, and 52%, respectively; Table 1, entries 1, 7, and 13). For 2X, with a methyl group at the C2 position, the trend differs, with the chloride salt being more active than the bromide salt: i.e., I⁻ \approx Cl⁻ > Br⁻ (50, 49 and 46%, respectively, Table 1, entries 2, 8 and 14). For 3X, which is fully substituted, the order differs again, i.e. Br⁻ > Cl⁻ \approx I⁻ (60, 53, and 51%, respectively; Table 1, entries 5, 11 and 17). Finally, for 4X, the benchmark tetrabutylammonium salt, the trend is completely reversed to that of the 1X series, with Cl⁻ > Br⁻ > I⁻ (56, 45, and 36%, respectively), which concurs with a previous study.⁴²

To rationalize the trends observed for the different catalysts with various halide anions, DFT calculations were performed and experiments were conducted with water added to the

reaction (employed as H-bond promoter). In order to quantify the nucleophilicity of the anion using DFT calculations, we employed a probe molecule, MeOH, and calculated the length of the H bond between the anion of the catalyst with the probe. As expected, the computations demonstrate that the Cl⁻ anion of the 3Cl ion pair forms a shorter (i.e., stronger) H bond with MeOH in comparison to the Cl⁻ anion of the 1Cl ion pair (2.050 Å vs 2.108 Å, respectively). Thus, the ability of the anion in 3Cl to donate its lone pair to the hydrogen atom of the -OH group is stronger than that of the same anion in 1Cl. Most probably, the same is the case with respect to the relative capacity of the anions in 3Cl and 1Cl to donate their lone pairs to the carbon atom of the epoxide ring, indicating that H bonds are potentially detrimental to the reaction and that 3Cl should be a better catalyst than 1Cl. However, experimentally, this is not the case, as both 1Cl and 3Cl demonstrated practically equivalent activity.

The addition of water as an external H-bond source was previously demonstrated to promote the CCE reaction when it was employed in ca. 30 mol % amount, regardless of the cation-anion combination in the 1X and 4X catalyst series. However, higher concentrations (100 mol % and above) are detrimental to the reaction and lead to unwanted side reactions.⁴³ We therefore decided to test the effect of a catalytic quantity of water (i.e., 5 mol %, the same concentration as the catalyst) as an external H-bond donor and its effect on the reaction to further probe the H-bond interactions between the epoxide, the halide anion, and the H-bond donor (water and/or the acidic protons in the imidazolium cation). Catalytic quantities of water (5 mol %) were added to the reactions employing the series of 1X and 4X halide catalysts (Table S2). The trend for the imidazolium salts 1X remained largely unchanged, with only a slight increase in yield obtained with 1Br (from 53% to 57%) and 1I (from 62% to 65%) and a slight decrease with 1Cl (from 52% to 46%). However, the order for the ammonium salt series 4X was reversed in the presence of 5 mol % water, with the order being 4I > 4Br > 4Cl. The yield also increases significantly with 4I from 36% in the absence of water to 68% with 5 mol % of water present (Table 1, entry 12, and Table S2, entry 6). A higher yield was also obtained with 4Br in the presence of 5 mol % of water (from 45 to 59%), whereas a slight detrimental effect was observed with the catalyst 4Cl (from 56 to 50%).

The difference in the magnitude of the change in the yield when water is present between the catalysts may be attributed to the different H-bonding strengths of the cation and solvation of the anion. With the tetrabutylammonium cation, which cannot form a H-bond with the substrate, the effect of the addition of water, which can form a H-bond with the substrate, is much more profound. With the imidazolium cation the effect of water is counterbalanced by the acidic ring protons on the cation. Additionally, the solvation enthalpy of the halide by water is important and follows the order chloride > bromide > iodide. Thus, the nucleophilicity of the anions is reduced, as discussed above, resulting in a decrease in reaction rate for all catalysts, with the effect being most pronounced for the chloride anion. The overall catalytic activity is therefore dependent on the balance between the nucleophilicity of the anion, which is reduced following solvation by water,⁴⁴ and the H-bond-induced activation of the epoxide ring, which promotes the reaction. Hence, the highest yields are obtained with iodide anions in the presence of H-bonding donors, as iodide is least

strongly solvated by water and benefits the most from H-bond-induced epoxide activation.³⁶

In summary, we have demonstrated that methyl groups on the cation of simple imidazolium salts do not significantly affect the efficacy of the CCE reaction. When acidic protons are present in the imidazolium ring of the cation (C2, C4, C5, or a combination thereof), the acidic protons simultaneously activate the epoxide (as demonstrated previously)³⁴ but interact with the halide ion to reduce its nucleophilicity (as we have shown here). In the absence of acidic protons (3X and 4X), the epoxide is presumably less well activated but the nucleophilicity of the halide is higher due to weaker cation-anion pairing, leading to higher activities, and the preferred anion is strongly cation dependent. The experimental data demonstrate that higher nucleophilicity (i.e. lower interactions between the anion and the cation) governs the activity of the catalyst. When H-bonding interactions between the cation and substrate are available, they are mostly counterbalanced by a decrease in nucleophilicity of the anion in the case of Cl⁻ and Br⁻ (both of which can interact with the H-bond donor). External H-bond donors can be used if they do not interact negatively with the anion (Cl⁻ is deactivated by water, as it is strongly solvated and therefore is less nucleophilic) and if they do not hinder the overall solubility of the catalyst into the epoxide. To confirm our hypotheses, we predicted the relative activity of three closely related catalysts, i.e. *N,N,N*-triethyl-*N*-hydroxyethylammonium iodide > *N,N,N*-triethyl-*N*-hydroxyethylammonium bromide⁴⁵ > 1-hydroxyethyl-3-methylimidazolium chloride.⁴⁶ Under the conditions described herein, the product yields for the three catalysts are 69, 55, and 31%, respectively, thus confirming our prediction (Table S3).

Further catalyst development should therefore strive to increase the nucleophilicity of the anion by minimizing ion-pairing interactions (e.g., having a buried or highly delocalized charge)^{47,48} as well as ensuring that the cation ensures high solubility of the salt in the epoxide (e.g., inclusion of hydrophobic groups), rather than incorporating additional H-bond donors, which has been the most widely employed strategy so far and usually leads to an overall lower solubility of the catalyst. Finally, this study also demonstrates that one of the first ILs reported to catalyze the CCE reaction is considerably more active than previously thought when it is applied under homogeneous conditions (i.e., with epichlorohydrin rather than propylene oxide), thus highlighting the need for benchmark conditions for the CCE reaction.^{22,32}

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b04389.

Experimental details, computational details, the effect of water, catalyst evaluation, and ¹H NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Hughes, T. P.; Kerry, J. T.; Álvarez-Noriega, M.; Álvarez-Romero, J. G.; Anderson, K. D.; Baird, A. H.; Babcock, R. C.; Beger, M.; Bellwood, D. R.; Berkemans, R.; Bridge, T. C.; Butler, I. R.; Byrne, M.; Cantin, N. E.; Comeau, S.; Connolly, S. R.; Cumming, G. S.; Dalton, S. J.; Diaz-Pulido, G.; Eakin, C. M.; Figueira, W. F.; Gilmour, J. P.; Harrison, H. B.; Heron, S. F.; Hoey, A. S.; Hobbs, J. A.; Hoogenboom, M. O.; Kennedy, E. V.; Kuo, C.; Lough, J. M.; Lowe, R. J.; Liu, G.; McCulloch, M. T.; Malcolm, H. A.; McWilliam, M. J.; Pandolfi, J. M.; Pears, R. J.; Pratchett, M. S.; Schoepf, V.; Simpson, T.; Skirving, W. J.; Sommer, B.; Torda, G.; Wachenfeld, D. R.; Willis, B. L.; Wilson, S. K. Global warming and recurrent mass bleaching of corals. *Nature* **2017**, *543*, 373–377.
- (2) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using carbon dioxide as a building block in organic synthesis. *Nat. Commun.* **2015**, *6*, 5933.
- (3) Beuls, A.; Swalus, C.; Jacquemin, M.; Heyen, G.; Karelovic, A.; Ruiz, P. Methanation of CO₂: Further insight into the mechanism over Rh/γ-Al₂O₃ catalyst. *Appl. Catal., B* **2012**, *113–114*, 2–10.
- (4) Studt, F.; Sharafutdinov, I.; Abild-Pedersen, F.; Elkjær, C. F.; Hummelshøj, J. S.; Dahl, S.; Chorkendorff, I.; Nørskov, J. K. Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol. *Nat. Chem.* **2014**, *6*, 320–324.
- (5) Huff, C. A.; Sanford, M. S. Cascade Catalysis for the Homogeneous Hydrogenation of CO₂ to Methanol. *J. Am. Chem. Soc.* **2011**, *133*, 18122–18125.
- (6) Moret, S.; Dyson, P. J.; Laurency, G. Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media. *Nat. Commun.* **2014**, *5*, 4017.
- (7) Zhao, Y.; Yu, B.; Yang, Z.; Zhang, H.; Hao, L.; Gao, X.; Liu, Z. A Protic Ionic Liquid Catalyzes CO₂ Conversion at Atmospheric Pressure and Room Temperature: Synthesis of Quinazoline-2,4(1H,3H)-diones. *Angew. Chem.* **2014**, *126*, 6032–6035.
- (8) Zhang, Z.; Liao, L.-L.; Yan, S.-S.; Wang, L.; He, Y.-Q.; Ye, J.-H.; Li, J.; Zhi, Y.-G.; Yu, D.-G. Lactamization of sp² C–H Bonds with CO₂: Transition-Metal-Free and Redox-Neutral. *Angew. Chem., Int. Ed.* **2016**, *55*, 7068–7072.
- (9) Whiteoak, C. J.; Nova, A.; Maseras, F.; Kleij, A. W. Merging sustainability with organocatalysis in the formation of organic carbonates by using CO₂ as a feedstock. *ChemSusChem* **2012**, *5*, 2032–2038.
- (10) Schäffner, B.; Verevkin, S. P.; Börner, A. Organische carbonate. Grüne Lösungsmittel für synthese und katalyse. *Chem. Unserer Zeit* **2009**, *43*, 12–21.
- (11) Schäffner, B.; Schäffner, F.; Verevkin, S. P.; Börner, A. Organic carbonates as solvents in synthesis and catalysis. *Chem. Rev.* **2010**, *110*, 4554–4581.
- (12) Du, Y.; Cai, F.; Kong, D.-L.; He, L.-N. Organic solvent-free process for the synthesis of propylene carbonate from supercritical carbon dioxide and propylene oxide catalyzed by insoluble ion exchange resins. *Green Chem.* **2005**, *7*, 518–523.
- (13) Darensbourg, D. J.; Wilson, S. J. What's new with CO₂? Recent advances in its copolymerization with oxiranes. *Green Chem.* **2012**, *14*, 2665–2671.
- (14) Wei-Li, D.; Bi, J.; Sheng-Lian, L.; Xu-Biao, L.; Xin-Man, T.; Chak-Tong, A. Functionalized phosphonium-based ionic liquids as efficient catalysts for the synthesis of cyclic carbonate from epoxides and carbon dioxide. *Appl. Catal., A* **2014**, *470*, 183–188.
- (15) Li, P. Z.; Wang, X. J.; Liu, J.; Lim, J. S.; Zou, R.; Zhao, Y. A Triazole-Containing Metal-Organic Framework as a Highly Effective and Substrate Size-Dependent Catalyst for CO₂ Conversion. *J. Am. Chem. Soc.* **2016**, *138*, 2142–2145.
- (16) Han, L.; Choi, H. J.; Kim, D. K.; Park, S. W.; Liu, B.; Park, D. W. Porous polymer bead-supported ionic liquids for the synthesis of cyclic carbonate from CO₂ and epoxide. *J. Mol. Catal. A: Chem.* **2011**, *338*, 58–64.
- (17) Wu, S. S.; Zhang, X. W.; Dai, W. L.; Yin, S. F.; Li, W. S.; Ren, Y. Q.; Au, C. T. ZnBr₂-Ph₄PI as highly efficient catalyst for cyclic carbonates synthesis from terminal epoxides and carbon dioxide. *Appl. Catal., A* **2008**, *341*, 106–111.
- (18) Han, L.; Choi, S.-J.; Park, M.-S.; Lee, S.-M.; Kim, Y.-J.; Kim, M.-I.; Liu, B.; Park, D.-W. Carboxylic acid functionalized imidazolium-based ionic liquids: efficient catalysts for cycloaddition of CO₂ and epoxides. *React. Kinet., Mech. Catal.* **2012**, *106*, 25–35.
- (19) Xu, B.-H.; Wang, J.-Q.; Sun, J.; Huang, Y.; Zhang, J.-P.; Zhang, X.-P.; Zhang, S.-J. Fixation of CO₂ into cyclic carbonates catalyzed by ionic liquids: a multi-scale approach. *Green Chem.* **2015**, *17*, 108–122.
- (20) Dean, R. K.; Devaine-Pressing, K.; Dawe, L. N.; Kozak, C. M. Reaction of CO₂ with propylene oxide and styrene oxide catalyzed by a chromium (iii) amine-bis (phenolate) complex. *Dalton Trans.* **2013**, *42*, 9233–9244.
- (21) Taherimehr, M.; Sertã, J. P. C. C.; Kleij, A. W.; Whiteoak, C. J.; Pescarmona, P. P. New Iron Pyridylamino-Bis (Phenolate) Catalyst for Converting CO₂ into Cyclic Carbonates and Cross-Linked Polycarbonates. *ChemSusChem* **2015**, *8*, 1034–1042.
- (22) Peng, J.; Deng, Y. Cycloaddition of carbon dioxide to propylene oxide catalyzed by ionic liquids. *New J. Chem.* **2001**, *25*, 639–641.
- (23) Caló, V.; Nacci, A.; Monopoli, A.; Fanizzi, A. Cyclic carbonate formation from carbon dioxide and oxiranes in tetrabutylammonium halides as solvents and catalysts. *Org. Lett.* **2002**, *4*, 2561–2563.
- (24) Sit, W. N.; Ng, S. M.; Kwong, K. Y.; Lau, C. P. J. Coupling Reactions of CO₂ with Neat Epoxides Catalyzed by PPN Salts To Yield Cyclic Carbonates. *J. Org. Chem.* **2005**, *70*, 8583–8586.
- (25) He, Q.; O'Brien, J. W.; Kitselman, K. A.; Tompkins, L. E.; Curtis, G. C. T.; Kerton, F. M. Synthesis of cyclic carbonates from CO₂ and epoxides using ionic liquids and related catalysts including choline chloride-metal halide mixtures. *Catal. Sci. Technol.* **2014**, *4*, 1513–1528.
- (26) Bobbink, F. D.; Dyson, P. J. Synthesis of carbonates and related compounds incorporating CO₂ using ionic liquid-type catalysts: State-of-the-art and beyond. *J. Catal.* **2016**, *343*, 52–61.
- (27) Sun, H.; Zhang, D. Density functional theory study on the cycloaddition of carbon dioxide with propylene oxide catalyzed by alkylmethylimidazolium chlorine ionic liquids. *J. Phys. Chem. A* **2007**, *111*, 8036–8043.
- (28) Girard, A.-L.; Simon, N.; Zanatta, M.; Marmitt, S.; Gonçalves, P.; Dupont, J. Insights on recyclable catalytic system composed of task-specific ionic liquids for the chemical fixation of carbon dioxide. *Green Chem.* **2014**, *16*, 2815–2825.
- (29) Marmitt, S.; Gonçalves, P. F. B. A DFT study on the insertion of CO₂ into styrene oxide catalyzed by 1-butyl-3-methyl-imidazolium bromide ionic liquid. *J. Comput. Chem.* **2015**, *36*, 1322–1333.
- (30) Katsyuba, S. A.; Vener, M. V.; Zvereva, E. E.; Fei, Z.; Scopelliti, R.; Brandenburg, J. G.; Siankevich, S.; Dyson, P. J. Quantification of Conventional and Nonconventional Charge-Assisted Hydrogen Bonds in the Condensed and Gas Phases. *J. Phys. Chem. Lett.* **2015**, *6*, 4431–4436.
- (31) Nelyubina, Y. V.; Korlyukov, A. A.; Lyssenko, K. A. Invariom approach as a new tool in electron density studies of ionic liquids: a model case of 1-butyl-2, 3-dimethylimidazolium chloride BDMIM [Cl]. *RSC Adv.* **2015**, *5*, 75360–75373.
- (32) Rintjema, J.; Kleij, A. W. Aluminum-Mediated Formation of Cyclic Carbonates: Benchmarking Catalytic Performance Metrics. *ChemSusChem* **2017**, *10*, 1274–1282.
- (33) Wilhelm, M. E.; Anthofer, M. H.; Reich, R. M.; D'Elia, V.; Basset, J.-M.; Herrmann, W. A.; Cokoja, M.; Kühn, F. E. Niobium (v) chloride and imidazolium bromides as efficient dual catalyst systems for the cycloaddition of carbon dioxide and propylene oxide. *Catal. Sci. Technol.* **2014**, *4*, 1638–1643.

(34) Anthofer, M. H.; Wilhelm, M. E.; Cokoja, M.; Markovits, I. I. E.; Pöthig, A.; Mink, J.; Herrmann, W. A.; Kühn, F. E. Cycloaddition of CO₂ and epoxides catalyzed by imidazolium bromides under mild conditions: influence of the cation on catalyst activity. *Catal. Sci. Technol.* **2014**, *4*, 1749–1758.

(35) Arnold, P. L.; Pearson, S. Abnormal N-heterocyclic carbenes. *Coord. Chem. Rev.* **2007**, *251*, 596–609.

(36) Wang, J.-Q.; Sun, J.; Cheng, W.-G.; Dong, K.; Zhang, X.-P.; Zhang, S.-J. Experimental and theoretical studies on hydrogen bond-promoted fixation of carbon dioxide and epoxides in cyclic carbonates. *Phys. Chem. Chem. Phys.* **2012**, *14*, 11021–11026.

(37) Liu, M.; Gao, K.; Liang, L.; Wang, F.; Shi, L.; Sheng, L.; Sun, J. Insights into hydrogen bond donor promoted fixation of carbon dioxide with epoxides catalyzed by ionic liquids. *Phys. Chem. Chem. Phys.* **2015**, *17*, 5959–5965.

(38) Gennen, S.; Alves, M.; Méreau, R.; Tassaing, T.; Gilbert, B.; Detrembleur, C.; Jerome, C.; Grignard, B. Fluorinated Alcohols as Activators for the Solvent-Free Chemical Fixation of Carbon Dioxide into Epoxides. *ChemSusChem* **2015**, *8*, 1845–1849.

(39) Girard, A.; Simon, N.; Zanatta, M.; Marmitt, S.; Gonçalves, P.; Dupont, J. Insights on recyclable catalytic system composed of task-specific ionic liquids for the chemical fixation of carbon dioxide. *Green Chem.* **2014**, *16*, 2815–2825.

(40) Luo, Z.; Wang, B.; Liu, Y.; Gao, G.; Xia, F. Reaction mechanisms of carbon dioxide, ethylene oxide and amines catalyzed by ionic liquids BmimBr and BmimOAc: a DFT study. *Phys. Chem. Chem. Phys.* **2016**, *18*, 27951–27957.

(41) Lee, E. H.; Ahn, J. Y.; Dharman, M. M.; Park, D. W.; Park, S. W.; Kim, I. Synthesis of cyclic carbonate from vinyl cyclohexene oxide and CO₂ using ionic liquids as catalysts. *Catal. Today* **2008**, *131*, 130–134.

(42) Wang, J.-Q.; Dong, K.; Cheng, W.-G.; Sun, J.; Zhang, S.-J. Water as an efficient medium for the synthesis of cyclic carbonate. *Catal. Sci. Technol.* **2012**, *2*, 1480–1484.

(43) Sun, J.; Ren, J.; Zhang, S.; Cheng, W. *Tetrahedron Lett.* **2009**, *50*, 423–426.

(44) Daguene, C.; Dyson, P. J. Inhibition of catalytic activity in ionic liquids: implications for catalyst design and the effect of cosolvents. *Organometallics* **2004**, *23*, 6080–6083.

(45) Cheng, W.; Xiao, B.; Sun, J.; Dong, K.; Zhang, P.; Zhang, S.; Ng, F. T. T. Effect of hydrogen bond of hydroxyl-functionalized ammonium ionic liquids on cycloaddition of CO₂. *Tetrahedron Lett.* **2015**, *56*, 1416–1419.

(46) Sun, J.; Zhang, S.; Cheng, W.; Ren, J. Hydroxyl-functionalized ionic liquid: a novel efficient catalyst for chemical fixation of CO₂ to cyclic carbonate. *Tetrahedron Lett.* **2008**, *49*, 3588–3591.

(47) Kaneko, S.; Shirakawa, S. Potassium Iodide-Tetraethylene Glycol Complex as a Practical Catalyst for CO₂ Fixation Reactions with Epoxides under Mild Conditions. *ACS Sustainable Chem. Eng.* **2017**, *5*, 2836–2840.

(48) Rulev, Y. A.; Gugkaeva, Z. T.; Lokutova, A. V.; Maleev, V. I.; Peregodov, A. S.; Wu, X.; North, M.; Belokon, Y. N. Carbocation/Polyol Systems as Efficient Organic Catalysts for the Preparation of Cyclic Carbonates. *ChemSusChem* **2017**, *10*, 1152–1159.