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**Ionic Catalysts for the Cycloaddition of Carbon Dioxide
with Epoxides and the Oxidation of Olefins**

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Most people say that it is the intellect which makes a great scientist.

They are wrong: it is character.

Albert Einstein

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Deutsches Abstract

Imidazoliumsalze werden als Katalysatoren und Lösemittel in vielseitigen Bereichen eingesetzt. In dieser Arbeit liegt das Hauptaugenmerk auf dem Zusammenhang der Struktur des Imidazoliumkations mit der Reaktivität des nukleophilen Anions als katalytisch aktive Spezies. Durch Modifizierung des Imidazoliumkerns mit organischen Substituenten werden die elektrostatische Wechselwirkung der Ionen und damit auch die Eigenschaften des Anions stark beeinflusst. Die wichtigsten Faktoren in Bezug auf die Reaktivität des Anions sind dabei sowohl die sterische Zugänglichkeit des C2 Protons, als auch dessen Azidität. Ferner hängt das Löslichkeitsverhalten von Imidazoliumsalzen vom Substitutionsmuster des Kations ab, was sich ebenfalls auf die Aktivität auswirkt.

Die Untersuchung der katalytischen Cycloaddition von Epoxiden mit Kohlenstoffdioxid stellt einen Großteil dieser Arbeit dar. Dabei wurden die Auswirkungen der Struktur des Kations auf die Aktivität von Imidazoliumhalogeniden als Katalysatoren analysiert. Die gewonnenen Erkenntnisse ermöglichen die Optimierung des Substitutionsmusters, sodass eine stärkere Aktivierung des Epoxids und eine höhere katalytische Aktivität erreicht werden. Des Weiteren wurden die Auswirkungen verschiedener Imidazoliumsubstituenten in einem binären Katalysatorsystem in Kombination mit Niob(V)-chlorid als *Lewis* Säure untersucht. Die sterischen und elektronischen Eigenschaften der Imidazoliumsalze sowie deren Löslichkeit konnten als entscheidende Aspekte für die Aktivität ermittelt werden. Durch Kombination eines Polyols, welches zur Aktivierung des Epoxids dient, mit einem Halogenid als Nukleophil wurde außerdem eine organokatalytische Alternative zu *Lewis*-aziden Metallen geschaffen. Darüber hinaus wurden Imidazoliumsalze für die Epoxidation von Olefinen mit wässrigem Wasserstoffperoxid benutzt. Durch säurefunktionalisierte Imidazoliumkationen konnten Polyoxomolybdate mit guter katalytischer Aktivität *in situ* aus günstigen und leicht verfügbaren Vorstufen erzeugt werden, wodurch die Reaktionsführung vereinfacht wurde. Zusätzlich wurde erstmals gezeigt, dass Imidazoliumperhenate als Katalysatoren für die Epoxidation von Olefinen fungieren können. Durch Strukturoptimierung des Kations konnten ein geringes Ausmaß an Ionenpaarung, und damit eine effiziente Aktivierung von H_2O_2 , sowie eine erhöhte Olefinlöslichkeit in der wässrigen Phase ermöglicht werden. Somit wurde ein aktives, einfaches und wiederverwendbares Katalysatorsystem für die zweiphasige Epoxidation von Olefinen erhalten.

English Abstract

Imidazolium salts are versatile compounds, being used as catalysts and solvents for a wide range of applications. The primary focus of this thesis is placed on the correlation between the imidazolium structure and the reactivity of the nucleophilic anion as catalytically active species. Upon modification of the imidazolium pattern with varying organic residues, the electrostatic interaction between the ions and thus the properties of the anion are significantly influenced. In particular, the steric accessibility and the acidity of the C2 proton are key factors affecting the anion reactivity. Furthermore, the solubility behavior of imidazolium salts depends on the cation structure to a large extent, which results in strong effects on the catalytic activity.

The major part of this work deals with the catalytic cycloaddition of epoxides with carbon dioxide towards cyclic carbonates. For this purpose, imidazolium halides were applied as organocatalysts and the impact of the cation structure on the activity was analyzed. Therefore, the optimization of the imidazolium ring substitution pattern was enabled, with respect to reinforced activation of the epoxide through hydrogen bonding. As a result, enhanced catalytic activity was achieved. Aside from imidazolium salts as single catalysts, the effects of various cation residues were investigated in combinations with niobium(V) chloride as *Lewis* acid. The changes in the steric and electronic properties and epoxide solubility were determined as the most important aspects influencing the activity of the binary catalyst system. Further, a binary mixture consisting of a polyol, as epoxide activator, and halides, as nucleophiles, was found to be a promising organocatalytic alternative to systems based on *Lewis* acidic metals.

Imidazolium salts were also employed as catalysts for the epoxidation of olefins with aqueous hydrogen peroxide. It was shown that catalytically active polyoxomolybdates can be generated *in situ* with carboxy-functionalized imidazolium salts. Consequently, the reaction procedure was facilitated and a good catalytic performance was obtained, whereby cost-efficient and readily available precursors were used. Additionally, it was demonstrated for the first time that imidazolium perrhenates are able to act as epoxidation catalysts. By optimizing the cation structure, a low degree of ion pairing, and hence strong H₂O₂ activation, as well as enhanced olefin solubility in the aqueous H₂O₂ phase were enabled. Finally, an active, simple and reusable catalyst system for the biphasic epoxidation of olefins with H₂O₂ was achieved.

Abbreviations

AER	anion exchange resin
APT	azaphosphatranes
BMim	1-butyl-3-methylimidazolium
CO ₂	carbon dioxide
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DFT	density functional theory
FTIR	fourier transform infrared spectroscopy
HB	hydrogen-bond
HFIP	1,1,1,3,3,3-hexafluoro <i>isopropanol</i>
HPPO	hydrogen peroxide propylene oxide
IL	ionic liquid
LCA	life-cycle-assessment
NMR	nuclear magnetic resonance
PC	propylene carbonate
PEG	polyethylene glycol
PETT	pentaerythritol
PO	propylene oxide
POM	polyoxometalate
PS	polystyrene
PTC	phase transfer catalysis
SC	styrene carbonate
SO	styrene oxide
TBAB	tetrabutylammonium bromide
TBAI	tetrabutylammonium iodide
TBD	triazabicyclo[4.4.0]dec-5-ene
TR	transfer reagent

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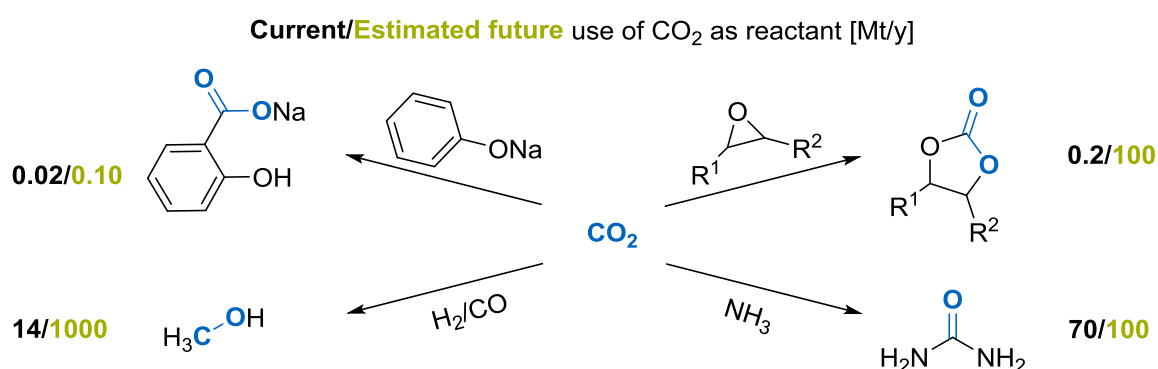
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1 Introduction

1.1 Organocatalytic Cyclic Carbonate Synthesis from Epoxides and CO₂

1.1.1 CO₂ as Sustainable Chemical Building Block

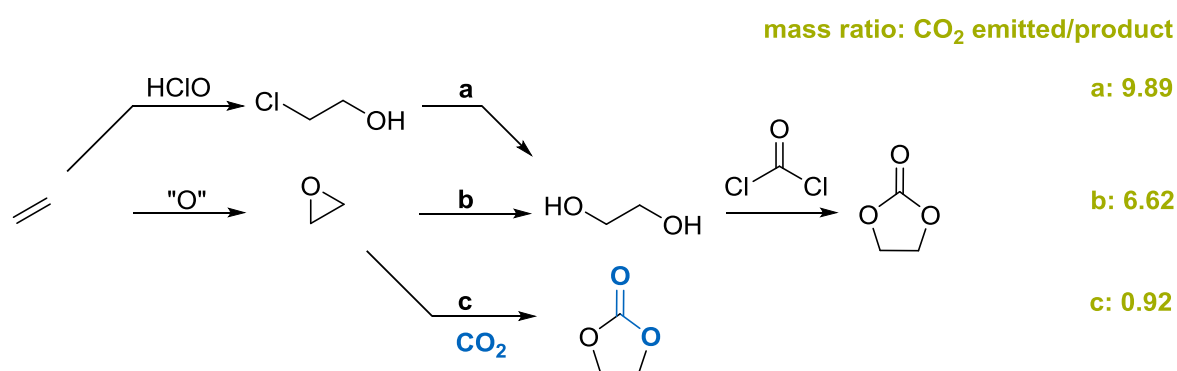
Chemistry strongly depends on the availability of fossil fuels, as they are used as raw materials for the preparation of the majority of available products.^[1] Additionally, many industrial processes are energy intensive, so that approximately 10 % of the global energy, which is mainly produced from fossil fuels, is consumed by the chemical industry.^[2] In order to alleviate the effects of growing fossil fuel depletion on the chemical industry, renewable carbon feedstocks represent a promising opportunity.^[3] In addition to ligno-cellulosic biomass,^[4] or oils and fats,^[5] the usage of carbon dioxide, as one of the most abundant renewable carbon sources, is of particular high interest.^[6] Besides the omnipresence of CO₂, to which the human emission amounts to more than 30 Gt/y, the greenhouse gas is non-toxic and cheap and therefore a suitable candidate as C1-feedstock in industry.^[7] The major drawback of CO₂ as a building block is its high stability and low reactivity originating from the carbon atom in the most oxidized state.^[8] Consequently, a vast amount of energy needs to be applied, which negatively affects the costs and environmental benignity.^[9] Therefore, less than 0.5 % of the anthropogenic CO₂ emissions are used as reactant in industry (appr. 110 Mt/y), whereby four major compound classes are produced so far (Scheme 1.1).^[8, 10]



Scheme 1.1: Industrial processes involving CO₂ as chemical building block.^[8]

To increase the utilization of CO₂ as a building block, catalysis research is a crucial factor. It is devoted to developing highly efficient processes, leading to lower energy input.^[11] One particular example for the catalytic chemical fixation of CO₂ represents its addition to epoxides as highly reactive starting materials. As shown in

Scheme 1.1, the prospective development of the scale for cyclic organic carbonate production (upper right) is expected to increase significantly.^[8] The corresponding cycloaddition of CO₂ to epoxides represents a 100 % atom economical reaction, which is highly desirable for industry.^[12] Further, highly toxic phosgene (route b, Scheme 1.2), is eliminated using this approach (route c, Scheme 1.2).^[13] Regarding the carbon footprint, life-cycle-assessment analysis (LCA) also shows that the coupling of CO₂ with ethylene oxide is the most desirable route towards ethylene carbonate as model product.^[14]



Scheme 1.2: Different routes towards ethylene carbonate with respective mass ratio of emitted CO₂/product (determined via LCA).^[14]

Cyclic organic carbonates, of which propylene carbonate (PC) is the most prominent example, can be used as high boiling polar aprotic solvents with low toxicity or as electrolytes in lithium batteries.^[15] Additionally, they can be applied as versatile feedstock for the manufacturing of polymers,^[16] linear organic carbonates^[17] or fine chemicals.^[18] Taking these facts into account, it can be stated that this reaction has great potential for the sustainable chemical fixation of CO₂.

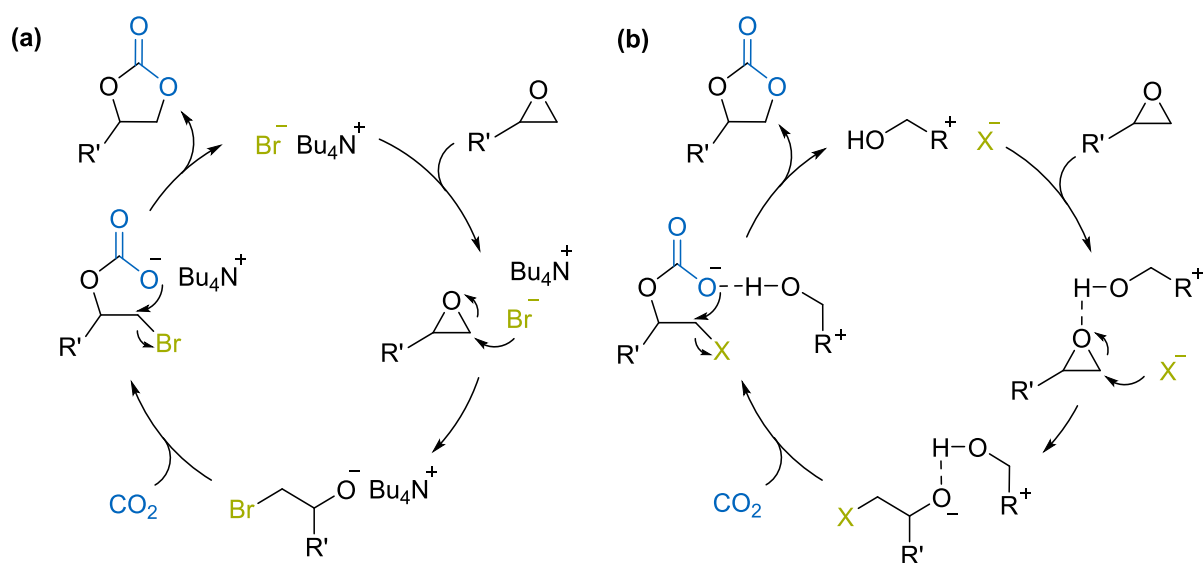
Unfortunately, harsh reaction conditions often have to be applied to convert the highly stable CO₂ to the corresponding cyclic carbonates.^[19] Thus, a multitude of catalyst systems, usually consisting of a combination of *Lewis* acids and nucleophiles, have been developed to optimize temperature, pressure and reaction time. Among several, Al,^[20] Co,^[21] Cr^[22] and Zn^[23] complexes, metal halide salts like ZnBr₂^[24] or (NbCl₅)₂,^[25] as well as metal oxides, e.g. MgO^[26], can be applied as *Lewis* acids. Onium, respectively imidazolium halide salts, or nucleophilic *N*-donor bases are often used as nucleophilic co-catalyst.^[13] The organocatalytic valorization of CO₂ with epoxides constitutes an alternative approach with vast research potential, particularly for the sustainability of the process. Generally, metal-free catalysts often benefit from being air- and moisture stable, allowing for an easy and cheap preparation, as well as a simple and

safe handling.^[27] A large part of organic compounds is comparably non-toxic and readily available from renewable carbon sources too.^[28] Therefore, organocatalysis can not only substantially improve the costs and the development time of processes, but also the required energy input.^[29] Further, the amount of chemical wastes can possibly be reduced and the experimental procedures can be simplified. Thus, the carbon footprint and sustainability of a variety of operations could be optimized, including the coupling reaction of CO₂ with epoxides to cyclic carbonates. This would offer the opportunity to use CO₂ as a reactant in an environmentally benign manner. However, this is only applicable if the demanding reaction conditions (> 120 °C, > 20 bar CO₂), under which these systems usually operate, can be enhanced significantly.

1.1.2 Ionic Organocatalysts for the Cycloaddition of CO₂ to Epoxides

The first report regarding metal-free conversion of epoxides with CO₂ to cyclic carbonates was published by Nishikubo et al. in 1993.^[30] Nearly a decade later, Calo et al. were able to transform styrene oxide (SO) to styrene carbonate (SC) in 83 % yield (120 °C, 4 h, 1 bar CO₂). A mixture of molten tetrabutylammonium bromide (TBAB) and iodide (TBAI) hereby served as solvent and catalyst.^[31] Moreover, the reaction mechanism for the organocatalytic cycloaddition of epoxides to CO₂ was initially postulated (Scheme 1.3, (a)). In the first step the epoxide ring is opened by nucleophilic attack of the halide anion at the sterically less hindered carbon atom. The resulting oxy-anion species attacks the electrophilic carbon atom of CO₂, forming an open-chain carbonate species. After intramolecular nucleophilic attack and elimination of the halide anion ('Back-biting'), the cyclic carbonate product is finally obtained. Further investigations by means of density functional theory (DFT) studies, combined with experiments, confirmed the postulated mechanism.^[32] Also the cation was found to influence the catalytic activity of ammonium halides, as the degree of ion pairing to the anion affects its nucleophilicity. Thus, TBAB shows considerably higher catalytic activity than the methyl analog arising from the sterically more demanding alkyl chains.^[33] The next step towards more active organocatalysts involves the introduction of tailored cations, being capable of acting as a synergistic structural component during the catalytic cycle. Therefore, OH-functionalized ammonium compounds were applied and found to be more efficient because of their hydrogen-bond (HB) donor ability.^[34] Sun et al. were able to show that PC yield increases from 74 to 96 % by

substituting TBAB with its corresponding hydroxyethyl analog (Figure 1.1, (a), 125 °C, 20 bar CO₂, 1 h, 1.6 mol %). Through coordination to the epoxide via HB, the C-O bond is polarized and the nucleophilic attack of the anion is facilitated, resulting in higher catalytic activity (Scheme 1.3, (b)).^[34] More recent investigations revealed that hydroxyethyl modified TBAI catalyzes the formation of PC at considerably milder reaction conditions (45 °C, 10 bar CO₂, 18 h, 5.0 mol %).^[35] This demonstrates the great potential of this class of catalysts. Additionally, betaine,^[36] choline,^[37] as well as amino acid based ammonium salts (Figure 1.1, (b))^[38] are reported as HB donor substituted catalysts for cyclic carbonate synthesis. However, their activity only slightly deviates in comparison to conventional hydroxyalkyl ammonium halides.



Scheme 1.3: Proposed mechanisms for the cycloaddition reaction of CO₂ with epoxides using (a) TBAB^[31] or (b) hydroxy functionalized ionic compounds^[34] as catalysts.

The immobilization of molecular catalysts on solid and insoluble carriers is a common possibility to enable easy catalyst recycling through e.g. filtration. For ammonium halide catalysts, a great variety of supporting materials have been applied: polymers like polystyrene (PS)^[39] or polyethylene glycols (PEG),^[40] biopolymers, e.g. cellulose^[41] and chitosan^[42], as well as different types of silica^[33] are reported in literature. As described for the homogeneous case, also immobilized OH-modified ammonium halides (Figure 1.1, (c)) lead to higher activities compared to unfunctionalized analogs.^[39b] Supporting materials bearing OH groups were also shown to have a comparable effect. Thus, silica^[33] as well as biopolymers^[41] (Figure 1.1, (d)) as carriers lead to a similar increase in catalytic activity.

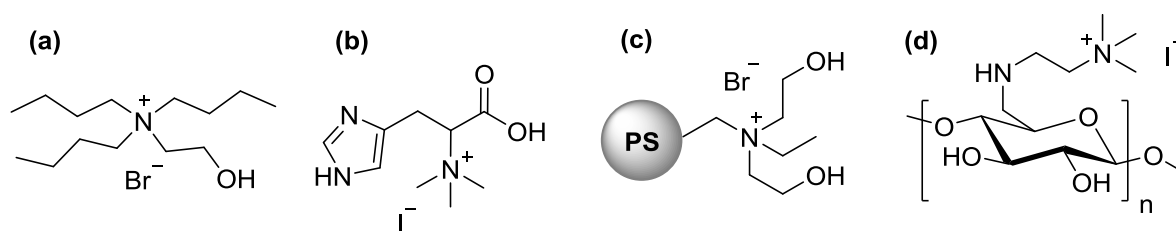


Figure 1.1: HB donor functionalized ammonium halide catalysts for cyclic carbonate synthesis.

In addition to ammonium halides based on conventional alkylamines, the protonation or quaternization of nitrogen superbases results in alternative catalysts. Therefore, guanidinium,^[43] pyridinium or pyrrolidinium^[44] and amidinium^[45] based derivatives have been synthesized. He et al. investigated a series of *Lewis* basic ionic catalysts and found the highest activity for protonated 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The resulting [HDBU]Cl is supposed to stabilize the intermediates to a greater extent, leading to a more efficient reaction.^[46] More recent studies by Tassaing et al. on the basis of protonated 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) have demonstrated that the HB properties of these catalysts are crucial. Hence, synergistic effects and higher activities are observed applying [HTBD]Br in comparison to TBAB.^[47] In addition to their initial studies regarding ammonium halides, Nishikubo et al. have also shown that phosphonium halides can be used as metal-free catalysts for the cycloaddition of CO₂ to epoxides.^[30] Generally, phosphonium halides show very similar catalytic activities compared to their ammonium counterparts. Furthermore, the introduction of HB donor functional groups at the cation likewise enhances the catalytic activity. By modification of PPH₃ with varying bromoethyl species, Lian et al. investigated the influence of HB donor groups on the catalytic activity.^[48] The tailored catalysts clearly outperformed the compounds without functionalization. Moreover, the respective carboxy substituted compound gave slightly higher yields than the amine or hydroxy analog, deriving from the higher polarization capability.^[48] Werner et al. further showed that hydroxyethyl modified P(*n*-Bu)₃, bearing iodide as nucleophilic counteranion (Figure 1.2, (a)), catalyzes the formation of PC under relatively mild reaction conditions (90 °C, 10 bar CO₂, 3 h, 2.0 mol %).^[49] As a novel cation structure of phosphonium based catalysts, Jain et al. synthesized a cyclotriphosphazene core carrying three molecules of [PPh₃]Cl. The multiple ion-pair motifs induce enhanced catalytic activity compared to conventional [PPh₃]Cl.^[50] Martinez and Dufaud et al. recently introduced azaphosphatranes (APT, Figure 1.2, (b)) as ionic organocatalysts with another structural motif. The proton of the N-P-H core is supposed to activate the epoxide via HB, while a hydrolysis sensitive carbamate species

forms through CO₂ insertion in the next step. By introduction of sterically demanding amine substituents, the degradation of this species is hindered, resulting in higher catalytic activity and stability.^[51] Designing molecular cavities around the P-H site can further stabilize the carbamate species because of their encapsulation in the generated cage. By creating a highly accessible HB center, the optimized hemicryptophane compound gave constant activity over 96 h and was applicable under relatively mild conditions (100 °C, 1 bar CO₂, 24 h, 1.0 mol %).^[52]

As described above regarding ammonium halides, the immobilization of phosphonium compounds is a feasible strategy to obtain heterogeneous catalysts for the cycloaddition of CO₂ to epoxides. Therefore, PS,^[30, 53] PEG,^[54] cross-linked polymeric nanoparticles^[55] as well as silica materials^[56] have been reported as carrier materials in literature. By using silica as support for P(*n*-Bu)₃ iodide (Figure 1.2, (c)), Sakakura et al. achieved an activating effect deriving from the silanol HB donor groups on the surface. This leads to significantly enhanced catalytic activity compared to the molecular compound. To demonstrate the long-time stability, the immobilized catalyst was applied under continuous flow conditions in a fixed-bed reactor, thereby converting > 80 % PO for more than 1000 h.^[57] By coupling of P(*n*-Bu)₃ chloride to a fluorinated copolymer (Figure 1.2, (d)), the same group was able to synthesize a compound, which combines the merits of homogeneous and heterogeneous catalysis. Under the applied supercritical CO₂ conditions (180 °C, 80 bar CO₂), the catalyst readily dissolves, while upon venting CO₂ it precipitates out of the reaction mixture and can be separated by simple filtration.^[58]

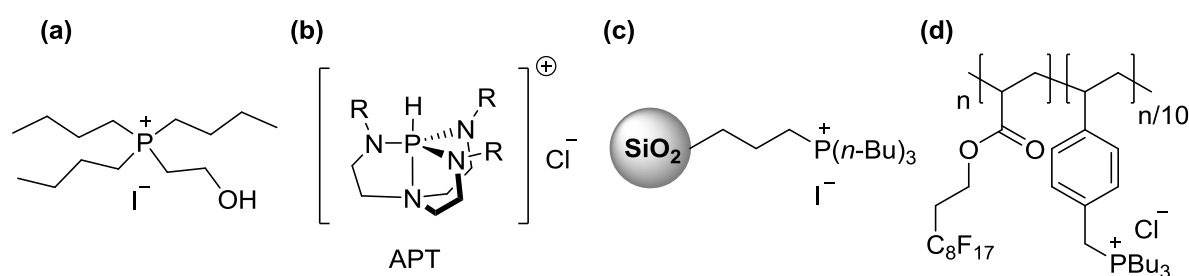


Figure 1.2: Phosphonium based halide catalysts for cyclic carbonate synthesis.

Imidazolium based systems constitute another widespread catalyst class with respect to metal-free mediated cycloaddition of CO₂ to epoxides. As their properties are strongly influenced by the easily tunable modification sites of the imidazolium cation structure (Figure 1.3), they can be adjusted towards the desired application. Thus, for example the solubility and the HB properties can be tailored through the choice of the

substitution pattern.^[59] As expected, increasing alkyl chain length of the substituents leads to enhanced lipophilicity.^[60] This also accounts for blocking the acidic C2 position with an alkyl group, whereby the HB strength decreases simultaneously.^[60-61]

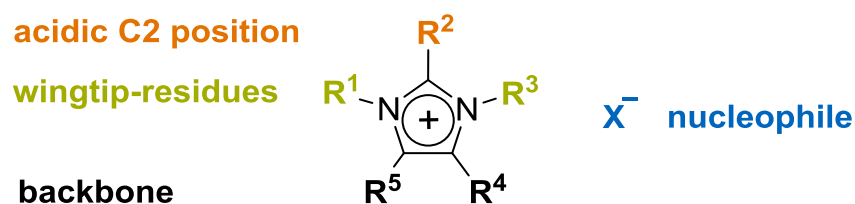


Figure 1.3: Modification sites of the imidazolium moiety for tailoring of the properties towards the desired application.

In the initial report dealing with imidazolium based organocatalysts for cycloaddition of CO₂ with epoxides, Peng and Deng introduced 1-butyl-3-methylimidazolium [BMIm] Cl⁻, [PF₆]⁻ and [BF₄]⁻ salts as first examples. A quantitative yield of PC was obtained applying [BMIm][BF₄], however at relatively harsh reaction conditions (110 °C, 25 bar CO₂, 6 h, 2.5 mol %).^[62] First attempts concerning the influence of the cation on the catalytic performance were carried out under supercritical conditions. Upon increasing the alkyl chain length at the wingtip position, CO₂ as well as PO solubility increase and higher yields are observed.^[63] Further, Park et al. have shown that sterically more demanding imidazolium cations lead to a lower degree of ion pairing and thus higher nucleophilicity of the anion. Also Cl⁻ gave a significantly better yield than [PF₆]⁻ and [BF₄]⁻, deriving from its higher nucleophilicity as decisive factor for the ring-opening of the epoxide.^[64] As aforementioned, HB donor groups at the cations of ammonium and phosphonium halides lead to an enhanced catalytic activity. The epoxide is activated in the first step, so that the following nucleophilic ring-opening is accelerated. This was also found for –OH and –COOH modified imidazolium halide catalysts. Thus, 2-hydroxyethyl wingtip substituted 3-methylimidazolium bromide gave 99 % yield of PC compared to 83 % applying the non-functionalized analog.^[34] The modification of the acidic C2 proton with a hydroxymethyl group represents another route towards HB donor carrying imidazolium catalysts. However, the catalytic activity was very similar compared to the wingtip functionalized compounds.^[65] As the Brønsted acidity and HB donor strength of carboxy groups are higher than for hydroxy groups, their synergistic effect is expected to be more pronounced.^[66] Consequently, a higher catalytic activity should be observed, which was confirmed by several studies.^[67] By introducing a –COOH functional group at both wingtips of the imidazolium cation, Zhang et al. could even further improve the cata-

lytic activity (Figure 1.4, (a)). It is assumed that the second carboxy unit has a reinforcing effect on the epoxide ring-opening, leading to higher conversions.^[67b] Wu et al. could also show that the catalytic activity strongly depends on the Brønsted acidity of the species used for functionalizing the imidazolium motif. A considerably decreased yield compared to a carboxy group is observed for a catalyst bearing a sulfonic acid motif. The HB between the epoxide and the very acidic sulfonic group is presumably too strong, so that CO₂ insertion is hindered, resulting in a lower catalytic activity.^[68] DFT studies from Zhang et al. revealed that the acidic proton in C2 position of the imidazolium cation is also capable to synergistically interact during the mechanism through HB. Thus, the reaction mechanism is modified and the energy barrier is reduced significantly.^[69] As the acidity of the C2 proton and therefore the HB donor strength is influenced by the substituents at the imidazolium ring, tailoring of the structure enables an improvement of the catalytic activity. To investigate the influence of the substituents in R¹, R² and R³ position, a series of ten imidazolium bromides was synthesized and used as catalysts for the cycloaddition of PO to CO₂.^[70] By substituting the acidic C2 position with alkyl residues, the PC yield declines. This is ascribed to the blocking of the most dominant HB donor site, leading to an essentially lower degree of epoxide activation. FTIR investigations underpin that although the whole imidazolium ring interacts with the epoxide, the most pronounced interaction derives from HB of the C2 proton. By modification of one of the wingtips with an electron withdrawing fluorinated benzyl group, the acidity and thus also the HB interaction and the catalytic activity were enhanced. For the further systematic structural optimization, a *n*-octyl alkyl side chain was introduced at the second wingtip site, leading to an enhanced solubility in the reaction medium. The obtained task specific ionic liquid catalyst (Figure 1.4, (b)) was able to catalyze the formation of PC in 91 % yield at very mild reaction conditions (70 °C, 4 bar CO₂, 22 h, 10.0 mol %).^[70] Comparable investigations were performed by Dupont et al. through comparison of the catalytic performance of 21 structurally varied imidazolium based ionic liquids.^[71] The HB donor activation of the epoxide by the imidazolium catalyst was found to be crucial for its nucleophilic ring-opening as the rate-determining step. Moreover, the nucleophilicity and leaving group ability of the anion are major factors towards high catalytic activity.^[71] More recently, hydroxy modified *bis*-imidazolium bromides were introduced as catalysts for the cycloaddition of CO₂ with epoxides.^[72] The three HB donor groups in spatial proximity lead to a more efficient epoxide activation and stabi-

lization of transition states and intermediates. This was corroborated by DFT calculations, thereby confirming previous studies regarding pyrogallol as component in binary catalyst systems.^[73] Through substitution of the second wingtip of the bisimidazolium bromide with a long alkyl chain (Figure 1.4, (c)), the solubility behavior is improved, which leads to an optimized catalytic activity.^[72]

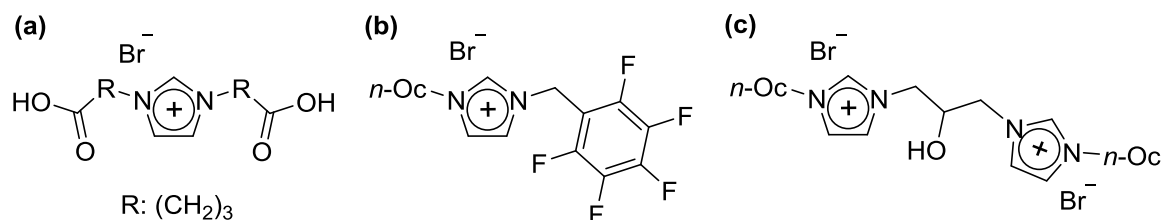


Figure 1.4: Tailored imidazolium bromide catalysts for the synthesis of cyclic carbonates through cycloaddition of CO₂ to epoxides.

The specifications of the imidazolium moiety to reach high catalytic activity change drastically by addition of (NbCl₅)₂ as *Lewis* acidic cocatalyst.^[25b] The coordination strength of the metal center to the epoxide is significantly stronger than the HB interaction of the imidazolium C2 proton. Hence, the nucleophilicity of the anion and thus the ion pairing is the decisive factor and alkyl substitution in C2 position leads to enhanced catalytic performance. The imidazolium solubility also influences the catalytic activity, so that long aliphatic wingtips improved reactivity compared to short alkyl chains or aromatic substituents.^[25b]

The easy modifiability of the imidazolium moiety opens the possibility for further tuning of their organocatalytic properties to enable even milder reaction conditions and minimized carbon footprint. Especially the modification of the backbone with functional groups capable of activating the epoxide through HB could lead to enhanced catalytic activity. In addition, the ion pairing to the anion could be weakened, leading to higher nucleophilicity and better catalytic performance. The variation of the bridging group between bisimidazolium salts could additionally result in more efficient catalysts.

To facilitate the recycling procedure, imidazolium based catalysts were also immobilized on a great variety of carrier materials. Therefore, polymers like PS^[74], PEG^[75] or carbon nanotubes^[76] as well as polymerized imidazolium salts^[77] have been used. As expected, supported hydroxy or carboxy functionalized imidazolium compounds gave higher catalytic activity caused by their HB properties.^[78] The immobilization of diol functionalized ionic liquids (Figure 1.5, (a)) leads to further improvement of the reac-

tivity, caused by the presence of two neighboring hydroxy groups as HB donors.^[79] Silica based materials represent another prominent class, regarding their use as carrier for imidazolium salt catalysts.^[80] As mentioned previously, carboxy groups are stronger HB donors than hydroxy groups, so that the epoxide is activated to a stronger extent. This results in higher catalytic activity, which is also observed for immobilized imidazolium salts on silica.^[66] A recent approach from Zhang et al. demonstrates the potential of silicon-based main-chain poly-imidazolium salts as catalysts for cyclic carbonate synthesis.^[81] In contrast to conventional heterogenized imidazolium compounds, the Si-OH groups are located in the main-chain, leading to higher catalytic activity at relatively mild conditions (Figure 1.5, (b)).^[81] As environmentally more benign alternatives, biopolymers like carboxymethylcellulose^[82] or chitosan (Figure 1.5, (c))^[83] can be used as support materials. Due to the multiple HB donor groups of the biopolymers, synergistic effects arise and high catalytic activities are observed under relatively mild conditions.^[82-83]

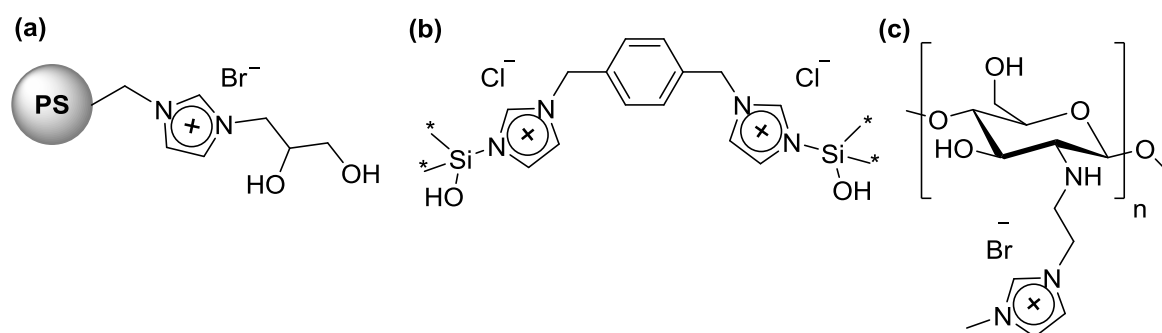


Figure 1.5: Supported imidazolium halide catalysts for the conversion of CO_2 with epoxides to cyclic carbonates.

Kleij et al. were able to reduce the required energy input by designing a heterogeneous catalyst based on a triazolium core immobilized on PS.^[84] The attached pyrogallol unit (Figure 1.6) efficiently activates the epoxide through HB, so that high catalytic activities at mild reaction conditions are made possible (96 % PC, 45 °C, 10 bar CO_2 , 8 h). However, the catalyst has to be reactivated with methyl iodide after five recycling runs, which is the major drawback of this system regarding the sustainability.^[84]

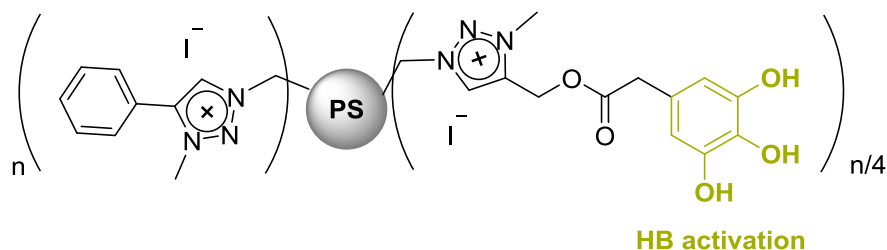
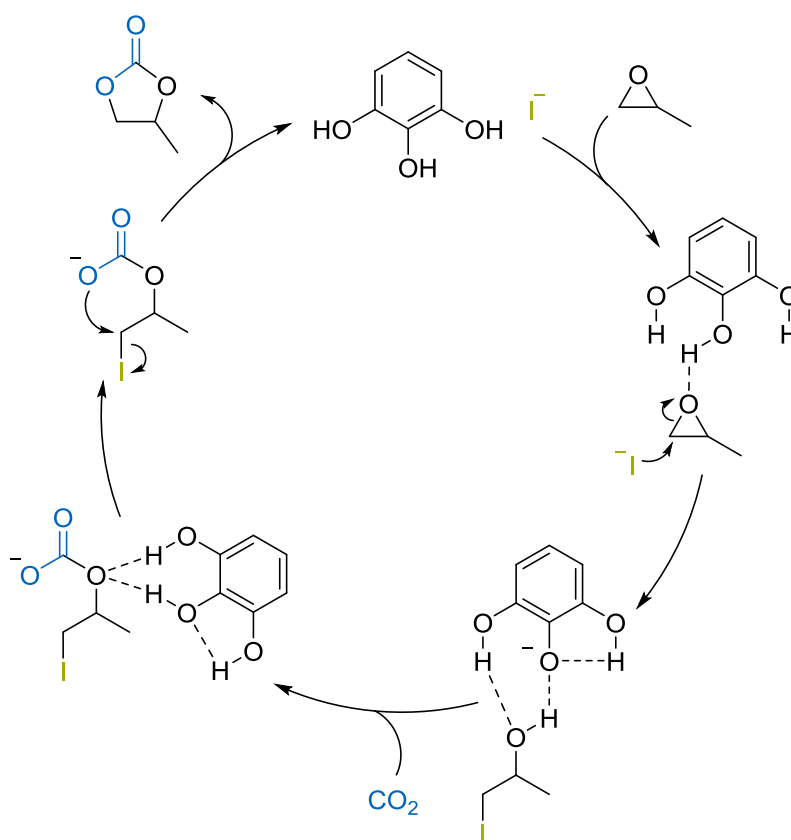


Figure 1.6: Pyrogallol-functionalized triazolium iodide based catalyst for the cycloaddition of CO_2 to epoxides supported on a polystyrene resin.

1.1.3 Synergistic Binary Systems

In addition to tailor-made bifunctional catalysts, the combination of two suitable compounds as mediators for the cycloaddition reaction represents an attractive alternative. Through proper choice of the respective single components, which are not or only slightly catalytically active themselves, synergistic effects can be created, leading to highly reactive systems. In most of these cases one component activates the epoxide through electrophilic interactions (mostly HB), while the second component serves as nucleophile for the subsequent ring-opening. Because of this simple concept and the easy accessibility of feasible single compounds, a myriad of combinations is possible. Bioavailable amino acids,^[85] as well as biopolymers like cellulose,^[86] lignin,^[87] or cyclodextrin^[88] bearing HB donor groups, are promising examples regarding their sustainability. Combined with KI or superbases, e.g. DBU, non-toxic, commercially available and relatively cost-efficient systems are obtained. However, demanding reaction conditions ($> 100\text{ }^{\circ}\text{C}$, $\geq 10\text{ bar CO}_2$) have to be applied in order to reach high cyclic carbonate yields in all cases. Regarding the reusability, *L*-tryptophan (Figure 1.7, (a)) represents the only amino acid, which was proven to show constant activity in five consecutive runs. But the related energy intensive vacuum distillation of the high boiling PC for isolating the KI/*L*-tryptophan system is its major drawback.^[85b] The recycling procedure is a great advantage of the biopolymer based systems, as they are insoluble and can thus be recovered through simple filtration. Consequently, e.g. the cyclodextrin system (Figure 1.7, (b)) can be recycled with low energy input and thus minimized carbon footprint.^[88] Initially, simple aliphatic or aromatic hydroxy compounds were used for epoxide activation in binary catalyst systems. It was found that phenol^[89] and *p*-methoxy-phenol^[90] can both act as suitable catalysts. Nevertheless, later studies showed that multiple hydroxy HB donor sites in spatial proximity have beneficial effects on the catalyst properties. Therefore, catechol shows higher selectivity than phenol in combination with TBAB,^[91] and ethylene glycol gave superior catalytic activity compared to ethanol when used with KI as nucleophile.^[86b] By systematic screening of a variety of largely commercially available compounds together with TBAI, Kleij et al. revealed that three neighboring aromatic hydroxy groups enhance the catalytic activity significantly. Consequently, pyrogallol (Figure 1.7, (c)) was found as the most active epoxide activating agent, enabling 96 % PC yield at room temperature (10 bar CO_2 , 18 h, 2.0 mol %). Further, DFT studies have shown that multiple OH-groups have cooperative effects on the epoxide

activation and transition state or intermediate stabilization during the mechanism (Scheme 1.4). Unfortunately, the catalyst system is not recyclable, which hinders it from being sustainable.^[73] A more promising example is the application of pentaerythritol (PETT, Figure 1.7, (d)) as multiple HB donor. In combination with TBAI, 96 % PC yield at mild reaction conditions (70 °C, 4 bar CO₂, 16 h) is enabled. Additionally, the catalyst system is highly stable and can be easily recycled through precipitation with diethyl ether, so that an energy demanding vacuum distillation is avoided. Moreover, the individual components are non-toxic, cost-efficient and readily available, leading to an overall highly sustainable system.^[92]



Scheme 1.4: Mechanism of PO with CO₂ catalyzed by pyrogallol as multiple HB donor in combination with TBAI as nucleophile (cation removed for clarity).

As an innovative approach towards binary organocatalytic systems, Mattson et al. used TBAI in combination with silanediols.^[93] These are capable of recognizing the epoxide, as well as the iodide through HB donor interaction. As a result, high catalytic activities for various epoxides were observed with the optimized silanediol catalyst (Figure 1.7, (e)) even under very mild reaction conditions (r.t.- 40 °C, 1 bar CO₂, 18 h). In conclusion, this is a very promising approach regarding the carbon footprint of the reaction, if the catalyst system is shown to be reusable in future works. If the

energetically disadvantageous vacuum distillation can be avoided during the recycling procedure, an exceptional sustainable process is obtained.^[93]

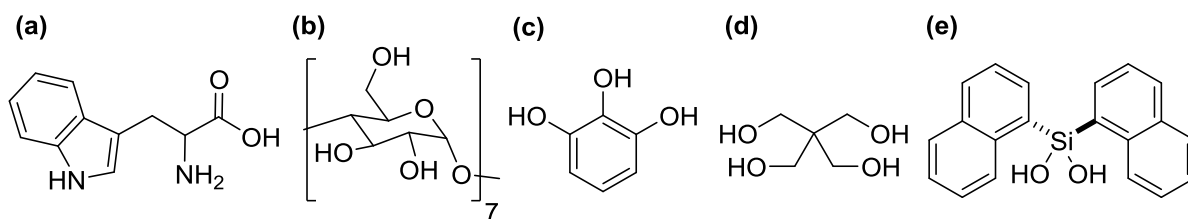


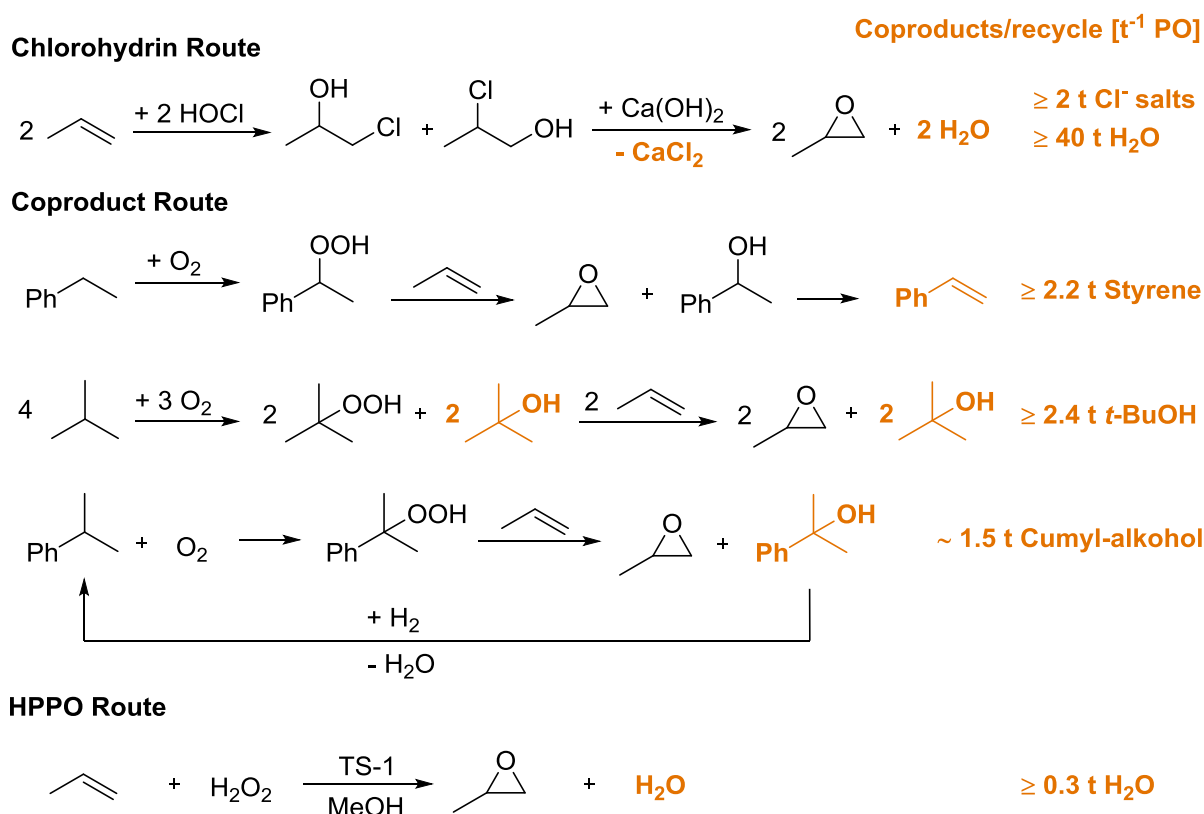
Figure 1.7: Selection of HB donor functionalized compounds used in combination with nucleophiles as binary catalytic systems for the cycloaddition of epoxides with CO₂.

1.2 Epoxidation of Olefins

1.2.1 Olefin Epoxidation in the Chemical Industry

The epoxidation of olefins is one of the most relevant transformations in the chemical industry and in academia.^[94] Epoxides are very important intermediates, mainly used as monomers for the production of polyglycols, polyurethanes and polyamides.^[95] Also a multitude of fine chemicals, like pharmaceuticals^[96] and surfactants^[94c], are synthesized using epoxides as feedstock. With an annual production capacity of 8 Mt/y in 2013 and an expected increase to approximately 9.6 Mt/y in 2018, PO represents one of the most important commodity chemicals.^[97] The main challenge regarding industrial PO production poses the necessity of suitable mediators that allow an economic process, as direct epoxidation in high yields is not yet possible with air or oxygen.^[98] Thus, a variety of reaction routes based on different mechanisms have been developed (Scheme 1.5).^[98] Through addition of hypochlorous acid to propene and subsequent dehydrochlorination under basic conditions, propylene oxide (PO) together with a great amount of harmful brine is obtained.^[98-99] In the so-called coproduct routes, hydroperoxides are generated in the first step through direct oxidation of precursors (ethylbenzene, *iso*-butane, cumene) with oxygen. During the epoxidation of propene, the corresponding alcohol is formed as coproduct, which can be dehydrated to the related olefin.^[100] To solve the problem of coproduct formation, the cumene hydroperoxide process was developed, whereby the initial precursor is recovered through reduction of the coproduct.^[101] Nevertheless, all of these approaches produce high amounts of by-products, thereby negatively affecting the environmental benignity and economy of the process. After oxygen, aqueous H₂O₂ represents the oxidant with the second highest oxygen availability.^[102] Moreover, in princi-

ple, water is generated as the only side product so that the amount of waste products compared to produced PO can be decreased significantly. Thus, the HPPO (hydrogen peroxide propylene oxide) process was developed as state-of-the-art technology.^[98, 100] Using a titanium doped MFI type zeolite catalyst (TS-1) and MeOH as solvent, 95 % PO selectivity under mild reaction conditions and > 99 % H₂O₂ conversions are achievable.^[103] With ≥ 0.3 t of H₂O as the major byproduct, the energy intensive purification of coproducts is redundant and the carbon footprint as well as the economic efficiency are optimized. Additionally, the process runs continuously with the heterogeneous catalyst packed in tubular reactors. The major drawbacks the HPPO process suffers from are the high price of the titanium used for doping the zeolite and the necessary regeneration of the TS-1 catalyst.^[100]



Scheme 1.5: Reaction routes for the production of PO in the chemical industry.^[98]

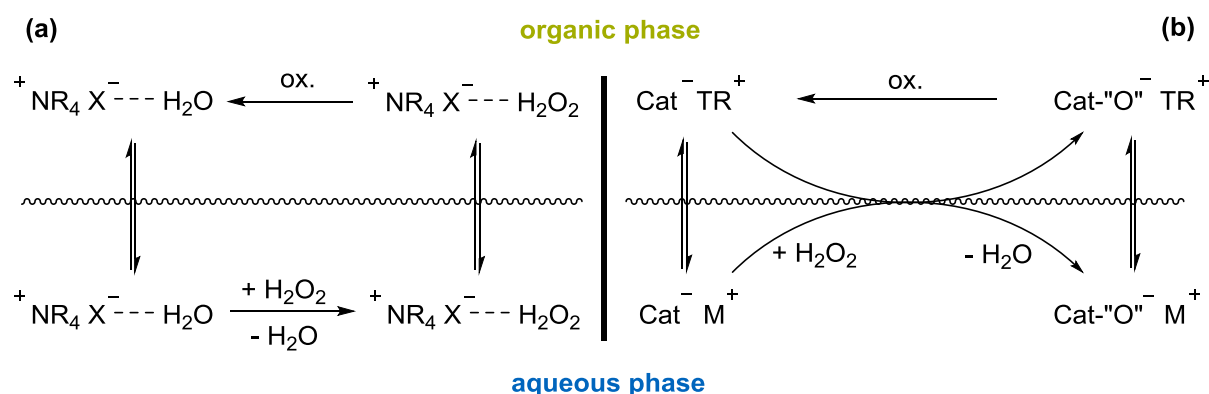
Besides the industrially used heterogeneous processes, vast numbers of homogeneous catalyst systems are described in literature.^[95, 104] However, these are limited to the synthesis of fine chemicals like enantiopure epoxides or other substrates requiring highly selective approaches.^[105] Nevertheless, molecular epoxidation catalysts have a highly promising potential regarding their tunability and reactivity and are hence extensively investigated especially in academia.^[95]

1.2.2 Multi-Phasic Olefin Epoxidation Using Ionic Compounds

Many high performance homogeneous catalysts have still not found their way to industrial applications because their separation from the products and reusability is rather difficult and cost-intensive.^[106] To solve this problem, the application of biphasic catalysis is a promising route, enabling simple catalyst recycling for a plethora of reactions.^[107] The catalyst remains in one phase, while the products are located in the other one, thus facilitating the separation procedure.^[108] Due to their unique physical properties like low volatility, thermal stability and low flashing points, ionic liquids (IL) possess some particular advantages over conventional organic solvents.^[109] Additionally, ILs often lead to enhanced reaction rates for several catalytic transformations.^[110] As these features are also strongly influenced by the chemical structure of the respective ions, they can be easily tuned towards the desired application, making them extremely versatile.^[111] Therefore, they are one of the most frequently used solvent classes for liquid-liquid biphasic transformations, including the oxidation of olefins.^[112] The initial report dealing with olefin epoxidation in ILs was published by Song and Roh.^[113] By applying NaOCl as oxidant and a Mn(III)salen complex in a mixture of DCM and an IL as solvent, a simple catalyst recycling procedure was made possible.^[113] Since then, numerous studies were presented dealing with transition metal epoxidation catalysts used in IL media. Most importantly, for Fe porphyrin,^[114] as well as for molybdenum complexes^[115] and methyltrioxorhenium,^[116] the catalytic activity is enhanced by using ILs instead of conventional solvents. However, the water content in the ILs has to be considered when using sensitive transition metal complexes. Additionally, e.g. $[\text{BF}_4]^-$ or $[\text{PF}_6]^-$ containing ILs hydrolyze during the reaction so that not all ILs can be used as suitable solvents when H_2O_2 is applied as oxidant.^[117] HF is thus produced, leading to reduced selectivity through by-product formation and decreased catalytic activity.^[112]

Aqueous H_2O_2 as oxidant frequently results in biphasic reactions, as olefins are often hydrophobic. Thus, the substrate is not located in the same phase as the oxidant and catalyst, leading to a decrease of the reaction rate. Phase transfer catalysis (PTC) is the most popular concept to ensure pronounced contact between the reaction partners and thus enable high reaction rates in multi-phase systems.^[118] Typically, ionic compounds like quaternary ammonium salts are used as transfer reagent (TR), forming an ion pair with an anionic reactant. An equilibrium between the organic and the water phase is formed and the transferred anionic compound reacts in the organic

phase. In this process the reactant is activated by the lower degree of hydration.^[119] Nevertheless, this mechanism is not limited to ionic compounds as shown by Dehm-low et al. for the extraction of H_2O_2 from aqueous solution in DCM or benzene (Scheme 1.6, (a)). By applying TBAB or $[\text{N}(n\text{-hex})_4]\text{Br}$, a significant amount of H_2O_2 was transferred in the organic phase through HB interactions of the halide to the oxidant. The amount extracted to the organic phase strongly depends on the cation, as longer alkyl chains and thus more lipophilic ammonium salts resulted in higher H_2O_2 content.^[120] Immense efforts concerning biphasic olefin epoxidation with aqueous H_2O_2 combined with PTC were undertaken by the groups of Venturello and Ishii through polyoxometalate (POM) catalysts.^[121] The combination of phosphate and tungstate or molybdate ions, respectively H_3PW_{12} or $\text{H}_3\text{PMo}_{12}$ as catalyst precursors, leads to water soluble peroxy intermediates upon treatment with aqueous H_2O_2 .^[122] By addition of a long alkyl chain ammonium TR, this precursor is transferred to the organic phase where it reacts with the lipophilic olefins (Scheme 1.6, (b)). The precursor is subsequently redissolved in the aqueous phase, closing the catalytic cycle.^[123]



Scheme 1.6: (a) Phase transfer of H_2O_2 by HB to quaternary ammonium salts^[120] and (b) biphasic catalyst system using a transfer reagent (TR) as counter cation additive.^[123]

Great research efforts were carried out to further improve this system in terms of higher catalytic activity and reusability. For instance, by application of task-specific ammonium salts, Zuwei et al. were able to prepare a reaction controlled self-separating catalyst for propene epoxidation.^[124] The salt precursor is insoluble in aqueous phase or organic solvents but reacts with H_2O_2 , forming a catalytic active and organic soluble species. After consumption of H_2O_2 , the insoluble catalyst precursor forms again, precipitates out of the reaction mixture and can thus be easily recycled through filtration.^[124] Therefore, propene, 1-hexene and cyclohexene can be

converted under mild reaction conditions (35 °C – 65 °C) with selectivities > 85 % towards the epoxide and > 95 % H₂O₂ conversion.^[124] The preparation of tetraalkylammonium salts of the divacant lacunary *Keggin*-type silica dodecatungstate [γ-SiW₁₀O₃₆]⁸⁻ under acidic conditions leads to alternative highly active catalysts. The POM synthesized at pH 2 with TBAB was able to epoxidize a variety of olefins with ≥ 99% selectivity and H₂O₂ utilization efficiency and was recycled with constant activity.^[125] It is important to note that the catalytic activity of this type of compounds strongly depends on the acidity of the reaction mixture used for the synthesis.^[125] Furthermore, acids are frequently used as an accelerator during catalysis.^[123]

Besides the possibility to introduce transition metals to tune the catalytic properties of POMs^[94b], the substitution of ammonium salts with imidazolium moieties is a prominent approach. By using [BMim] as countercation for [W₁₀O₂₃]⁴⁻ or [PW₁₂O₄₀]³⁻ and simultaneous application of the respective [BF₄]⁻ and [PF₆]⁻ IL as solvent, easily reusable and highly active systems could be generated.^[126] Utilization of an IL did not only facilitate the recycling procedure, but also created a beneficial chemical environment regarding the formation of the active species.^[126] Hou et al. could further show that a long chain imidazolium salt of a Ti substituted POM as heterogeneous epoxidation catalyst clearly outperformed the TBA analog. This was ascribed to the higher flexibility and accessibility of the imidazolium catalyst.^[127] The same group further accomplished a room temperature IL catalyst based on a dodecylimidazolium cation and a tungstate POM, showing a reaction-induced phase separation behavior. Thereby, the recycling procedure is significantly facilitated, as the catalyst separation can be conducted through simple decantation.^[128] A comparable effect can also be achieved by using bisimidazolium salts bridged with a PEG unit as a countercation for the system originally presented by Venturello et al.^[129] More recently, Hou and coworkers used the same imidazolium compounds for the synthesis of [W₂O₁₁]²⁻ salts, thereby yielding thermoregulated catalysts for olefin epoxidation with aqueous H₂O₂. Upon heating the reaction mixture to the desired temperature, the catalyst dissolves in ethyl acetate. After the epoxidation is completed, cooling to 0 °C leads to the precipitation of the IL catalyst, whereby a separation by simple decantation is enabled. As a result, the catalyst can be recycled efficiently and remains its activity for 17 consecutive runs.^[130] As aforementioned, a multitude of functional groups can be easily introduced to the imidazolium moiety to design the properties towards the desired application. This also applies for POM catalysts, where amino functionalized imidazolium

cations can be used to synthesize heterogeneous *Keggin*-type catalyst analogs by combination with $\text{H}_3\text{PW}_{12}\text{O}_{40}$. The structure of this insoluble POM ionic hybrid consists of nanospheres with partly protonated ammonium imidazolium cations and non-protonated amino units. The authors assume that the amino-functionalized cations interact with the POM anion through HB, which leads to superior catalytic activity compared to imidazolium compounds without functional groups. Additionally, the HB properties stabilize the nanosphere structure, leading to an easily recyclable insoluble solid catalyst system.^[131] Triethoxysilylpropyl wingtip modified imidazolium salts can also be used to immobilize peroxotungstate as counter anion on silica supports. Therefore, Mizuno et al. first prepared the respective $[\text{PF}_6]^-$ salt, covalently anchored the resulting IL on the carrier material and finally exchanged the anion with the POM. The prepared heterogeneous catalyst was able to epoxidize a broad scope of substrates and was recyclable through simple filtration with constant activity over four runs.^[132] Alternatively, vinyl substituted imidazolium salts can be used to synthesize POM containing organic inorganic hybrid materials. In the first step mono- and divinyl modified imidazolium bromide salts are radically copolymerized, while the POM unit is subsequently introduced through anion exchange.^[133] These heterogeneous catalysts can be separated by filtration and are reusable without losing catalytic activity for at least three runs.^[133b] Apart from tungstate compounds, POM based on octamolybdates are prepared in an easy and cost-efficient manner under acidic conditions with defined pH values. Recently, it was found that POM bearing 1-hexyl-3-methylimidazolium or 1-hexyl-2,3-dimethylimidazolium cations are applicable as self-separating catalysts for the epoxidation of olefins using aqueous H_2O_2 as oxidant.^[134] The catalyst directly precipitates out of the reaction mixture upon completion of the respective run, so that no addition of organic solvent is required. Followed by washing with water, the recovered catalyst is reused for the next catalytic cycle, thereby showing nearly quantitative epoxide yield for at least ten consecutive runs (60 °C, 1 h, 1.5 mol %).^[134] In order to facilitate the reaction procedure, carboxy functionalized imidazolium salts can be used to synthesize catalytic active molybdate based POMs *in situ*.^[135] Hence, the system is simplified considerably as the utilization of additional acids becomes redundant. The catalytic activity depends on the pH value, which is controlled by varying the carboxy-imidazolium/ Na_2WO_4 ratio used for generating the catalyst. At tenfold excess of imidazolium salt, the optimum catalytic performance was obtained and 68 % cyclooctene oxide yield could be achieved (60 °C,

24 h, 0.1 mol %). Moreover, the catalyst system could be reused for five runs with a negligible loss of activity.^[135]

1.2.3 Activation of H₂O₂ by Hydrogen Bonding

Conventionally, metal catalysts form peroxo species as active sites through reaction with the oxidant. As an alternative, H₂O₂ in aqueous solution can be activated by compounds forming HB. The initial studies dealing with alkene epoxidation solely catalyzed by this mode of action were conducted by Neumann et al. using fluorinated alcohol solvents as HB donors.^[136] The strong electron withdrawing effect of the fluorine substituents in combination with the HB donor ability of the hydroxy group leads to the electrophilic activation of H₂O₂. The reactivity also depends on the degree of fluorination, as 2,2,2-trifluoroethanol shows inferior catalytic activity compared to 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP). Thus, the cyclooctene oxide yield could be increased from 66 % to 99 % under the applied reaction conditions with HFIP as solvent and epoxidation mediator (60 °C, 20 h).^[136] Shortly afterwards, R. A. Sheldon et al. confirmed the catalytic activity of these solvents and proved their inert nature during the course of the reaction. Therefore, oxidation products are not involved in the formation of the catalytic active species, meaning that only HB interactions are responsible for H₂O₂ activation.^[137] DFT calculations shed some light onto the mechanism and particularly on the role of HFIP, which was found to provide a complementary charge template for the transition state. Thus, the bond deformations are reduced and the electronic interactions between the fluorine residues and the hydrogen atoms of the alkene and H₂O₂ stabilize the transition state (Figure 1.8, (a)).^[138] The influence of solvent clusters was revealed through kinetic investigations of the catalytic performance, depending on the concentration of HFIP in the epoxidation of *cis*-cyclooctene.^[139] Significantly enhanced catalytic activity was only observed for high HFIP concentrations, where coordination spheres of multiple HFIP molecules are assumed to cause the rate acceleration.^[139] Moreover, aggregates of HFIP and especially its di- and trimers show an elevated positive partial charge at the free hydroxy group and thus stronger HB donor properties.^[140] On the basis of these results, the mechanism of the HFIP catalyzed olefin epoxidation was reinvestigated by Berkessel et al. with DFT methods.^[141] It was shown that the energy activation barrier decreased by approx. 15 kcal/mol, when two or three HFIP molecules are involved in the reaction (Figure 1.8, (b,c)). This strongly suggests the participation of coordinated

HB networks during the catalytic cycle.^[141] The major drawback regarding fluorinated alcohols as catalytic active solvents is the large amount used for the reaction combined with their extensive costs. To overcome this challenge, dendritic catalysts were developed, which possess a high local concentration of fluororoalcohols on the polymer surface. Hence, a comparable interaction to the multiple HB network of conventional HFIP as solvent and high catalytic activity is enabled for olefin epoxidation with aqueous H_2O_2 . Consequently, 20 mol % HFIP analogs can be applied as substoichiometric catalyst for quantitative cyclooctene oxide yield instead of using an excess of HFIP as solvent.^[142]

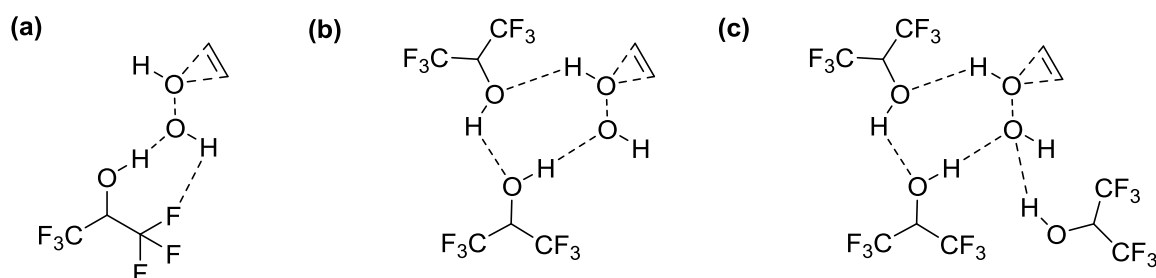
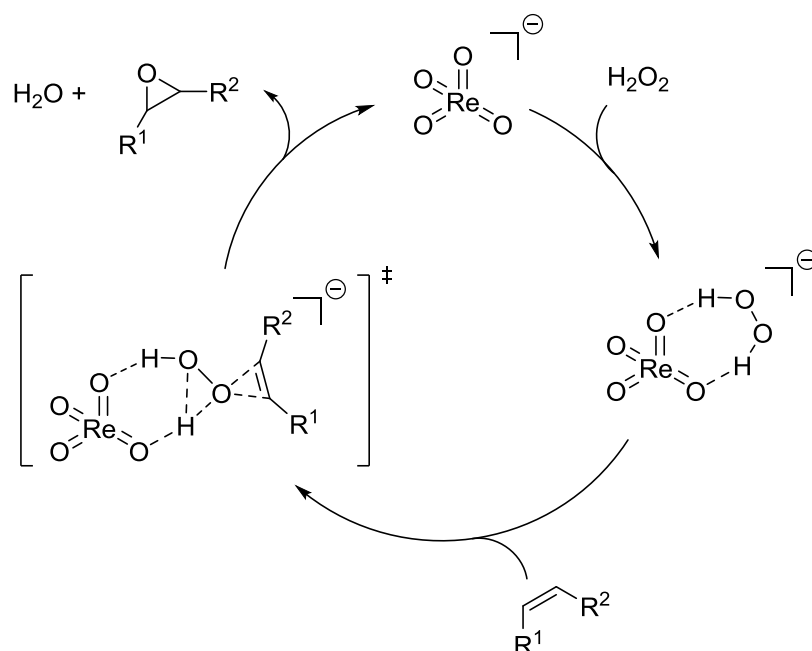


Figure 1.8: Possible transition states during the epoxidation of olefins with HB activated H_2O_2 involving (a) one, (b) two or (c) three molecules of HFIP according to DFT calculations.

In addition to HB donors, it was shown that HB acceptors are capable of activating H_2O_2 for the oxidation of sulfides to the respective sulfoxides.^[143] Vibrational and NMR spectroscopic studies have depicted that the $[\text{BF}_4]^-$ anion of imidazolium salts as solvent interacts with the hydrogen atoms of H_2O_2 through HB. Hence, the IL serves as an activator, leading to a higher electrophilicity of the H_2O_2 oxygen atom and participating in the cleavage of water as leaving group from the intermediate.^[143] More recently, it was firstly reported that HB acceptors are also able to mediate the epoxidation of olefins with H_2O_2 . Therefore, imidazolium perrhenates were synthesized in high purities by a simple procedure using an anion exchange resin (AER). The obtained ILs were used in equimolar amounts for the epoxidation of *cis*-cyclooctene, whereby nearly quantitative conversion to the epoxide was observed (70 °C, 4 h, 2.5 eq. aq. H_2O_2).^[144] This is a counterintuitive result, as perrhenates show no activity towards olefin epoxidation under common reaction conditions because of the interaction with the solvation shell.^[145] To investigate the role of the chemical environment on the catalytic performance in detail, NH_4^+ , K^+ and imidazolium perrhenates were used as H_2O_2 activators for the epoxidation of *cis*-cyclooctene. It was found that the imidazolium cation has a strong beneficial effect on the reaction

outcome, as the perrhenate anion is dissolved without the formation of a solvent shell. Consequently, the HB acceptor ability of the perrhenate anion is not passivated and a peroxide complex can be formed. The reaction mechanism was analyzed by extensive IR, Raman and NMR spectroscopic studies. As the symmetry of $[\text{ReO}_4]^-$ changes after the addition of H_2O_2 from T_d to C_{2v} , while the local symmetry of the Re center is unaffected, the formation of Re peroxo species was excluded. This was corroborated by ^{17}O labeled NMR spectroscopy. Therefore, the metal center is not involved in the reaction and an outer sphere mechanism can be stated. The energetically most feasible scenario for the reaction mechanism was determined through DFT calculations with ethene as a model substrate (Scheme 1.7). The first step involves the formation of an outer-sphere complex between $[\text{ReO}_4]^-$ and H_2O_2 through HB interactions, thereby activating the oxidant. The extent of this effect is strongly influenced by the polarity of the cation and thus the ion pairing. Subsequently, the transition state results from the addition of the olefin. Finally, an oxygen atom of the pre-coordinated H_2O_2 is transferred to the olefin and the epoxide is obtained with water as the only by-product. The IL mediators are also easily recyclable through extraction with *n*-hexane and can be reused for at least eight consecutive without loss of activity. This clearly demonstrates their inertness under oxidative reaction conditions.^[144]

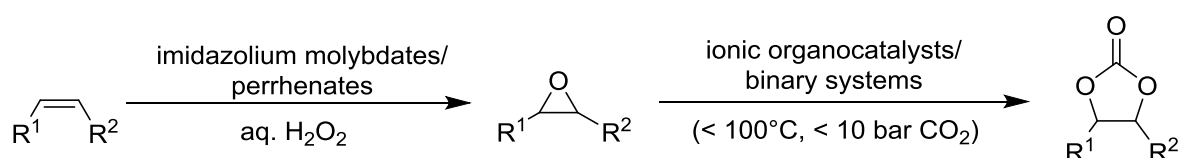


Scheme 1.7: Mechanism of olefin epoxidation with H_2O_2 activated through HB to perrhenate anions.^[144]

However, equimolar amounts of imidazolium perrhenates have to be used to reach quantitative conversions.^[144] This is highly undesirable because of the costs associated with the rhenium containing counter anion. In order to improve their activity, the easily tunable imidazolium moiety enables the tailoring of the IL properties, e.g. ion pairing and solubility. This opens the possibility to use these compounds in catalytic amounts, thereby decreasing the amount of rhenium in the reaction mixture.

2 Objective of the Thesis

The main focus of this work was the development of organocatalytic systems for the sustainable chemical fixation of CO₂ as cyclic carbonates, which represent highly desirable products. In contrast to the majority of organocatalysts reported in literature, the aim of the newly designed systems is to provide high catalytic activity at mild reaction conditions (< 100 °C, < 10 bar CO₂). Thus, the carbon footprint of the process can be minimized, thereby improving the overall sustainability. Although imidazolium halides are frequently used organocatalysts for cyclic carbonate synthesis, the role of the cation during the catalytic cycle has not been examined in detail. Therefore, mechanistic investigations were carried out to understand the influence of the cation, in order to design task-specific catalysts through structural optimization. Additionally, binary synergistic catalyst systems were designed through combination of commercially available compounds as epoxide activators with suitable nucleophiles. In this process, simple, cost-efficient and sustainable systems for cyclic carbonate synthesis should be enabled.



Scheme 2.1: Catalytic systems investigated within this work for the conversion of olefins to epoxides and subsequent cycloaddition reaction with CO₂ to the respective carbonate.

In the second part of this work, imidazolium molybdates and perrhenates were synthesized and examined as catalysts for olefin epoxidation with aqueous H₂O₂ as oxidant. Carboxy functionalized imidazolium salts were applied for the *in situ* synthesis of catalytically active polyoxomolybdates. Hence, the reaction procedure was expected to be facilitated, as the need of additional acids for the catalyst preparation prior to olefin epoxidation is eliminated. The key objective of the studies regarding imidazolium perrhenates was to evaluate their potential as epoxidation catalysts and to analyze the influence of the cation structure on the catalytic performance. By tailoring of the imidazolium residue, it was intended to optimize the properties of these ionic compounds and thus the catalytic activity. The long-term goal of this thesis is to combine all findings to develop catalysts for the one-pot synthesis of cyclic carbonates from olefins, an oxidant and CO₂ in a sustainable manner.

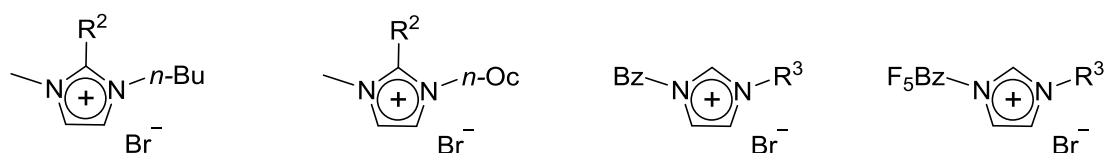
3 Results and Discussion

3.1 Publication Summaries

This chapter shortly summarizes the crucial aspects of the publications prepared during the course of this dissertation. The bibliographic data of the complete manuscripts can be found in Chapter 5 of this thesis.

3.1.1 Cycloaddition of CO₂ and Epoxides Catalyzed by Imidazolium Bromides under Mild Conditions: Influence of the Cation on Catalyst Activity

To evaluate the influence of the cation on the catalytic cycloaddition of CO₂ to epoxides, systemically varied imidazolium bromides with different alkyl chain lengths and aromatic residues were initially synthesized and characterized (Figure 3.1). Therefore, ¹H and ¹³C-NMR spectroscopy as well as elemental analysis were used, while the structure of **10** was also determined by single X-ray diffraction. Subsequently, the catalytic activity of the obtained series was tested under mild reaction conditions (70 °C, 4 bar CO₂, 22 h, 10 mol %) for the cycloaddition of CO₂ with PO to PC.



R²: H (**1**), Me (**2**), Et (**3**) R²: H (**4**), Me (**5**), Et (**6**) R³: *n*-Bu (**7**), *n*-Oc (**8**) R³: *n*-Bu (**9**), *n*-Oc (**10**)

Figure 3.1: Synthesized imidazolium bromide catalysts for PC formation (BzF₅: 1-(2,3,4,5,6-pentafluoro)benzyl).

All investigated catalysts are liquid at 70 °C and thus able to dissolve CO₂ under reaction conditions. However, the difference of CO₂ solubility in **4**, **5**, **6**, **8** and **10** was found to be insignificant so that an influence on the activity can be neglected. Regarding the impact of R² on the catalytic activity for **1-3** and **4-6**, it was shown that an acidic C2 proton has a beneficial effect compared to an alkyl substituent. As free carbenes can be excluded, because **2-3** and **5-6** are active although their C2 position is alkylated, the HB properties of the C2 proton cause the higher catalytic activity. This is supported by the improved reactivity upon modification with the electron withdrawing fluorinated aromatic wingtip. Thus, the acidity of the C2 proton increases, leading to a stronger HB donor ability and interaction strength. Consequently, **10** showed the

highest catalytic activity under the applied conditions. To investigate the HB interaction of **10** in more detail, FTIR studies were performed upon addition of PO to the neat catalyst at room temperature. The frequency of the vibration band at 3064 cm^{-1} , which is assigned to the stretching mode of the catalyst C2 proton, shifts by 24 cm^{-1} and broadens by a factor of 3 (Figure 3.2). This can be ascribed to intermolecular HB of **10** to PO. As other imidazolium-ring vibrations are also shifted, it is difficult to exactly specify which structural elements interact with PO. Nevertheless, the most pronounced contact is observed between the acidic C2 proton and the oxygen atom of PO, deriving from HB. On the basis of these results, the mechanism for PC formation catalyzed by imidazolium halides bearing an acidic C2 proton is proposed (Scheme 3.1). The HB interaction weakens the PO C-H bond, thereby facilitating the nucleophilic ring-opening through the halide. Additionally, transition states and intermediates are stabilized, so that higher catalytic activity is observed. After optimization of the reaction parameters (T, t, cat. loading), catalyst **10** was able to mediate PC formation in 91 % yield at mild conditions ($70\text{ }^{\circ}\text{C}$, 4 bar CO_2 , 22 h, 10 mol %). Moreover, the recycling can be conducted through simple precipitation with remaining activity for ten consecutive cycles. Aside from PO, a broad scope of epoxides can further be converted to the respective cyclic carbonates applying **10** as catalyst. Thus, **10** represents a versatile and sustainable organocatalyst for the cycloaddition of epoxides with CO_2 .

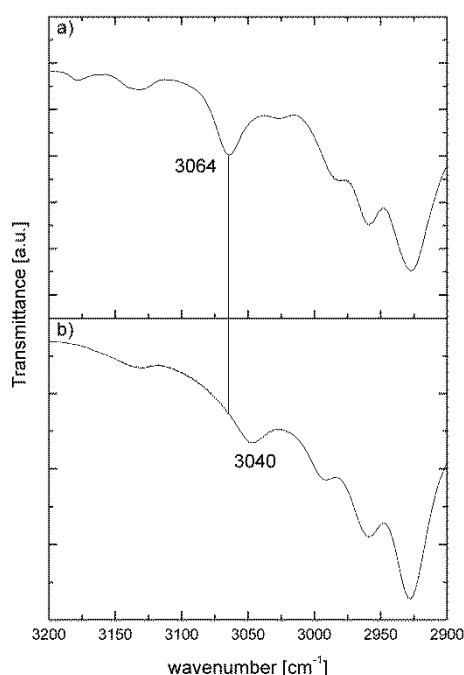
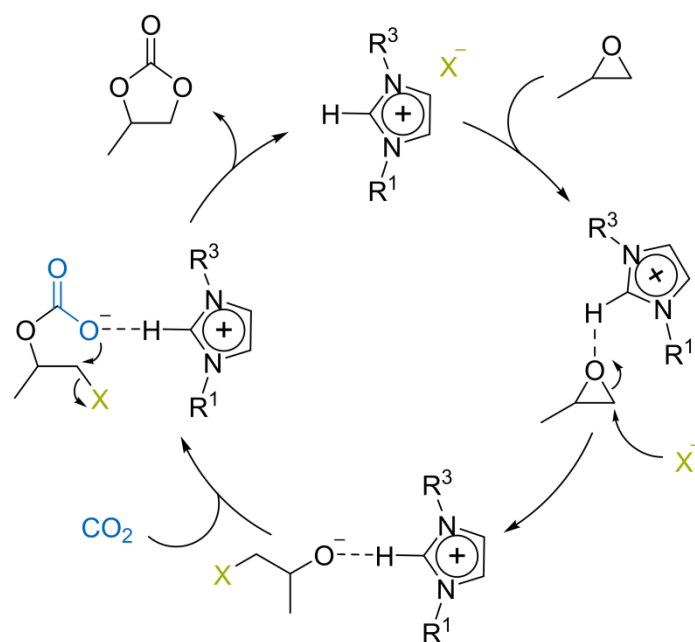


Figure 3.2: FTIR spectrum of **a)** neat catalyst **10** and **b)** **10** with excess of PO.



Scheme 3.1: Mechanism for the cycloaddition reaction of PO with CO_2 catalyzed by imidazolium halides.

3.1.2 Hydroxy-Functionalized Imidazolium Bromides as Catalysts for the Cycloaddition of CO₂ and Epoxides to Cyclic Carbonates

As previously mentioned, the acidic C2 proton of the imidazolium moiety synergistically interacts through HB during the mechanism of cyclic carbonate formation. Further, organocatalysts with three hydroxy groups in spatial proximity are more efficient compared to single or double functionalized analogs.^[73, 84] Therefore, imidazolium bromides with three (11-13) or two (14-16) HB donor sites were synthesized (Figure 3.3) and characterized by ¹H, ¹³C-NMR, IR and mass spectroscopy as well as by elemental analysis. Subsequently, the impact of the multiple HB donor sites was evaluated through comparison of the catalytic activities with 1-10 and 17 as benchmark single HB donor based systems. In order to ensure a proper comparison, the aforementioned mild reaction conditions (70 °C, 4 bar CO₂, 10 mol % halide) were also applied for 11-17.

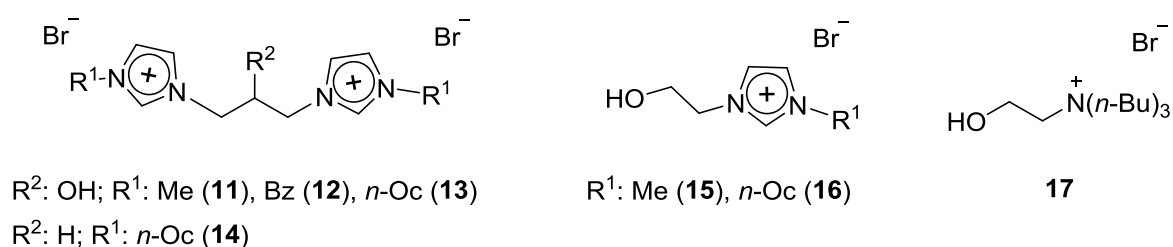
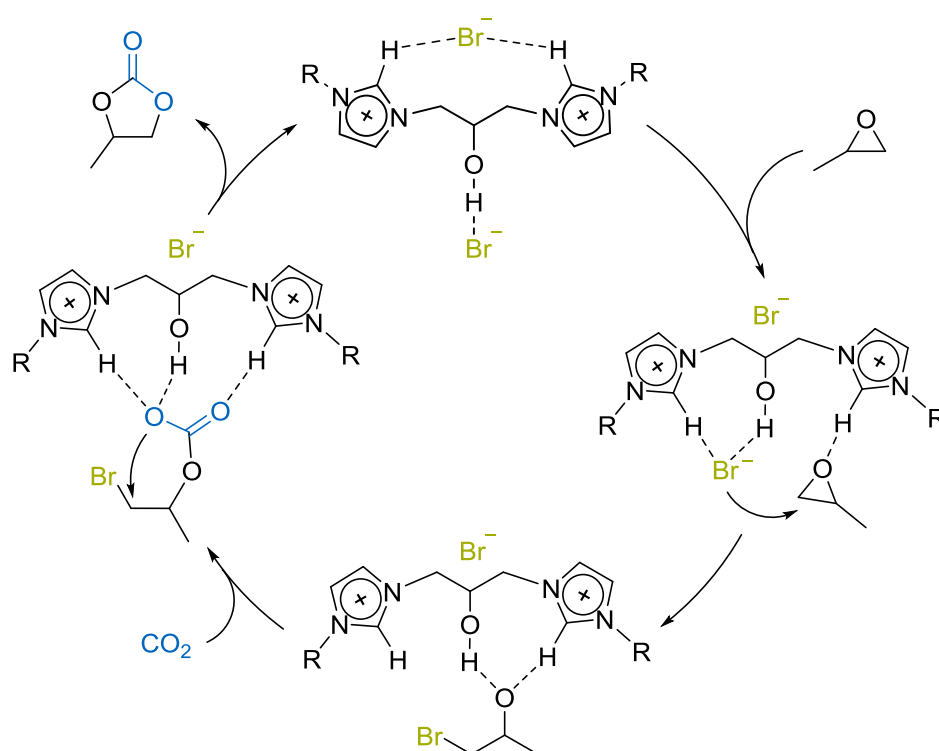


Figure 3.3: Investigated catalysts to determine the impact of multiple HB donor sites on the activity.

It was shown that the variation of the wingtip residue results in an increased catalytic activity in the order of Me < Bz < *n*-Oc (11-13). This is caused by the significantly higher solubility of 13 in the reaction mixture. Additionally, 13 is the most active organocatalyst among the investigated compounds, as 95 % PC yield were observed after 16 h. Consequently, the reaction time was reduced by 6 h compared to catalyst 10. The high catalytic activity arises from the triple HB donor motif (two acidic C2 protons and one hydroxy group), leading to an efficient epoxide activation and stabilization of intermediates and transition states. The PC yields for the double HB analogs 14 and 16 amount to only 58 % and respectively 79 %, thereby underlining the positive effect of three neighboring HB sites. Compared to 17 as an ammonium based benchmark system (92 % PC), the application of 13 further gave a slightly higher yield under the applied conditions. Moreover, the catalytic activity of 13 was compared with [HDBU]Cl as a state-of-the-art organocatalysts. As described in literature,^[46] more demanding conditions but shorter reaction times are used (140 °C,

10 bar CO₂, 2 h, 1 mol %). In consequence, identical catalytic activity of **13** and [HDBU]Cl was observed. For the potential application in larger scale and concerning the sustainability, the recycling procedure and catalyst reusability are crucial. By addition of diethyl ether, **13** is easily precipitated from the reaction mixture and can be reused after filtration. Hence, energy-intensive distillation of PC is avoided. As no leaching phenomena or decomposition processes occur, the catalyst is reusable for at least ten times without loss of activity. The facile recyclability demonstrates the main advantage of catalyst **13** over **17** or [HDBU]Cl. Catalyst **13** can also be used for the efficient conversion of a wide range of epoxides to their corresponding cyclic carbonates, including functionalized substrates. To shine some light onto the mechanism for catalyst **13**, DFT calculations were carried out, leading to the proposed cycle shown in Scheme 3.2. It was confirmed that all HB donor sites show an interaction during the mechanism. This leads to more efficient epoxide activation, a stabilization of intermediates and thus a high catalytic activity. In conclusion, **13** is a very promising organocatalyst for cyclic carbonate formation under mild reaction conditions because of its high activity, stability and easy reusability. Therefore, the gap between bifunctional and binary organocatalyst systems is minimized.



Scheme 3.2: Proposed mechanism for the cycloaddition of CO₂ with PO catalyzed by **13**.

3.1.3 Niobium(V)chloride and Imidazolium Bromides as Efficient Dual Catalyst Systems for the Cycloaddition of Carbon Dioxide and Propylene Oxide

The combination of the transition metal salt niobium(V)chloride (NbCl_5)₂ as *Lewis* acid with nucleophiles like TBAB results in highly reactive catalyst systems for cyclic carbonate formation. The metal center activates the epoxide through coordination to the oxygen atom, which results in a polarized C-O bond and enhanced ring-opening by the halide anion. Thus, the system shows high catalytic activity, even when the reaction is carried out under ambient conditions. Herein, imidazolium bromides were investigated as nucleophiles instead of using TBAB, with particular focus on the impact of the imidazolium substitution pattern on the catalytic activity. Therefore, a series of 31 imidazolium bromides with varying aliphatic and aromatic residues (Figure 3.4) was synthesized and applied as a catalyst systems for PC formation in combination with (NbCl_5)₂ (r.t., 4 bar CO₂, 2 h).

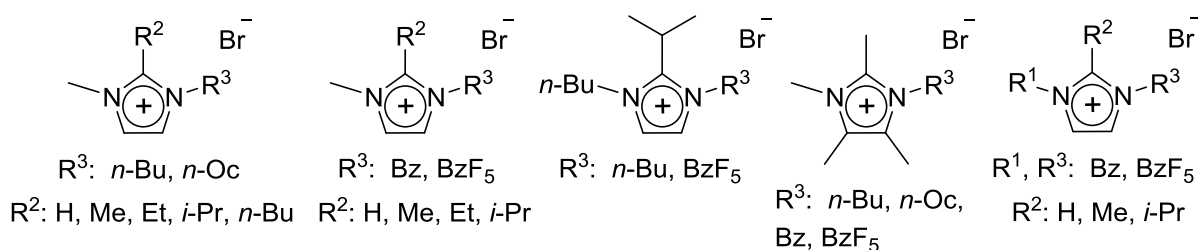


Figure 3.4: Imidazolium bromides used as nucleophiles in combination with (NbCl_5)₂.

It was shown that the investigated imidazolium bromides with aliphatic residues gave very high yields, whereby the catalytic activity varies in dependency of the R² substituent. In contrary to imidazolium bromides as single catalysts without involving *Lewis* acids, the presence of an acidic C2 proton results in lower activities. Due to the strong interaction of the metal center and PO compared to the C2 proton HB, additional activation of PO by the imidazolium cation is negligible. However, the ion-pairing of the imidazolium moiety to the anion decreases upon C2 alkyl substitution as the strong HB interaction site is eliminated. This leads to a lower degree of electrostatic interaction, thus higher anion nucleophilicity and catalytic activity. As a result, the PC yield increases in the order of R²: H < Me ≤ Et ~ *i*-Pr ~ *n*-Bu according to the steric demand of the residue. The most active imidazolium bromide (R¹: Me, R²: *i*-Pr, R³: *n*-Bu) was used for the determination of the optimal catalyst loading and ratio of NbCl_5 /nucleophile, which was found to be 1.0/2.0 mol-%. *In situ* IR measurements further revealed that the imidazolium bromide/ NbCl_5 system constitutes con-

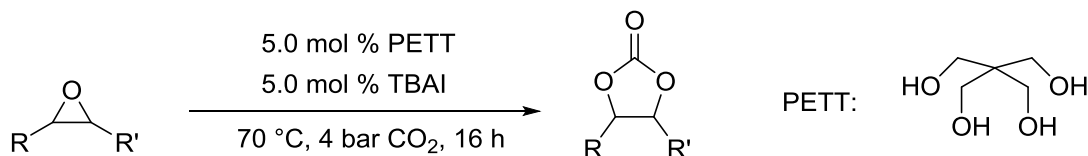
siderably higher turnovers in the beginning of the reaction compared to TBAB. But during the course of the reaction, the activity of the imidazolium system drops quickly, while the loss of activity for TBAB is less pronounced. This is ascribed to the shift of the chemical environment from slightly polar (PO) to polar (PC).

The use of imidazolium bromides bearing aliphatic and aromatic residues generally resulted in lower PC yields compared to cations exclusively substituted with aliphatic side-chains. This is caused by the rather poor solubility in the reaction mixture. Through introduction of BzF₅, the solubility and catalytic activity could be increased compared to the corresponding non-fluorinated Bz compounds. As observed for aliphatic cations, the substitution in C2 position leads to a higher catalytic activity due to a lower degree of ion pairing. As a result, the same order of reactivity was observed for the respective R² residues. Finally, combinations of (NbCl₅)₂ with imidazolium bromides bearing two aromatic wingtips were used as catalyst systems for PC synthesis, leading to poor conversions. Due to the formation of Coulomb networks, which are comparatively stable because of the aryl substituents, these imidazolium bromides are barely soluble in the reaction mixture. Nevertheless, it was confirmed that alkyl substitution in C2 position leads to enhanced catalytic activity because of the reduced electrostatic interaction between the ions. Additionally, fluorination of the aromatic rings again leads to a higher solubility and activity. The (NbCl₅)₂/imidazolium bromide catalyst system was also applied for the conversion of a variety of epoxides to their cyclic carbonates. The reaction conditions were chosen according to the previously studied (NbCl₅)₂/TBAB system (40 °C and 8 h).^[25a] The investigated aliphatic and aromatic epoxides were converted efficiently with the exception of epichlorohydrin. The chloro group presumably interacts with the metal center and therefore competes with the oxygen atom of the epoxide.

In summary, combinations of imidazolium bromides with (NbCl₅)₂ enable high catalytic activities under very mild reaction conditions. The *Lewis* acidic metal center activates the epoxide and the imidazolium bromide provides the nucleophile for subsequent ring-opening. The ion pairing and the solubility are the main factors that affect the catalytic activity regarding the imidazolium structure. Whereas C2 alkyl substitution results in decreased ion pairing and higher catalytic activity, alkyl wingtips lead to better solubility and conversions in comparison to aryl residues.

3.1.4 Cycloaddition of Carbon Dioxide and Epoxides Using Pentaerythritol and Halides as Dual Catalyst System

Combinations of PETT and a variety of halide based nucleophiles, like TBAI, were used as binary organocatalysts to synthesize cyclic carbonates (Scheme 3.3).



Scheme 3.3: Cyclic carbonate synthesis using PETT/Nu as binary organocatalytic system.

The cycloaddition of PO and CO₂ was used to determine the influence of the presence of both compounds and the nature of the nucleophilic component on the reactivity. It was clearly shown that synergistic effects are responsible for the activity as no or very small conversions are observed when only PETT or TBAI are used as single catalysts. This is ascribed to the HB abilities of PETT, leading to lower energy barriers for epoxide ring-opening and the stabilization of intermediates and transition states. Thus, the reaction can be carried out with excellent conversions under mild reaction conditions (70 °C, 4 bar CO₂) with PETT/TBAI as a binary system. Further, the catalytic activity strongly depends on the cation of the halide nucleophile. Using KI instead of TBAI significantly reduces the PC yield from 96 to 6 % under the investigated conditions. This derives from the lower degree of ion pairing in TBAI, leading to higher anion nucleophilicity and catalytic activity. Moreover, imidazolium bromides were used as nucleophilic components to investigate the role of the cation in more detail, whereby lower catalytic activities were observed. On the one hand, this arises from the higher bulkiness of the tetrabutylammonium cation, resulting in higher nucleophilicity. On the other hand, the imidazolium cation also bears HB sites, which presumably stabilize the halide anion and compete with the hydroxy groups of PETT. This is supported by the higher yields obtained when C2- or tetramethyl-substituted imidazolium analogs with weaker HB donor abilities are used in this binary system. Both TBAI and TBAB lead to nearly quantitative yields in combination with PETT after 22 h and thus, superior catalytic activity compared to the other cations investigated. Therefore, time dependent analysis of the PC yield was carried out with TBAI and TBAB in order to examine the influence of the anion on the reactivity. At any time of the reaction, the yields of the TBAI system were higher compared to TBAB. As the bromide anion possesses a stronger HB acceptor effect, the interaction strength to

PETT is higher compared to iodide. As a result, it is stabilized to a greater extent and is less nucleophilic and reactive. Additionally, the activation of the epoxide through PETT is hindered because of the more pronounced competitive HB of bromide compared to iodide. Consequently, the reaction time can be decreased from 22 h for PETT/TBAB to 16 h for PETT/TBAI. By systematic variation of the temperature and the catalyst loading, the reaction conditions were further optimized. Finally 96 % PC yield could be achieved at 70 °C by using 5.0 mol-% of PETT and TBAI.

The reusability and the recycling procedure are crucial regarding the catalyst sustainability. Especially binary organocatalysts like pyrrogallol/TBAI are consumed or decompose during the reaction, so that the activity drops already in the second run. However, this not observed for the PETT/TBAI catalyst system, which can be reused for at least eight runs with remaining activity (Figure 3.5, (a)). In addition, the separation from the reaction mixture is conducted by simple precipitation with diethyl ether and subsequent filtration, so that energy intensive distillation is avoided. Moreover, PETT/TBAI converts a broad scope of substrates efficiently to their respective cyclic carbonates. Besides aromatic and aliphatic epoxides, the system also tolerates functional groups (Figure 3.5 (b), Entry 4 and 5) and thus covers a wide range.

Conclusively, the PETT/TBAI binary organocatalyst system efficiently mediates the cycloaddition reaction of epoxides with CO₂ under mild reaction conditions. It consists of cost-efficient, commercially available and non-toxic components and is easily reusable for eight consecutive runs without loss of activity. Therefore, it represents an exceptional sustainable approach towards cyclic carbonate synthesis using CO₂.

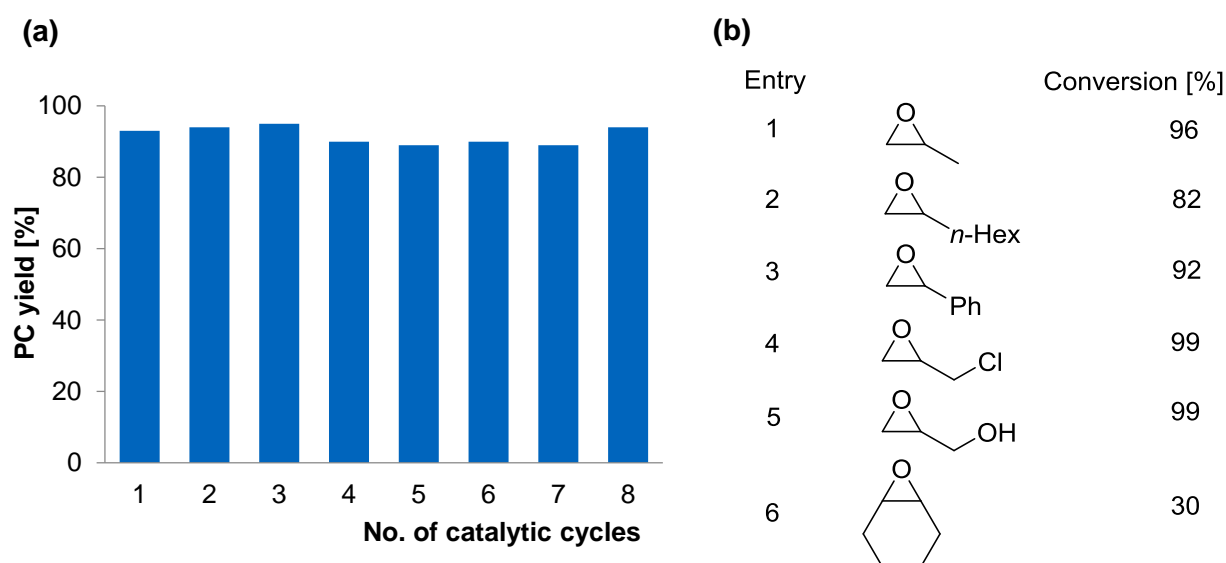
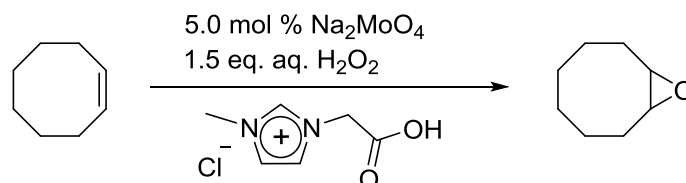


Figure 3.5: (a) Influence of the PETT/TBAI catalyst recycling on the PC yield and (b) conversions of different substrates, selectivities $\geq 99\%$ for all investigated epoxides (reaction conditions in both cases: 70 °C, 4 bar CO₂, 16 h, 10 mmol epoxides and 0.5 mmol catalysts).

3.1.5 Epoxidation of Olefins Catalyzed by Polyoxomolybdates Formed *in situ* in Ionic Liquids

Carboxy-functionalized ILs were used for the *in situ* formation of a catalyst system based on polyoxomolybdates. The resulting system was tested for the epoxidation of *cis*-cyclooctene using aqueous H₂O₂ (Scheme 3.4). Consequently, organic acids, usually used for adjusting the pH value, can be avoided, leading to facilitated catalyst preparation.



Scheme 3.4: Catalytic epoxidation of *cis*-cyclooctene with polyoxomolybdates prepared *in situ*.

In order to find the optimum reaction conditions, the ratio IL to molybdate, the molybdate concentration itself and the reaction temperature were systematically varied. As expected, the catalytic activity is strongly influenced by the amount of acid-functionalized IL because the pH value controls the structure of the formed polyoxomolybdates. By adjusting the pH value to 3.5, corresponding to an IL/molybdate ratio of 10/1, the highest catalytic activity was observed. It is supposed that these conditions result in the formation of [Mo_xO_y]²⁻ clusters, which are responsible for the catalytic activity. Moreover, no cyclooctene-1,2-diol is formed so that the selectivity for all reactions amounts to > 99%. The molybdate concentration in the reaction mixture also heavily impacts the catalytic activity. In absence of a molybdate precursor, the olefin conversion drops rapidly, so that peracids as potential alternative catalytic active species can be excluded. Besides, using an excess of molybdate also gave a decreased cyclooctene oxide yield because of the solubility behavior. The resulting slurry of undissolved sodium molybdate rapidly decomposes H₂O₂ and thus, low yields are observed. Finally, a catalyst loading of 5.0 mol % was found as the optimum value regarding the catalytic activity of the system. Furthermore, variations of the reaction temperature were found to substantially affect the outcome of the reaction (Figure 3.6, (a)). This can be attributed to changes in the solubility behavior of the polyoxometalate in the water/IL phase and the olefin in the reaction mixture. At T < 50 °C a slurry was formed because of the solubility of the IL in the aqueous phase. When the temperature was increased to 70 °C, the H₂O₂ decomposition is

presumably the favored reaction route, as strong gas evolution was observed. Finally, a reaction temperature of 60 °C gave the highest cyclooctene oxide yield among the investigated reaction conditions. With the optimum reaction conditions in hand (60 °C, 24 h, 1.5 eq. H₂O₂, IL/Na₂MoO₄: 10.0/1.0 mol %), the recycling procedure and reusability of the catalyst system were investigated. Therefore, the organic phase containing the product was extracted with *n*-hexane and separated from the aqueous phase, which was simply dried in high vacuum at 80 °C. Consequently, the catalyst system could be reused for six reaction runs with negligible loss of activity (Figure 3.6, (b)).

The epoxidation of *cis*-cyclooctene can be conducted under relatively mild reaction conditions, using the *in situ* prepared catalyst system. Although the system is not as active as molecular systems, the use of readily available and cost-efficient precursors and the reusability without considerable loss of activity are attractive aspects.

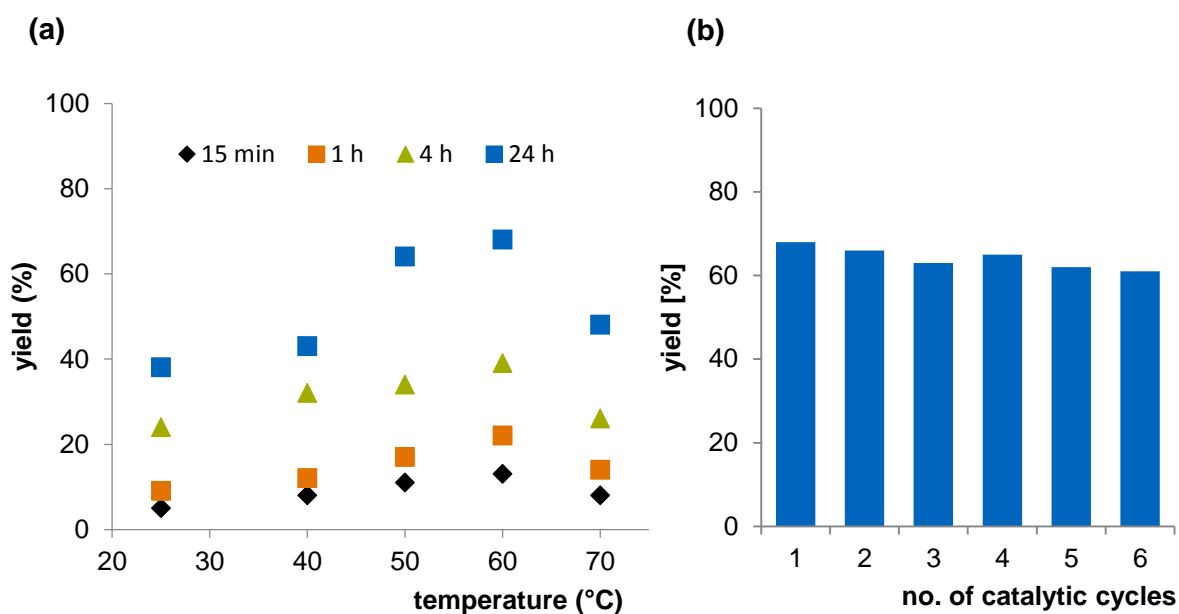
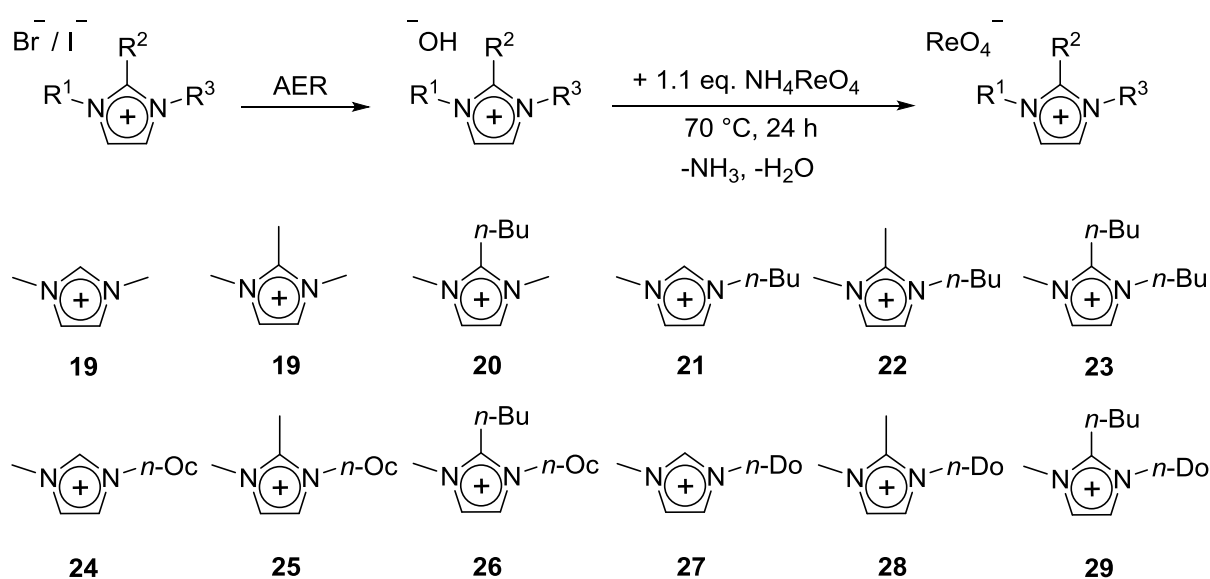


Figure 3.6: (a) Effect of the reaction temperature and reaction time on the cyclooctene oxide yield (2.00 mmol *cis*-cyclooctene, 0.1 mmol Na₂MoO₄, 1.0 mmol IL, 3 mL deionized water); (b) reusability of the catalyst system for *cis*-cyclooctene epoxidation (60 °C, 24 h).

3.2 Epoxidation of Olefins Using Ionic Liquids as Phase Transfer Catalysts

3.2.1 Results and Discussion

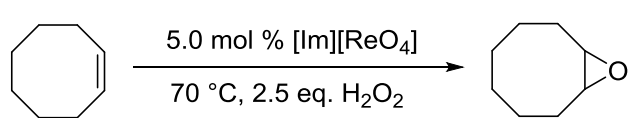
As mentioned in Chapter 1.2.3, equimolar amounts of imidazolium perrhenates are able to mediate the epoxidation of *cis*-cyclooctene using aqueous H₂O₂ as oxidant. Due to the chemical environment created by the IL, the [ReO₄]⁻ anion is capable of activating H₂O₂ by HB, leading to a facilitated oxygen atom transfer to the olefin. Herein, imidazolium perrhenates as olefin epoxidation catalysts were investigated for the first time. In particular, the influences of the imidazolium cation on the environment, e.g. solubility, ion pairing and thus, on the catalytic activity, were investigated. Therefore, various alkyl substituted imidazolium perrhenates were synthesized (Scheme 3.5) using a literature known procedure based on halide anion exchange to the corresponding hydroxide.^[144] By conversion with ammonium perrhenate, the target compounds are finally obtained together with water and ammonia as the only by-products.

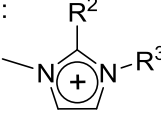


Scheme 3.5: Synthesis procedure and overview of all synthesized imidazolium perrhenate catalysts within this work (AER: anion exchange resin).

The catalytic activity was investigated with *cis*-cyclooctene as a model substrate and 50 wt. % aq. H₂O₂ (Table 3.1) as the oxidant. It is noteworthy that the selectivity for cyclooctene oxide was $\geq 99\%$ for all investigated catalysts as no epoxide ring-opening was detected.

Table 3.1: Epoxidation of *cis*-cyclooctene catalyzed by imidazolium perchrenates.



[Im] : 

R²: H, Me, *n*-Bu
R³: Me, *n*-Bu, *n*-Oc, *n*-Do

Catalyst	R ³	R ²	Yield [%] after 4 h ^[a]	Yield [%] after 24 h ^[a]
18	Me	H	3	22
19	Me	Me	4	60
20	Me	<i>n</i> -Bu	5	60
21	<i>n</i> -Bu	H	7	55
22	<i>n</i> -Bu	Me	8	70
23	<i>n</i> -Bu	<i>n</i> -Bu	24	100
24	<i>n</i> -Oc	H	44	98
25	<i>n</i> -Oc	Me	88	100
26	<i>n</i> -Oc	<i>n</i> -Bu	21	34
27	<i>n</i> -Do	H	64	96
28	<i>n</i> -Do	Me	85	100
29	<i>n</i> -Do	<i>n</i> -Bu	2	8

Reaction conditions: 10 mmol *cis*-cyclooctene, 0.5 mmol catalyst (5.0 mol %), 25 mmol aq. H₂O₂ (50 wt. %), T = 70 °C; [a] yields based on GC analysis.

Regarding the influence of the substitution pattern on the reaction outcome, it was found that imidazolium cations with short alkyl wingtips and a C2 proton result in low activities (Table 3.1, catalysts **18**, **21**). The strong HB donor ability of the acidic C2-H presumably causes a high degree of ion pairing to [ReO₄]⁻. Thus, the activation of H₂O₂ by the anion as HB acceptor is hindered, leading to low conversions. However, alkyl chains in R² position do not enhance the catalytic activity significantly (Table 3.1, catalysts **19**, **20**, **22**, **23**). Consequently, the electrostatic interaction between the ions is not the only factor affecting the activity of the catalyst. As wingtip substitution with elongated alkyl chains leads to substantially improved activity (Table 3.1, catalysts **24**, **25**, **27**, **28**), the hydrophobicity of the IL catalysts is another key factor. Nevertheless, a *n*-Bu residue in C2 position results in a strongly decreased catalytic activity in these cases (Table 3.1, catalysts **26**, **29**), presumably because of the too high hydrophobicity. However, the corresponding C2 methylated analogs represent the most active epoxidation catalysts among the investigated compounds (Table 3.1,

catalysts **25**, **28**). They exhibit the proper solubility behavior and the degree of ion pairing is low, thereby enabling efficient activation of H_2O_2 by $[\text{ReO}_4]^-$ as HB acceptor. To understand the impact of the hydrophobicity on the activity in detail, the quantitative solubility of the R^3 : *n*-Oc series was determined in *cis*-cyclooctene, water and aqueous H_2O_2 . The investigated ILs are almost insoluble in *cis*-cyclooctene (< 50 ppm) and only barely soluble (**24**, 2 wt. %, **25**, 1 wt. %) or even insoluble (**26**) in water. These solubilities change drastically in presence of the oxidant in the aqueous phase. Whereas the behavior of **26** remains unchanged, **24** is entirely soluble and 25 wt. % of **25** are dissolved in 50 wt. % aq. H_2O_2 . Consequently, **24** and **25** are entirely dissolved in the aq. H_2O_2 phase under catalytic conditions, which is caused by the strong HB interactions of $[\text{ReO}_4]^-$ to H_2O_2 . Moreover, the solubility of *cis*-cyclooctene in the biphasic system is affected by the ILs (Figure 3.7, (a)). Compared to the absence of IL, the substrate solubility in aq. H_2O_2 under reaction conditions is enhanced by the factor of 50 using **24**, and 20 for **25**. In contrast, addition of **26** even lowers the olefin solubility in aq. H_2O_2 because of the three-phasic reaction mixture. Thus, the most active catalyst **25** (Figure 3.7, (b)) is entirely soluble in aq. H_2O_2 and is able to transfer the substrate in the aqueous phase. Further, the alkyl substitution in C2 position leads to low electrostatic interactions between the ions, which in turn enables more pronounced HB to H_2O_2 and therefore a more efficient activation.

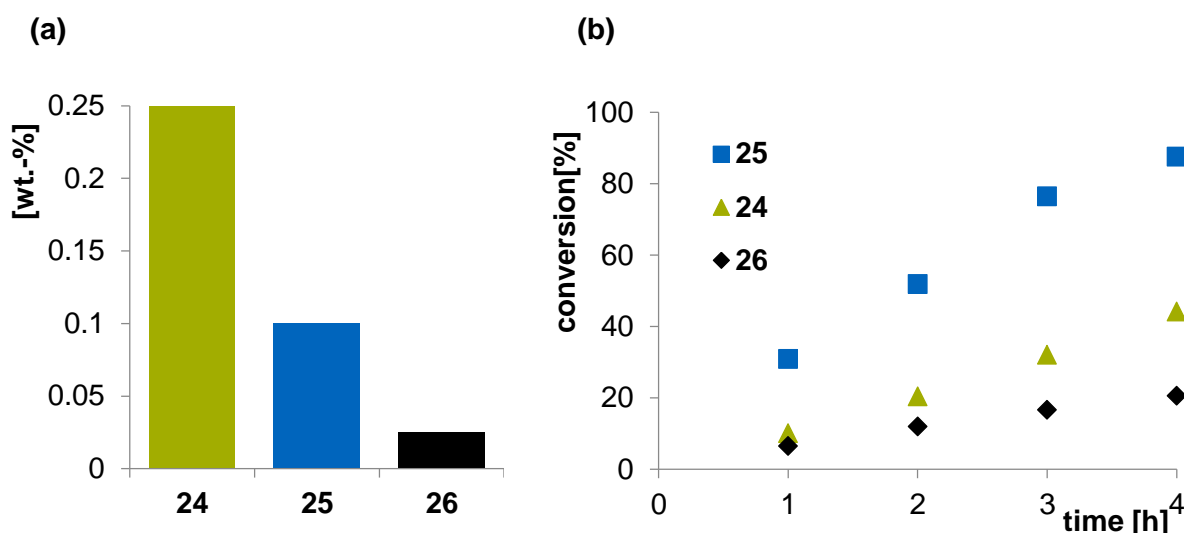


Figure 3.7: (a) *cis*-cyclooctene solubility in a mixture of 0.5 mmol catalysts and 25 mmol 50 wt. % aqueous H_2O_2 ; (b) time-dependent conversion of *cis*-cyclooctene with IL catalysts **24**, **25** and **26** (10 mmol *cis*-cyclooctene, 0.5 mmol ILs, 70 °C, 2.5 eq. H_2O_2).

For the investigation of the stability and the reusability of the catalysts, **24** and **25** were used as test compounds. After the recycling by extraction and subsequent dry-

ing in vacuum, the next catalytic run was started under standard conditions and 4 h reaction time. No decomposition reactions or leaching was observed and at least ten consecutive runs were possible without loss of activity (Figure 3.8).

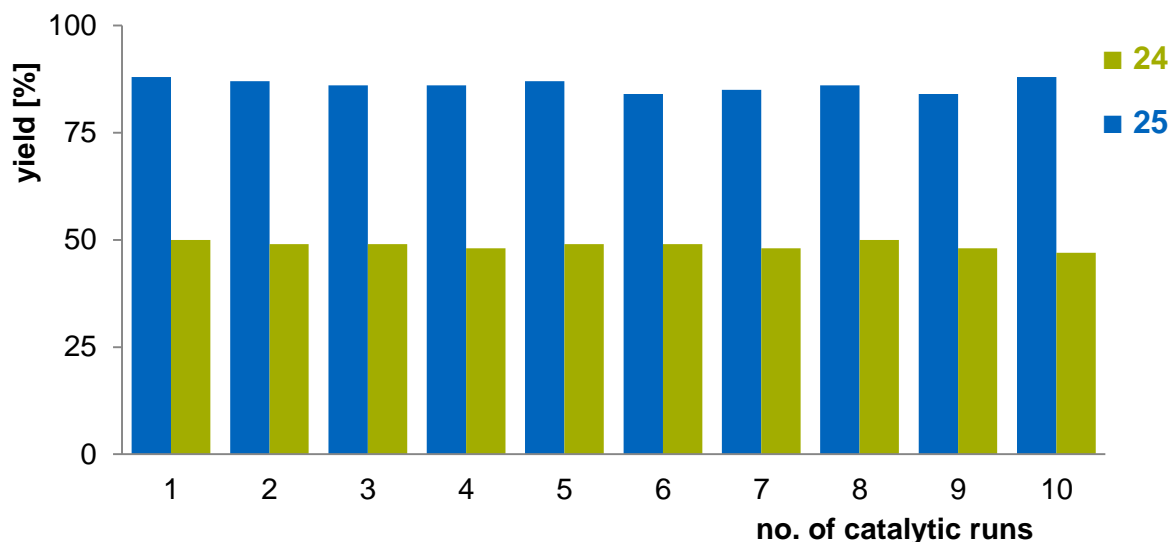


Figure 3.8: Yields of cyclooctene oxide for ten consecutive reaction with catalyst **24** and **25**, reaction conditions: 10 mmol *cis*-cyclooctene, 25 mmol aq. H₂O₂ (50 wt.%), 0.5 mmol catalysts, 4 h, 70 °C.

In addition, catalyst **25** was used for the oxidation of various olefins with aqueous H₂O₂ as oxidant. Given the different reactivities and solubilities of substrates other than *cis*-cyclooctene, more demanding reaction conditions were applied (70 °C, 24 h, 2.5 eq. H₂O₂, 20 mol % catalyst loading). All tested substrates could be efficiently converted, albeit to the corresponding diol products (Table 3.2). This derives from the higher sensitivity towards nucleophilic ring-opening of the respective epoxides compared to cyclooctene oxide. To challenge this problem, the structure of the applied imidazolium perrhenate catalysts can be individually tuned for each substrate, which will be the subject of future investigations.

Table 3.2: Epoxidation of various olefins with catalyst **25**.^[a]

Substrate	Conversion [%] ^[b]	Selectivity Diol [%] ^[b]
1-Octene	≥ 99 %	≥ 99 %
Styrene	≥ 99 %	≥ 99 %
Allyl alcohol	≥ 99 %	≥ 99 %
Cyclohexene	≥ 99 %	≥ 99 %

[a] Reaction conditions: 10 mmol olefin, 2.0 mmol catalyst (20 mol %), 25 mmol aq. H₂O₂ (50 wt. %), T = 70 °C; 24 h; [b] conversions and selectivities determined by integration of the olefin, diol and epoxide peaks in the ¹H NMR spectra.

In summary, these studies have shown for the first time that imidazolium perrhenates can be used as catalysts for the epoxidation of unfunctionalized olefins with aq. H_2O_2 . The catalytic activity is strongly influenced by the interactions between the ions and the catalyst hydrophobicity, which can both be controlled by systematic variation of the imidazolium pattern. Upon substitution of the C2 position with alkyl residues, the degree of ion pairing decreases, while the HB acceptor interaction strength of $[\text{ReO}_4]^-$ to H_2O_2 is enhanced. In order to allow a pronounced contact, the catalyst has to be soluble in the aqueous phase containing the oxidant. However, good activity is only achieved when the catalyst transfers the olefinic substrate in the aqueous phase, where the reaction takes place. Thus, the cation hydrophobicity has to be properly tuned so that the imidazolium perrhenate is soluble in aqueous H_2O_2 and is simultaneously able to act as phase transfer catalyst.

3.2.2 Experimental Details

All syntheses and catalytic reactions were carried out under air, if not stated otherwise. 1,2-Dimethylimidazole, hydrogen peroxide (50 % in water), *n*-hexane, acetonitrile, ethyl acetate were purchased from *Acros Organics*. NaOH pellets were purchased from *J. T. Baker*. 1-Bromobutane, 1-bromooctane and 1-bromododecane were received from *Merck*. *Cis*-cyclooctene (95 %), acetone and Amberlite IRA-400 (OH) were purchased from *Sigma-Aldrich*. All chemicals were used as received without further purification.

Analytical Equipment

^1H - and ^{13}C -NMR spectra were recorded on a 400 MHz *Bruker* Advance DPX-400 spectrometer and calibrated to the corresponding solvent signals (CDCl_3 : 7.26 ppm for ^1H , 77.16 ppm for ^{13}C ; DMSO: 2.50 ppm for ^1H , 39.52 ppm for ^{13}C). Microanalysis was performed at the Mikroanalytisches Labor of the Technische Universität München in Garching. The melting points were determined with a MPH-H2 melting point meter from *Schorpp Gerätetechnik*. Catalytic runs were performed on a cycler “Carousel 12 plus” from *Radleys* and monitored via GC methods on a *Hewlett-Packard* HP 5890 Series II instrument equipped with a FID, *Superlco* column Alphadex 120 and a *Hewlett-Packard* integration unit HP 3396 Series II.

Experimental Procedure for Catalytic Olefin Epoxidation

The corresponding catalyst (0.5 mmol or 2.0 mmol) was placed in a glass tube equipped with a magnetic stirring bar. Subsequently, the substrate (10.0 mmol) was added and the reaction mixture was heated to 70 °C. Finally, the oxidant (25.0 mmol) was added and the reaction mixture was kept at 70 °C for 4 and 24 hours. Continuous samples (0.1 mL) were taken from the top phase (substrate and product), mixed with an internal standard (1.0 mL) and analyzed by GC for *cis*-cyclooctene. The reaction outcome for all other substrates was determined by integration of the olefin, diol and epoxide peaks in the ¹H-NMR spectra.

Experimental Procedure for Catalyst Recycling

Recycling experiments were performed in a round-bottomed flask equipped with a magnetic stirring bar under the same conditions as mentioned above. After each run, *cis*-cyclooctene and cyclooctene oxide were extracted at 70 °C with *n*-hexane (2 x 2.5 mL). The residual solvent, water and hydrogen peroxide were subsequently removed under reduced pressure at 70 °C for 4 h.

Solubility Measurements

The solubility measurements were performed by Dipl.-Chem. Johannes Schäffer at the Chair of Chemical Engineering of Prof. Dr.-Ing. Andreas Jess at the Faculty of Engineering Sciences from the University of Bayreuth.

3.2.3 Synthesis and Characterization of the Catalysts

Preparation of Imidazolium Bromides

The imidazolium bromides and iodides (for **18**, **19** and **20**) were synthesized according to literature procedures.^[25b, 146] The purity of the compounds was determined with ¹H- and ¹³C-NMR spectroscopy as well as with elemental analysis.

Preparation of Imidazolium Perrhenate Catalysts

The imidazolium perrhenates were prepared according to a literature known procedure.^[144] The previously synthesized imidazolium bromides were first transformed to the corresponding hydroxide analogs through an anion exchange resin. Subsequently, an excess of NH₄ReO₄ (1.10 eq.) was added and the resulting reaction mixture was stirred at 70 °C for 24 h leading to water and ammonia as only by-products. Af-

terwards, all volatiles were removed in high vacuum at elevated temperatures and dichloromethane was added to the resulting mixture of imidazolium perrhenate and excess of NH_4ReO_4 . Finally, the insoluble NH_4ReO_4 was filtered off and the target catalyst was received after removing the volatiles in vacuo. The purity of the synthesized compounds was analyzed by means of ^1H -, ^{13}C -NMR and IR spectroscopy, as well as with elemental analysis and melting point determination.

Characterization Data

1,3-Dimethylimidazolium perrhenate (18):

$\text{C}_5\text{H}_9\text{N}_2\text{O}_4\text{Re}$ (347.34 g/mol); colorless powder; 89 % yield; m.p.: 90 °C;

^1H NMR ([d6]DMSO, 400 MHz, RT, ppm): δ = 9.02 (s, 1H, CH), 7.67 (d, $^3J(\text{H,H}) = 2$ Hz, 2 H, CH), 3.84 (s, 6H, CH_3);

^{13}C -NMR (100.28 MHz, CDCl_3 , RT, ppm) δ = 137.0, 123.5, 35.7;

IR (ATR, diamond crystal, neat): ν = 905 (Re=O asymmetric);

Elemental analysis calcd. (%) for $\text{C}_5\text{H}_9\text{N}_2\text{O}_4\text{Re}$: C 17.29, H 2.61, N 8.07, O 18.42, Re 53.61; found: C 17.77, H 2.70, N 8.15, Re 52.75.

1,2,3-Trimethylimidazolium perrhenate (19):

$\text{C}_6\text{H}_{11}\text{N}_2\text{O}_4\text{Re}$ (361.37 g/mol); colorless powder; 33 % yield; m.p.: 191 °C;

^1H NMR ([d6]DMSO, 400 MHz, RT, ppm): δ = 7.24 (s, 2H, CH), 3.92 (s, 6H, CH_3), 2.76 (s, 3H, CH_3);

^{13}C -NMR ([d6]DMSO, 100 MHz, RT, ppm) δ = 144.8, 122.0, 34.8, 9.2;

IR (ATR, diamond crystal, neat): ν = 900 (Re=O asymmetric);

Elemental analysis calcd. (%) for $\text{C}_6\text{H}_{11}\text{N}_2\text{O}_4\text{Re}$: C 19.94, H 3.07, N 7.75, O 17.71, Re 51.53; found: C 20.10, H 2.98, N 7.72, Re 51.63.

2-Butyl-1,3-dimethylimidazolium perrhenate (20):

$\text{C}_9\text{H}_{17}\text{N}_2\text{O}_4\text{Re}$ (403.45 g/mol); colorless powder; 86 % yield; m.p.: 93 °C;

^1H NMR ([d6]DMSO, 400 MHz, RT, ppm): δ = 7.60 (s, 2H, CH), 3.79 (s, 6H, CH_3), 2.99 (t, $^3J(\text{H,H}) = 8$ Hz, 2H, CH_2), 1.60-1.50 (m, 2H, CH_2), 1.42-1.30 (m, 2H, CH_2), 0.91 (t, $^3J(\text{H,H}) = 7$ Hz, 3H, CH_3);

^{13}C -NMR ([d6]DMSO, 100 MHz, RT, ppm) δ = 144.8, 122.0, 34.8, 9.2;

IR (ATR, diamond crystal, neat): ν = 897 (Re=O asymmetric);

Elemental analysis calcd. (%) for $C_9H_{17}N_2O_4Re$: C 26.79, H 4.25, N 6.94, O 15.86, Re 46.15; found: C 26.99, H 4.25, N 6.95, Re 45.92.

1-Butyl-3-methylimidazolium perrhenate (21):

$C_8H_{15}N_2O_4Re$ (389.42 g/mol); yellow liquid; 86 % yield;

1H NMR ($CDCl_3$, 400 MHz, RT, ppm): δ = 8.92 (s, 1 H, CH), 7.39 (s, 1 H, CH), 7.36 (s, 1 H, CH), 4.24 (t, $^3J(H,H) = 8$ Hz, 2 H, CH_2), 4.02 (s, 3 H, CH_3), 1.89-1.81 (m, 2 H, CH_2), 1.39-1.30 (m, 2 H, CH_2), 0.97 (t, $^3J(H,H) = 7$ Hz, 3 H, CH_3);

^{13}C NMR ($CDCl_3$, 100 MHz, RT, ppm) δ = 136.5, 123.9, 122.5, 50.3, 36.7, 32.1, 19.6, 13.5;

IR (ATR, diamond crystal, neat): $\nu = 892$ (Re=O asymmetric);

Elemental analysis calcd. (%) for $C_8H_{15}N_2O_4Re$: C 24.67, H 3.88, N 7.19, O 16.43, Re 47.82; found: C 24.98, H 3.81, N 7.06, Re 43.38.

3-Butyl-1,2-dimethylimidazolium perrhenate (22):

$C_9H_{17}N_2O_4Re$ (403.45 g/mol); colorless powder; 90 % yield; m.p.: 68 °C

1H NMR ($CDCl_3$, 400 MHz, RT, ppm): δ = 7.28 (d, $^3J(H,H) = 2$ Hz, 1H, CH), 7.22 (d, $^3J(H,H) = 2$ Hz, 1H, CH), 4.12 (t, $^3J(H,H) = 8$ Hz, 2H, CH_2), 3.89 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 1.84-1.76 (m, 2H, CH_2), 1.42-1.35 (m, 2H, CH_2), 1.00 (t, $^3J(H,H) = 7$ Hz, 3H, CH_3);

^{13}C -NMR ($CDCl_3$, 100 MHz, RT, ppm) δ = 149.6, 122.8, 121.1, 48.9, 35.5, 31.7, 19.8, 13.7, 9.7;

IR (ATR, diamond crystal, neat): $\nu = 898$ (Re=O asymmetric);

Elemental analysis calcd. (%) for $C_9H_{17}N_2O_4Re$: C 26.79, H 4.25, N 6.94, O 15.86, Re 46.15; found: C 26.73, H 4.19, N 6.84, Re 46.90.

1,2-Dibutyl-3-methylimidazolium perrhenate (23):

$C_{12}H_{23}N_2O_4Re$ (445.53 g/mol); red oil; 80 % yield;

1H NMR ($CDCl_3$, 400 MHz, RT, ppm): δ = 7.36 (s, 1H, CH), 7.31 (s, 1H, CH), 4.09 (t, $^3J(H,H) = 8$ Hz, 2H, CH_2), 3.88 (s, 3H, CH_3), 3.00 (t, $^3J(H,H) = 8$ Hz, 2H, CH_2), 1.83-1.75 (m, 2H, CH_2), 1.63-1.55 (m, 2H, CH_2), 1.50-1.35 (m, 4H, CH_2), 0.98 (t, $^3J(H,H) = 8$ Hz, 6H, CH_3);

^{13}C -NMR($CDCl_3$, 100 MHz, RT, ppm) δ = 146.9, 123.2, 121.1, 48.5, 35.3, 32.1, 29.2, 23.1, 22.6, 19.8, 13.7, 13.6;

IR (ATR, diamond crystal, neat): $\nu = 894$ (Re=O asymmetric);

Elemental analysis calcd. (%) for $C_{12}H_{23}N_2O_4Re$: C 32.50, H 4.77, N 6.32, O 14.43, Re 41.98; found: C 32.47, H 5.07, N 6.21, Re 41.89.

1-Methyl-3-octylimidazolium perrhenate (24):

$C_{12}H_{23}N_2O_4Re$ (445.53 g/mol); pale yellow liquid; 90 % yield;

1H NMR ($CDCl_3$, 400 MHz, RT, ppm): $\delta = 8.85$ (s, 1 H, CH), 7.41 (s, 1 H, CH), 7.36 (s, 1 H, CH), 4.20 (t, $^3J(H,H) = 8$ Hz, 2 H, CH_2), 4.00 (s, 3 H, CH_3), 1.89-1.79 (m, 2 H, CH_2), 1.35-1.20 (m, 10 H, CH_2), 0.84 (t, $^3J(H,H) = 8$ Hz, 3 H, CH_3);

^{13}C NMR ($CDCl_3$, 100 MHz, RT, ppm) $\delta = 136.2, 124.0, 122.5, 50.5, 36.6, 31.7, 30.2, 29.0, 28.9, 26.3, 22.6, 14.1$;

IR (ATR, diamond crystal, neat): $\nu = 895$ (Re=O asymmetric);

Elemental analysis calcd. (%) for $C_{12}H_{23}N_2O_4Re$: C 32.35, H 5.20, N 6.29, O 14.36, Re 41.79; found: C 32.60, H 5.30, N 6.31, Re 42.53.

1,2-Dimethyl-3-octylimidazolium perrhenate (25):

$C_{12}H_{25}N_2O_4Re$ (459.56 g/mol); pale yellow oil; 87 % yield;

1H NMR ($CDCl_3$, 400 MHz, RT, ppm): $\delta = 7.33$ (d, $^3J(H,H) = 2$ Hz, 1H, CH), 7.25 (d, $^3J(H,H) = 2$ Hz, 1H, CH), 4.09 (t, $^3J(H,H) = 8$ Hz, 2H, CH_2), 3.87 (s, 3H, CH_3), 2.67 (s, 3H, CH_3), 1.81-1.71 (m, 2H, CH_2), 1.40-1.20 (m, 10H, CH_2), 0.86 (t, $^3J(H,H) = 7$ Hz, 3H, CH_3);

^{13}C -NMR ($CDCl_3$, 100 MHz, RT, ppm) $\delta = 143.7, 122.7, 120.9, 48.8, 35.3, 31.6, 29.6, 28.9, 26.3, 22.5, 14.0, 9.5$;

IR (ATR, diamond crystal, neat): $\nu = 895$ (Re=O asymmetric);

Elemental analysis calcd. (%) for $C_{12}H_{25}N_2O_4Re$: C 33.98, H 5.48, N 6.10, O 13.93, Re 40.52; found: C 34.00, H 5.42, N 6.05, Re 40.50.

2-Butyl-1-methyl-3-octylimidazolium perrhenate (26):

$C_{16}H_{31}N_2O_4Re$ (501.64 g/mol); colorless powder; 85 % yield; m.p.: 53 °C;

1H NMR ($CDCl_3$, 400 MHz, RT, ppm): $\delta = 7.33$ (d, $^3J(H,H) = 2$ Hz, 1H, CH), 7.28 (d, $^3J(H,H) = 2$ Hz, 1H, CH), 4.04 (t, $^3J(H,H) = 8$ Hz, 2H, CH_2), 3.84 (s, 3H, CH_3), 2.96 (t, $^3J(H,H) = 8$ Hz, 2H, CH_2), 1.80-1.75 (m, 2H, CH_2), 1.63-1.55 (m, 2H, CH_2), 1.47-1.37 (m, 2H, CH_2), 1.31-1.21 (m, 10H, CH_2), 0.93 (t, $^3J(H,H) = 7$ Hz, 3H, CH_3), 0.81 (t, $^3J(H,H) = 7$ Hz, 3H, CH_3);

^{13}C -NMR (CDCl_3 , 100 MHz, RT, ppm) δ = 146.6, 123.1, 120.9, 48.6, 35.2, 31.6, 30.0, 29.1, 28.9, 28.9, 26.4, 23.0, 22.5, 22.4, 14.0, 13.5;

IR (ATR, diamond crystal, neat): ν = 894 (Re=O asymmetric);

Elemental analysis calcd. (%) for $\text{C}_{16}\text{H}_{31}\text{N}_2\text{O}_4\text{Re}$: C 38.31, H 6.23, N 5.58, O 12.76, Re 37.12; found: C 38.43, H 6.71, N 5.64, Re 36.41.

1-Dodecyl-3-methylimidazolium perrhenate (27):

$\text{C}_{16}\text{H}_{31}\text{N}_2\text{O}_4\text{Re}$ (501.64 g/mol); colorless powder; 95 % yield; m.p.: 49 °C;

^1H NMR (CDCl_3 , 400 MHz, RT, ppm): δ = 8.85 (s, 1 H, CH), 7.40 (m, 1 H, CH), 7.34 (m, 1 H, CH), 4.21 (t, $^3J(\text{H,H})$ = 8 Hz, 2 H CH_2), 4.01 (s, 3 H, CH_3), 1.89 (t, $^3J(\text{H,H})$ = 8 Hz, 2 H CH_2), 1.33–1.24 (m, 18 H CH_2), 0.86 (t, $^3J(\text{H,H})$ = 8 Hz, 3 H, CH_3);

^{13}C NMR (CDCl_3 , 100 MHz, RT, ppm): δ = 136.4, 123.9, 122.4, 50.6, 36.7, 32.0, 30.3, 29.7, 29.7, 29.6, 29.5, 29.4, 29.1, 26.4, 22.8, 14.2;

IR (ATR, diamond crystal, neat): ν = 900 (Re=O asymmetric);

Elemental analysis calcd. (%) for $\text{C}_{16}\text{H}_{31}\text{N}_2\text{O}_4\text{Re}$: C 38.31, H 6.23, N 5.58, O 12.76, Re 37.12; found: C 38.52, H 6.31, N 5.57, Re 37.14.

1,2-Dimethyl-3-dodecylimidazolium perrhenate (28):

$\text{C}_{17}\text{H}_{33}\text{N}_2\text{O}_4\text{Re}$ (515.66); colorless powder; 90 % yield; m.p.: 50 °C;

^1H NMR (CDCl_3 , 400 MHz, RT, ppm): δ = 7.31 (d, $^3J(\text{H,H})$ = 2 Hz, 1H, CH), 7.23 (d, $^3J(\text{H,H})$ = 2 Hz, 1H, CH), 4.06 (t, $^3J(\text{H,H})$ = 8 Hz, 2H, CH_2), 3.84 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 1.79-1.70 (m, 2H, CH_2), 1.30-1.20 (m, 18H, CH_2), 0.84 (t, $^3J(\text{H,H})$ = 7 Hz, 3H, CH_3);

^{13}C -NMR (CDCl_3 , 100 MHz, RT, ppm) δ = 143.8, 122.8, 121.0, 48.9, 35.3, 31.9, 29.8, 29.6, 29.6, 29.4, 29.3, 29.1, 26.4, 22.7, 14.2, 9.5;

IR (ATR, diamond crystal, neat): ν = 895 (Re=O asymmetric);

Elemental analysis calcd. (%) for $\text{C}_{17}\text{H}_{33}\text{N}_2\text{O}_4\text{Re}$: C 39.60, H 6.45, N 5.43, O 12.41, Re 36.11; found: C 39.91, H 6.47, N 5.33, Re 36.44.

2-Butyl-1-dodecyl-3-methylimidazolium perrhenate (29):

$\text{C}_{20}\text{H}_{39}\text{N}_2\text{O}_4\text{Re}$ (557.75 g/mol); off-white powder; 72 % yield; m.p.: 76 °C;

^1H NMR (CDCl_3 , 400 MHz, RT, ppm): δ = 7.38 (d, $^3J(\text{H,H})$ = 2 Hz, 1H, CH), 7.28 (d, $^3J(\text{H,H})$ = 2 Hz, 1H, CH), 4.07 (t, $^3J(\text{H,H})$ = 8 Hz, 2H, CH_2), 3.90 (s, 3H, CH_3), 3.01 (t, $^3J(\text{H,H})$ = 8 Hz, 2H, CH_2), 1.90-1.80 (m, 2H, CH_2), 1.68-1.58 (m, 2H, CH_2), 1.53-1.42

(m, 2H, CH_2), 1.40-1.20 (m, 18H, CH_2), 0.99 (t, $^3J(H,H) = 7$ Hz, 3H, CH_3), 0.87 (t, $^3J(H,H) = 7$ Hz, 3H, CH_3);

^{13}C -NMR ($CDCl_3$, 100 MHz, RT, ppm) $\delta = 146.9, 123.3, 121.0, 48.8, 35.4, 32.0, 30.2, 29.7, 29.6, 29.5, 29.4, 29.2, 29.1, 26.6, 23.2, 22.6, 14.3, 13.7$;

IR (ATR, diamond crystal, neat): $\nu = 902$ (Re=O asymmetric);

Elemental analysis calcd. (%) for $C_{20}H_{39}N_2O_4Re$: C 43.07, H 7.05, N 5.02, O 11.47, Re 33.39; found: C 43.45, H 7.17, N 5.06, Re 32.57.

4 Summary and Outlook

The catalytic cycloaddition of CO₂ with epoxides to cyclic carbonates is a sustainable possibility for the utilization of this greenhouse gas as a chemical building block. Organocatalysts bear a great potential, because of the easy availability and handling, as well as the lower price and toxicity compared to metal based systems. However, efficient conversions for this reaction with metal-free catalysts are only possible by applying high temperatures and pressures, as they are generally less active. Hence, the major part of this thesis focuses on the development of tailored organocatalysts, which allow milder reaction conditions and lead to a minimized carbon footprint of the process. The long-term objective is thereby to achieve a comparable catalytic activity to metal based systems in order to conduct cyclic carbonate synthesis at ambient conditions with organocatalysts.

Although imidazolium halides are known metal-free catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides, the impact of the cation on the catalytic activity was not understood in detail. Thus, imidazolium bromides with varying imidazolium residues were synthesized and applied as catalysts for the synthesis of PC to investigate the resulting effects on the reaction outcome. It was shown that the C2 proton at the imidazolium ring activates the epoxide by HB, which leads to facilitated nucleophilic ring-opening and enhanced catalytic activity. This was corroborated by FTIR studies of a mixture of catalyst and epoxide. Further, the formation of a free carbene as a catalytic active species can be excluded as a C2 alkyl substituent only slightly reduces the observed yields. On the basis of these results, the structure of the imidazolium substitution pattern was tailored to reach higher catalytic activity. The introduction of an electron-withdrawing wingtip results in higher acidity of the C2 proton and thus in a stronger HB donor capability and more pronounced activation of the epoxide. In addition, the solubility of the catalyst in the reaction mixture was improved by a long alkyl residue at the second wingtip position. Finally, the optimized catalyst 1-(2,3,4,5,6-pentafluorobenzyl)-3-octylimidazolium bromide (Figure 4.1) is able to efficiently mediate the formation of a variety of cyclic carbonates under mild reaction conditions (70 °C, 4 bar CO₂, 16 h). Moreover, the catalyst can be easily recycled, it remains constantly active for at least ten runs and no solvents or metals are required. Consequently, an overall green approach for the cycloaddition of CO₂ and epoxides with minimized energy-input and carbon footprint was achieved.

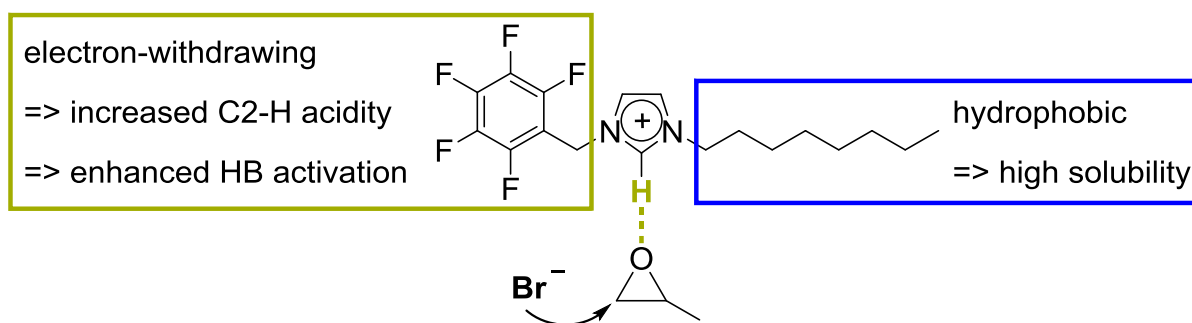


Figure 4.1: Optimized imidazolium bromide catalyst structure for the cycloaddition of CO_2 with epoxides.

In order to further increase the catalytic activity of imidazolium halide based catalysts, the structural motif of the cation was modified. As aforementioned, the presence of three hydroxy groups in spatial proximity leads to particularly effective organocatalysts because of the synergism deriving from the multiple HB donor groups. Therefore, two imidazolium moieties were coupled with a hydroxy functionalized propylene bridging unit. The resulting catalysts bear two acidic C2 protons and one hydroxy group as three neighboring HB donor functionalities that are capable of interacting during the cycloaddition reaction. DFT calculations have revealed that these three HB donor groups activate the epoxide more efficiently and also stabilize intermediates, so that an enhanced catalytic activity is achieved. To ensure high solubility in the reaction mixture, the remaining second wingtips of the imidazolium cations were again functionalized with *n*-octyl groups, leading to the optimized bisimidazolium bromide catalyst (Figure 4.2). Compared to the previously described most active single imidazolium bromide, the reaction time could be reduced to 73 % by using the newly developed system under identical conditions. In addition, the catalyst is applicable without solvents or metals for a broad scope of epoxides and reusable for a least ten reaction runs without loss of activity. Consequently, the carbon footprint and sustainability of the reaction were successfully improved.

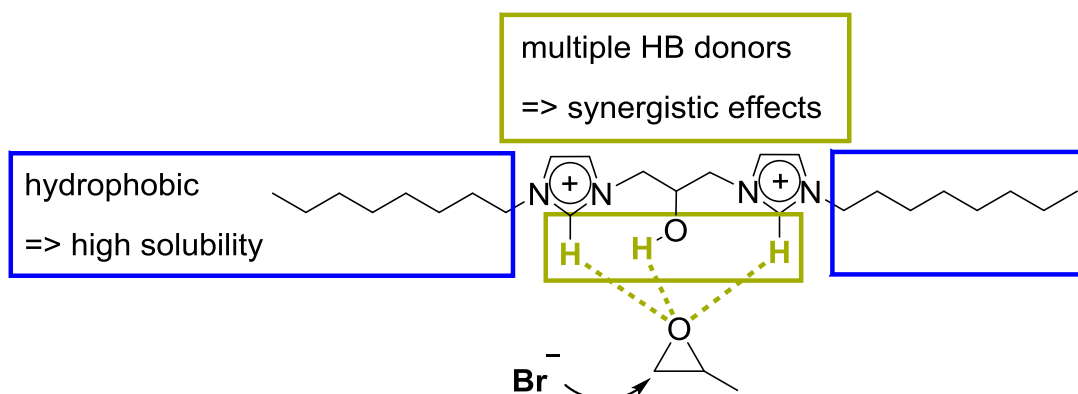


Figure 4.2: Bisimidazolium bromide catalyst bearing three neighboring HB donor groups.

The simple and versatile possibilities for the modification of imidazolium halides are their main advantage for further investigations towards even more active organocatalysts. By introducing new structural motifs for an enhanced epoxide or CO₂ activation, high catalytic efficiency at ambient conditions could be reached. As a result, the activity gap between metal-based and metal-free systems could be minimized, leading to more sustainable organocatalytic processes.

Binary mixtures consisting of niobium(V)chloride and nucleophiles like TBAB are known to efficiently mediate the catalytic cycloaddition of CO₂ and epoxides at room temperature and under one atmosphere CO₂ pressure. By using imidazolium bromides as nucleophilic components instead of TBAB, alternative catalyst systems are obtained, whereby the activity strongly depends on the imidazolium substituents. Unlike imidazolium bromides as single catalysts, the presence of a C2 proton reduces the activity. Due to the much stronger epoxide interaction of the *Lewis* acidic (NbCl₅)₂, the HB activation by the cation is negligible. However, the degree of ion pairing is higher when the imidazolium ring bears a C2 proton, which results in a lower anion nucleophilicity. Thus, imidazolium salts with alkyl substituents in C2 position gave higher catalytic activities. Besides the ion pairing, the solubility of the imidazolium bromides in the reaction mixture was determined as a crucial factor regarding the activity. Therefore, imidazolium patterns based on aliphatic substituents generally show better catalytic performance compared to aromatic wingtips. By tailoring the imidazolium structure towards high solubility and small interionic attractions, a promising alternative to common TBAB as nucleophile was finally obtained (Figure 4.3). However, the (NbCl₅)₂/nucleophile catalyst systems cannot be recycled without loss of activity, which is a serious disadvantage. Future studies should hence focus on suitable structural motifs for nucleophilic components that allow facile recycling procedures and constant catalytic activity for multiple runs at the same time. Consequently, not only a cost-efficient binary catalyst with high catalytic activity, but also a large sustainability could be realized.

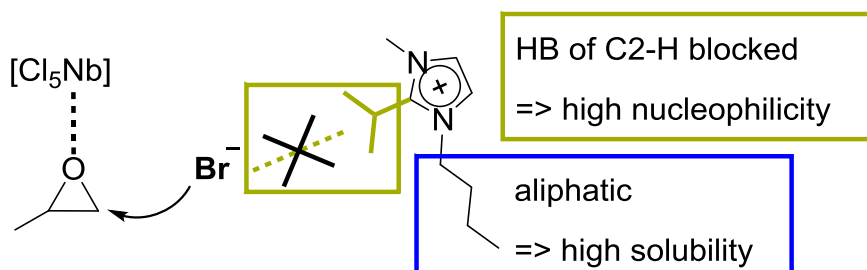


Figure 4.3: Binary catalyst system by combination of (NbCl₅)₂ and imidazolium bromides.

As a metal-free alternative to the $(\text{NbCl}_5)_2$ binary catalyst systems, the polyol PETT was used as an activation agent for epoxides in combination with nucleophiles. The four hydroxy groups activate the epoxide by HB interactions, so that the nucleophilic ring-opening is facilitated. It was shown that the cation structure of the nucleophile has a major influence on the catalytic activity. This is particularly obvious if TBAI is used instead of KI in combination with PETT, as the cyclic carbonate yield increases by a factor of 16. The resulting PETT/TBAI system (Figure 4.4) is applicable for the conversion of a variety of epoxides to their corresponding cyclic carbonates in high yields at mild reaction conditions (70 C, 4 bar CO_2 , 16 h, 5 mol % catalysts). In contrast to other binary organocatalytic systems, the PETT/TBAI mixture is also easily recyclable and can be reused without loss of activity for a minimum of eight consecutive reaction runs. Additionally, no metals or solvents are needed and the compounds are non-toxic, cost-efficient and readily available. Taking all these aspects into account, a highly sustainable catalyst system for the coupling of CO_2 and epoxides with low carbon footprint was achieved.

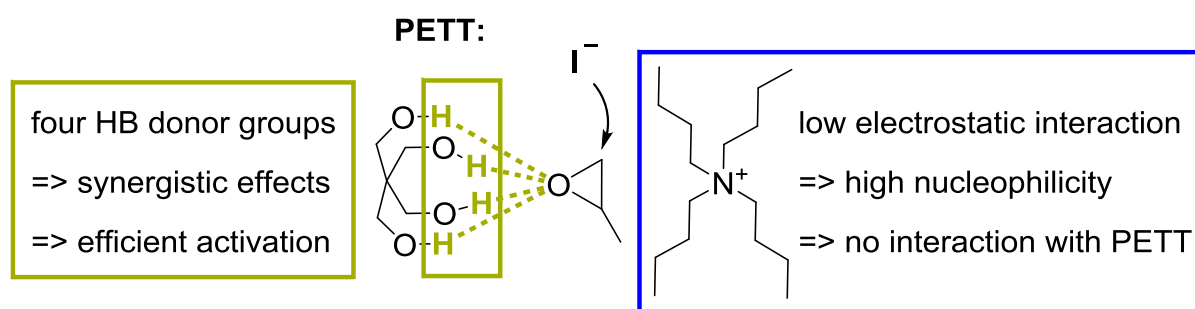


Figure 4.4: PETT/TBAI binary catalyst system for the cycloaddition of CO_2 and epoxides.

However, more demanding reaction conditions for the PETT system have to be applied compared to the $(\text{NbCl}_5)_2$ binary mixtures, as efficient conversions at ambient conditions are not yet possible. Nevertheless, the air and moisture stable metal-free approach does not require elaborated inert gas techniques or water free reactants or solvents. Therefore, time consuming preparations are redundant and safety problems are avoided. This demonstrates the great potential of organocatalytic binary catalysts as a sustainable approach. To minimize the carbon footprint of the process, new structural motifs for more efficient epoxide activation should be the focus of further investigations. As a result, high catalytic activity at ambient reaction conditions should be the long-term goal regarding the cycloaddition of CO_2 and epoxides by organocatalysts.

In the second part of this thesis, the biphasic epoxidation of olefins, with aqueous H_2O_2 as sustainable oxidant, was investigated using imidazolium based catalyst systems.

For this purpose, carboxy-functionalized imidazolium salts were employed to form catalytic active polyoxomolybdates *in situ* (Figure 4.5). Thus, additional organic acids for lowering the pH value are redundant and the reaction procedure is simplified significantly. Nevertheless, the catalytic activity depends on the acidity of the reaction mixture and thereby on the ratio of imidazolium salt to metal precursor. The optimal catalyst performance was determined with a tenfold excess of imidazolium salt, leading to good yields for the epoxidation of *cis*-cyclooctene (60 °C, 24 h, 1.5 eq. H_2O_2 , 5.0 mol %). The presumably formed $[\text{Mo}_x\text{O}_y]^{2-}$ clusters were determined as the catalytic active species, as it was shown that oxygen transfer of potentially *in situ* generated peracids can be excluded. Moreover, the catalyst system could be recycled by extraction and was reusable with negligible loss of activity for six reaction runs. Conclusively, simple and cost-efficient precursors were used to create a catalyst system for the epoxidation of *cis*-cyclooctene with aqueous H_2O_2 in an environmentally benign manner.

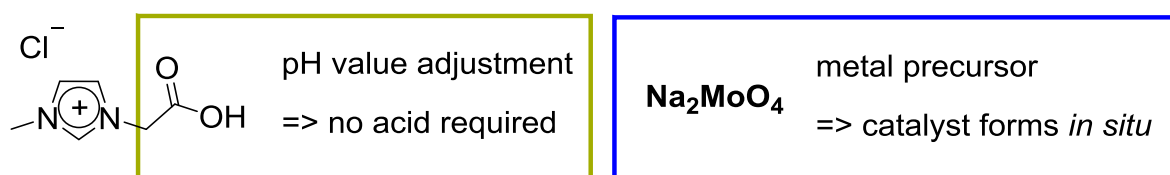


Figure 4.5: System for the *in situ* generation of catalytic active polyoxomolybdate species using a carboxy-functionalized imidazolium salt.

To enhance the catalytic activity of this system, more comprehensive studies dealing with the exact structure of the catalytic active species are needed. This would allow the tailoring of the imidazolium substitution pattern towards the actual catalyst, leading to more efficient conversion rates for the epoxidation reaction. The scope of this system should further be extended to show the applicability for other olefins than *cis*-cyclooctene. Aside from molybdate precursors, other metal salts could also be used to possibly generate even more active epoxidation catalysts *in situ*.

As an alternative system for the epoxidation of olefins with aqueous H_2O_2 , imidazolium perrhenates were used as catalysts for the first time. In contrast to earlier studies regarding their equimolar application, it was demonstrated that also substoichiometric amounts are capable of efficiently mediating the epoxidation reaction. To reveal the

impact of the cation on the activity, a database of imidazolium perrhenates with varying substitution patterns was synthesized and used as catalysts. As the reaction mechanism is based on the activation of H_2O_2 by the $[\text{ReO}_4]^-$ HB acceptor ability, the shielding of the anion caused by interionic attractions has a major influence. Therefore, alkyl substituents in C2 position of the imidazolium cation instead of a C2 proton positively affect the reaction outcome, caused by the lower degree of ion pairing. This results in a more reactive anion and hence more efficient H_2O_2 activation. The hydrophobicity of the catalysts is another fundamental factor for the activity of imidazolium perrhenates in the biphasic epoxidation reaction of olefins with aqueous H_2O_2 . For suitable functionalization, it was found that HB interactions of the anion to H_2O_2 enable high solubility in the aqueous phase. This is not observed in the absence of the oxidant or imidazolium cations with a too high hydrophobicity. However, it was shown that proper modification of the solubility enables the imidazolium perrhenate to act as a phase transfer catalyst, thereby transferring the olefin in the aqueous phase. This assumes that the cation provides a catalyst hydrophobicity, which is not too low, so that interaction with the olefin is possible. The optimized catalyst (Figure 4.6), regarding ion pairing and solubility, catalyzes the formation of cyclooctene oxide in 88 % yield (70 °C, 4 h, 2.5 eq. H_2O_2 (50 wt. %), 5.0 mol %). Additionally, the catalyst was easily separated from the reaction mixture and exhibits high stability, as well as constant catalytic activity for at least ten consecutive runs.

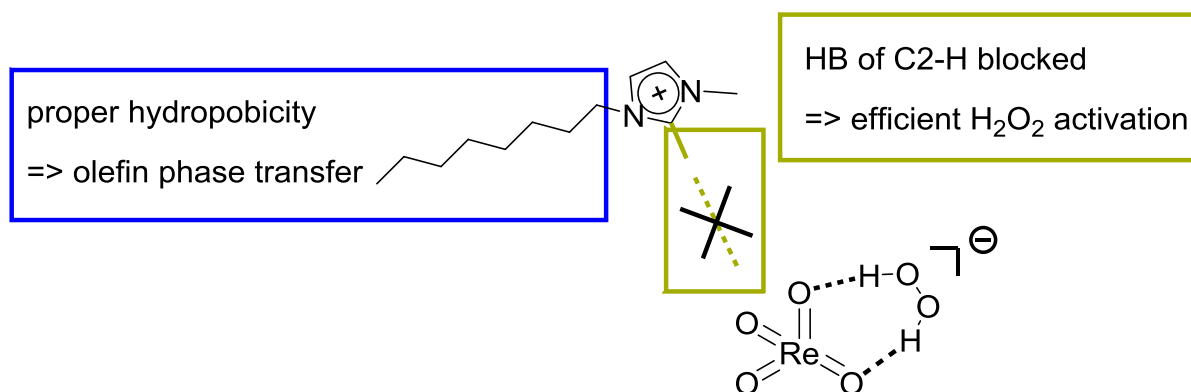


Figure 4.6: Optimized imidazolium perrhenate catalyst for olefin epoxidation with aqueous H_2O_2 .

Also a variety of other olefins was converted efficiently, but with high selectivities for the corresponding diols. The aim of future investigations could be to tailor the imidazolium structure towards the desired substrate in order to reach higher selectivities for the epoxide product. The introduction of functional groups at the cation moiety could further lead to enhanced catalytic activity caused by more pronounced phase transfer

of the olefin or stronger H_2O_2 activation. Apart from the modification of the imidazolium pattern, the substitution of $[\text{ReO}_4]^-$ as HB acceptor for H_2O_2 activation bears a vast potential. It is known from mechanistic investigations that the metal center does not participate in the catalytic cycle, which proceeds via an outer-sphere mechanism. This enables the possibility to exchange the expensive transition metal with metal-free, much more cost-efficient and eco-friendly analogs like the omnipresent nitrate $[\text{NO}_3]^-$, sulfate $[\text{SO}_4]^{2-}$, phosphate $[\text{PO}_4]^{3-}$ or acetate $[\text{OAc}]^-$ anions. Initial studies have shown that such imidazolium salts are catalytically active for the epoxidation of *cis*-cyclooctene. This paves the way to innovative, cost-efficient, readily available and highly sustainable organocatalysts for the epoxidation of olefins with aqueous H_2O_2 . The future objective of this thesis is to develop a process, which enables direct cyclic carbonate synthesis from olefins, CO_2 and H_2O_2 or oxygen as eco-friendly oxidants. For this purpose, the achieved results have to be combined to design a catalyst, which is able to mediate both reactions consecutively at identical reaction conditions. Another possibility could be the simultaneous application of two individual catalysts, whereby the respective single compounds have to be compatible and do not disrupt each other. When these challenges are solved, the synthesis of cyclic carbonates is facilitated considerably and superior possibilities for more sustainable processes will be provided.

5 Bibliographic Data of Complete Publications

This chapter provides the reader with the bibliographic details of the publications summarized in Chapter 3 of this thesis to facilitate the retrieval of the complete manuscripts and supporting information.

5.1 Cycloaddition of CO₂ and Epoxides Catalyzed by Imidazolium Bromides Under Mild Conditions: Influence of the Cation on Catalyst Activity

*Michael H. Anthofer,^{‡a} Michael E. Wilhelm,^{‡a} Mirza Cokoja,^{*a} Iulius I. E. Markovits,^a
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DOI: 10.1039/C3CY01024D

Hyperlink: <http://pubs.rsc.org/en/Content/ArticleLanding/2014/CY/c3cy01024d#!divAbstract>

5.2 Hydroxy-Functionalized Imidazolium Bromides as Catalysts for the Cycloaddition of CO₂ and Epoxides to Cyclic Carbonates

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DOI: 10.1002/cctc.201402754

Hyperlink: <http://onlinelibrary.wiley.com/doi/10.1002/cctc.201402754/abstract>

5.3 Niobium(V)chloride and Imidazolium Bromides as Efficient Dual Catalyst Systems for the Cycloaddition of Carbon Dioxide and Propylene Oxide

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Originally published in: Catal. Sci. Technol. **2014**, *4*, 1638 – 1643.

DOI: 10.1039/C3CY01057K

Hyperlink: <http://pubs.rsc.org/en/Content/ArticleLanding/2014/CY/c3cy01057k#!divAbstract>

5.4 Cycloaddition of Carbon Dioxide and Epoxides Using Pentaerythritol and Halides as Dual Catalyst System

*Michael E. Wilhelm,^{‡a} Michael H. Anthofer,^{‡a} Mirza Cokoja,^{*a} Iulius I. E. Markovits,^a Wolfgang A. Herrmann^a and Fritz E. Kühn^a*

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5.5 Epoxidations of Olefins Catalyzed by Polyoxomolybdates Formed *in situ* in Ionic Liquids

Lilian R. Graser,^a Sophie Jürgens,^a Michael E. Wilhelm,^a Mirza Cokoja,^a
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7 References

- [1] E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazabal, J. Perez-Ramirez, *Energy & Environmental Science* **2013**, *6*, 3112-3135.
- [2] W. V. o. t. C. I. ICAA, *Technology Roadmaps on Energy & Climate Change* **2013**.
- [3] a) C. R. A. G., van Santen, *Catalysis for Renewables: From Feedstock to Energy Production*, Wiley-VCH, **2007**; b) D. M. Alonso, J. Q. Bond, J. A. Dumesic, *Green Chemistry* **2010**, *12*, 1493-1513.
- [4] D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Chemical Society Reviews* **2012**, *41*, 8075-8098.
- [5] J. K. Satyarthi, T. Chiranjeevi, D. T. Gokak, P. S. Viswanathan, *Catalysis Science & Technology* **2013**, *3*, 70-80.
- [6] C. Maeda, Y. Miyazaki, T. Ema, *Catalysis Science & Technology* **2014**, *4*, 1482-1497.
- [7] IEA, *CO2 Emission from Fuel Combustion Highlights* **2013**.
- [8] M. Mikkelsen, M. Jorgensen, F. C. Krebs, *Energy & Environmental Science* **2010**, *3*, 43-81.
- [9] S. Suib, *New and Future Developments in Catalysis Activation of Carbon Dioxide*, **2013**.
- [10] M. Aresta, A. Dibenedetto, *Dalton Transactions* **2007**, *0*, 2975-2992.
- [11] G. Centi, E. A. Quadrelli, S. Perathoner, *Energy & Environmental Science* **2013**, *6*, 1711-1731.
- [12] M. North, R. Pasquale, C. Young, *Green Chemistry* **2010**, *12*, 1514-1539.
- [13] A. Decortes, A. M. Castilla, A. W. Kleij, *Angewandte Chemie International Edition* **2010**, *49*, 9822-9837.
- [14] M. Aresta, A. Dibenedetto, A. Angelini, *Chemical Reviews* **2013**, *114*, 1709-1742.
- [15] a) K. Xu, *Chemical Reviews* **2004**, *104*, 4303-4418; b) H. L. Parker, J. Sherwood, A. J. Hunt, J. H. Clark, *ACS Sustainable Chemistry & Engineering* **2014**, *2*, 1739-1742.
- [16] D. J. Darensbourg, W. Choi, O. Karroonnirun, N. Bhuvanesh, *Macromolecules* **2008**, *41*, 3493-3502.
- [17] T. Tatsumi, Y. Watanabe, K. A. Koyano, *Chemical Communications* **1996**, 2281-2282.
- [18] J. H. Clements, *Industrial & Engineering Chemistry Research* **2003**, *42*, 663-674.
- [19] L. Wang, L. Lin, G. Zhang, K. Kodama, M. Yasutake, T. Hirose, *Chemical Communications* **2014**, *50*, 14813-14816.
- [20] R. Luo, X. Zhou, S. Chen, Y. Li, L. Zhou, H. Ji, *Green Chemistry* **2014**, *16*, 1496-1506.
- [21] A. Sibaouih, P. Ryan, M. Leskelä, B. Rieger, T. Repo, *Applied Catalysis A: General* **2009**, *365*, 194-198.
- [22] R. L. Paddock, S. T. Nguyen, *Journal of the American Chemical Society* **2001**, *123*, 11498-11499.
- [23] A. Decortes, M. Martinez Belmonte, J. Benet-Buchholz, A. W. Kleij, *Chemical Communications* **2010**, *46*, 4580-4582.
- [24] H. Xie, S. Li, S. Zhang, *Journal of Molecular Catalysis A: Chemical* **2006**, *250*, 30-34.

- [25] a) A. Monassier, V. D'Elia, M. Cokoja, H. Dong, J. D. A. Pelletier, J.-M. Basset, F. E. Kühn, *ChemCatChem* **2013**, *5*, 1321-1324; b) M. E. Wilhelm, M. H. Anthofer, R. M. Reich, V. D'Elia, J.-M. Basset, W. A. Herrmann, M. Cokoja, F. E. Kühn, *Catalysis Science & Technology* **2014**, *4*, 1638-1643.
- [26] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chemical Communications* **1997**, 1129-1130.
- [27] a) D. W. C. MacMillan, *Nature* **2008**, *455*, 304-308; b) J. G. Hernandez, E. Juaristi, *Chemical Communications* **2012**, *48*, 5396-5409.
- [28] a) B. L. M. Reetz, S. Jaroch, H. Weinmann, *Organocatalysis*, Springer-Verlag, **2008**; b) P. MacLellan, *Nat Chem* **2013**, *5*, 896-897.
- [29] a) H. G. A. Berkessel, *Asymmetric Organocatalysis: From Biomimetic Concepts to Applications in Asymmetric Synthesis* Wiley-VCH Verlag GmbH & Co. , **2005**; b) E. N. Jacobsen, D. W. C. MacMillan, *Proceedings of the National Academy of Sciences* **2010**, *107*, 20618-20619.
- [30] T. Nishikubo, A. Kameyama, J. Yamashita, M. Tomoi, W. Fukuda, *Journal of Polymer Science Part A: Polymer Chemistry* **1993**, *31*, 939-947.
- [31] V. Calo, A. Nacci, A. Monopoli, A. Fanizzi, *Organic Letters* **2002**, *4*, 2561-2563.
- [32] J.-Q. Wang, K. Dong, W.-G. Cheng, J. Sun, S.-J. Zhang, *Catalysis Science & Technology* **2012**, *2*, 1480-1484.
- [33] J.-Q. Wang, D.-L. Kong, J.-Y. Chen, F. Cai, L.-N. He, *Journal of Molecular Catalysis A: Chemical* **2006**, *249*, 143-148.
- [34] J. Sun, S. Zhang, W. Cheng, J. Ren, *Tetrahedron Letters* **2008**, *49*, 3588-3591.
- [35] H. Büttner, K. Lau, A. Spannenberg, T. Werner, *ChemCatChem* **2015**, *7*, 459-467.
- [36] a) Y. Zhou, S. Hu, X. Ma, S. Liang, T. Jiang, B. Han, *Journal of Molecular Catalysis A: Chemical* **2008**, *284*, 52-57; b) Y. Tsutsumi, K. Yamakawa, M. Yoshida, T. Ema, T. Sakai, *Organic Letters* **2010**, *12*, 5728-5731.
- [37] A. J. R. Amaral, J. F. J. Coelho, A. C. Serra, *Tetrahedron Letters* **2013**, *54*, 5518-5522.
- [38] a) J. Tharun, G. Mathai, R. Roshan, A. C. Kathalikkattil, K. Bomi, D.-W. Park, *Physical Chemistry Chemical Physics* **2013**, *15*, 9029-9033; b) K. R. Roshan, T. Jose, D. Kim, K. A. Cherian, D. W. Park, *Catalysis Science & Technology* **2014**, *4*, 963-970.
- [39] a) Y. Du, F. Cai, D.-L. Kong, L.-N. He, *Green Chemistry* **2005**, *7*, 518-523; b) X. Chen, J. Sun, J. Wang, W. Cheng, *Tetrahedron Letters* **2012**, *53*, 2684-2688.
- [40] Y. Du, J.-Q. Wang, J.-Y. Chen, F. Cai, J.-S. Tian, D.-L. Kong, L.-N. He, *Tetrahedron Letters* **2006**, *47*, 1271-1275.
- [41] K. R. Roshan, T. Jose, A. C. Kathalikkattil, D. W. Kim, B. Kim, D. W. Park, *Applied Catalysis A: General* **2013**, *467*, 17-25.
- [42] a) J. Tharun, Y. Hwang, R. Roshan, S. Ahn, A. C. Kathalikkattil, D.-W. Park, *Catalysis Science & Technology* **2012**, *2*, 1674-1680; b) Y. Zhao, J.-S. Tian, X.-H. Qi, Z.-N. Han, Y.-Y. Zhuang, L.-N. He, *Journal of Molecular Catalysis A: Chemical* **2007**, *271*, 284-289.
- [43] D. Wei-Li, J. Bi, L. Sheng-Lian, L. Xu-Biao, T. Xin-Man, A. Chak-Tong, *Journal of Molecular Catalysis A: Chemical* **2013**, *378*, 326-332.
- [44] a) W.-L. Wong, P.-H. Chan, Z.-Y. Zhou, K.-H. Lee, K.-C. Cheung, K.-Y. Wong, *Chemsuschem* **2008**, *1*, 67-70; b) W.-L. Wong, L. Y. S. Lee, K.-P. Ho, Z.-Y.

- Zhou, T. Fan, Z. Lin, K.-Y. Wong, *Applied Catalysis A: General* **2014**, *472*, 160-166.
- [45] T. Yu, R. G. Weiss, *Green Chemistry* **2012**, *14*, 209-216.
- [46] Z.-Z. Yang, L.-N. He, C.-X. Miao, S. Chanfreau, *Advanced Synthesis & Catalysis* **2010**, *352*, 2233-2240.
- [47] a) S. Foltran, J. Alsarraf, F. Robert, Y. Landais, E. Cloutet, H. Cramail, T. Tassaing, *Catalysis Science & Technology* **2013**, *3*, 1046-1055; b) S. Foltran, R. Mereau, T. Tassaing, *Catalysis Science & Technology* **2014**, *4*, 1585-1597.
- [48] D. Wei-Li, J. Bi, L. Sheng-Lian, L. Xu-Biao, T. Xin-Man, A. Chak-Tong, *Applied Catalysis A: General* **2014**, *470*, 183-188.
- [49] T. Werner, H. Büttner, *ChemSusChem* **2014**, *7*, 3268-3271.
- [50] P. K. Khatri, S. L. Jain, K. T. Lim, *Tetrahedron Letters* **2013**, *54*, 6648-6650.
- [51] B. Chatelet, L. Joucla, J.-P. Dutasta, A. Martinez, K. C. Szeto, V. Dufaud, *Journal of the American Chemical Society* **2013**, *135*, 5348-5351.
- [52] B. Chatelet, L. Joucla, J.-P. Dutasta, A. Martinez, V. Dufaud, *Chemistry – A European Journal* **2014**, *20*, 8571-8574.
- [53] Y. Xiong, F. Bai, Z. Cui, N. Guo, R. Wang, *Journal of Chemistry* **2013**, *2013*, 9.
- [54] Y. P. Patil, P. J. Tambade, S. R. Jagtap, B. M. Bhanage, *Journal of Molecular Catalysis A: Chemical* **2008**, *289*, 14-21.
- [55] a) Y. Xiong, H. Wang, R. Wang, Y. Yan, B. Zheng, Y. Wang, *Chemical Communications* **2010**, *46*, 3399-3401; b) Y. Xiong, Y. Wang, H. Wang, R. Wang, *Polymer Chemistry* **2011**, *2*, 2306-2315.
- [56] T. Sakai, Y. Tsutsumi, T. Ema, *Green Chemistry* **2008**, *10*, 337-341.
- [57] T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, *Chemical Communications* **2006**, *0*, 1664-1666.
- [58] Q.-W. Song, L.-N. He, J.-Q. Wang, H. Yasuda, T. Sakakura, *Green Chemistry* **2013**, *15*, 110-115.
- [59] a) J. D. Holbrey, R. D. Rogers, R. A. Mantz, P. C. Trulove, V. A. Cocalia, A. E. Visser, J. L. Anderson, J. L. Anthony, J. F. Brennecke, E. J. Maginn, T. Welton, R. A. Mantz, in *Ionic Liquids in Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA, **2008**, pp. 57-174; b) T. Peppel, C. Roth, K. Fumino, D. Paschek, M. Köckerling, R. Ludwig, *Angewandte Chemie International Edition* **2011**, *50*, 6661-6665.
- [60] M. G. Freire, L. M. N. B. F. Santos, A. M. Fernandes, J. A. P. Coutinho, I. M. Marrucho, *Fluid Phase Equilibria* **2007**, *261*, 449-454.
- [61] A. Wulf, K. Fumino, R. Ludwig, *Angewandte Chemie International Edition* **2010**, *49*, 449-453.
- [62] J. Peng, Y. Deng, *New Journal of Chemistry* **2001**, *25*, 639-641.
- [63] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, *Chemical Communications* **2003**, 896-897.
- [64] D.-W. Park, N.-Y. Mun, K.-H. Kim, I. Kim, S.-W. Park, *Catalysis Today* **2006**, *115*, 130-133.
- [65] J.-Q. Wang, W.-G. Cheng, J. Sun, T.-Y. Shi, X.-P. Zhang, S.-J. Zhang, *RSC Advances* **2014**, *4*, 2360-2367.
- [66] L. Han, H.-J. Choi, S.-J. Choi, B. Liu, D.-W. Park, *Green Chemistry* **2011**, *13*, 1023-1028.
- [67] a) L. Han, S.-J. Choi, M.-S. Park, S.-M. Lee, Y.-J. Kim, M.-I. Kim, B. Liu, D.-W. Park, *Reac Kinet Mech Cat* **2012**, *106*, 25-35; b) J. Sun, L. Han, W. Cheng, J. Wang, X. Zhang, S. Zhang, *ChemSusChem* **2011**, *4*, 502-507.
- [68] L.-F. Xiao, D.-W. Lv, D. Su, W. Wu, H.-F. Li, *Journal of Cleaner Production* **2014**, *67*, 285-290.

- [69] H. Sun, D. Zhang, *The Journal of Physical Chemistry A* **2007**, *111*, 8036-8043.
- [70] M. H. Anthofer, M. E. Wilhelm, M. Cokoja, I. I. E. Markovits, A. Pöthig, J. Mink, W. A. Herrmann, F. E. Kühn, *Catalysis Science & Technology* **2014**, *4*, 1749-1758.
- [71] A.-L. Girard, N. Simon, M. Zanatta, S. Marmitt, P. Goncalves, J. Dupont, *Green Chemistry* **2014**, *16*, 2815-2825.
- [72] M. H. Anthofer, M. E. Wilhelm, M. Cokoja, M. Drees, W. A. Herrmann, F. E. Kühn, *ChemCatChem* **2015**, *7*, 94-98.
- [73] C. J. Whiteoak, A. Nova, F. Maseras, A. W. Kleij, *ChemSusChem* **2012**, *5*, 2032-2038.
- [74] Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu, K. Ding, *Angewandte Chemie International Edition* **2007**, *46*, 7255-7258.
- [75] H.-J. Choi, M. Selvaraj, D.-W. Park, *Chemical Engineering Science* **2013**.
- [76] L. Han, H. Li, S.-J. Choi, M.-S. Park, S.-M. Lee, Y.-J. Kim, D.-W. Park, *Applied Catalysis A: General* **2012**, *429-430*, 67-72.
- [77] Z.-Z. Yang, Y. Zhao, G. Ji, H. Zhang, B. Yu, X. Gao, Z. Liu, *Green Chemistry* **2014**, *16*, 3724-3728.
- [78] a) J. Sun, W. Cheng, W. Fan, Y. Wang, Z. Meng, S. Zhang, *Catalysis Today* **2009**, *148*, 361-367; b) T.-Y. Shi, J.-Q. Wang, J. Sun, M.-H. Wang, W.-G. Cheng, S.-J. Zhang, *RSC Advances* **2013**, *3*, 3726-3732.
- [79] R. A. Watile, K. M. Deshmukh, K. P. Dhake, B. M. Bhanage, *Catalysis Science & Technology* **2012**, *2*, 1051-1055.
- [80] a) J.-Q. Wang, X.-D. Yue, F. Cai, L.-N. He, *Catalysis Communications* **2007**, *8*, 167-172; b) L. Han, S.-W. Park, D.-W. Park, *Energy & Environmental Science* **2009**, *2*, 1286-1292; c) S. Udayakumar, V. Raman, H.-L. Shim, D.-W. Park, *Applied Catalysis A: General* **2009**, *368*, 97-104; d) J. N. Appaturi, F. Adam, *Applied Catalysis B: Environmental* **2013**, *136-137*, 150-159; e) C. Aprile, F. Giacalone, P. Agrigento, L. F. Liotta, J. A. Martens, P. P. Pescarmona, M. Gruttadauria, *ChemSusChem* **2011**, *4*, 1830-1837.
- [81] J. Wang, J. Leong, Y. Zhang, *Green Chemistry* **2014**, *16*, 4515-4519.
- [82] K. R. Roshan, G. Mathai, J. Kim, J. Tharun, G.-A. Park, D.-W. Park, *Green Chemistry* **2012**, *14*, 2933-2940.
- [83] J. Sun, J. Wang, W. Cheng, J. Zhang, X. Li, S. Zhang, Y. She, *Green Chemistry* **2012**, *14*, 654-660.
- [84] C. J. Whiteoak, A. H. Henseler, C. Ayats, A. W. Kleij, M. A. Pericas, *Green Chemistry* **2014**, *16*, 1552-1559.
- [85] a) K. R. Roshan, A. C. Kathalikkattil, J. Tharun, D. W. Kim, Y. S. Won, D. W. Park, *Dalton Transactions* **2014**, *43*, 2023-2031; b) Z. Yang, J. Sun, W. Cheng, J. Wang, Q. Li, S. Zhang, *Catalysis Communications* **2014**, *44*, 6-9.
- [86] a) J. Sun, W. Cheng, Z. Yang, J. Wang, T. Xu, J. Xin, S. Zhang, *Green Chemistry* **2014**, *16*, 3071-3078; b) S. Liang, H. Liu, T. Jiang, J. Song, G. Yang, B. Han, *Chemical Communications* **2011**, *47*, 2131-2133.
- [87] Z. Wu, H. Xie, X. Yu, E. Liu, *ChemCatChem* **2013**, *5*, 1328-1333.
- [88] J. Song, Z. Zhang, B. Han, S. Hu, W. Li, Y. Xie, *Green Chemistry* **2008**, *10*, 1337-1341.
- [89] J.-W. Huang, M. Shi, *The Journal of Organic Chemistry* **2003**, *68*, 6705-6709.
- [90] Y.-M. Shen, W.-L. Duan, M. Shi, *Advanced Synthesis & Catalysis* **2003**, *345*, 337-340.
- [91] J.-Q. Wang, J. Sun, W.-G. Cheng, K. Dong, X.-P. Zhang, S.-J. Zhang, *Physical Chemistry Chemical Physics* **2012**, *14*, 11021-11026.

- [92] M. E. Wilhelm, M. H. Anthofer, M. Cokoja, I. I. E. Markovits, W. A. Herrmann, F. E. Kühn, *ChemSusChem* **2014**, *7*, 1357-1360.
- [93] A. M. Hardman-Baldwin, A. E. Mattson, *ChemSusChem* **2014**, *7*, 3275-3278.
- [94] a) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, *The Journal of Organic Chemistry* **1996**, *61*, 8310-8311; b) N. Mizuno, K. Yamaguchi, K. Kamata, *Coordination Chemistry Reviews* **2005**, *249*, 1944-1956; c) K. Kamata, M. Kotani, K. Yamaguchi, S. Hikichi, N. Mizuno, *Chemistry – A European Journal* **2007**, *13*, 639-648.
- [95] S. A. Hauser, M. Cokoja, F. E. Kühn, *Catalysis Science & Technology* **2013**, *3*, 552-561.
- [96] S. T. Oyama, in *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis* (Ed.: S. T. Oyama), Elsevier, Amsterdam, **2008**, pp. 3-99.
- [97] M. R. Consulting, *World Propylene Oxide (PO) Market to See Sustained Growth in Years Ahead* **2014**.
- [98] P. Bassler, H.-G. Göbbel-, M. Weidenbach, *Chemical Engineering Transactions* **2010**, *21*, 571-576.
- [99] T. A. Nijhuis, M. Makkee, J. A. Moulijn, B. M. Weckhuysen, *Industrial & Engineering Chemistry Research* **2006**, *45*, 3447-3459.
- [100] V. Russo, R. Tesser, E. Santacesaria, M. Di Serio, *Industrial & Engineering Chemistry Research* **2013**, *52*, 1168-1178.
- [101] L. Sumitomo Chemical Co., J. Tsuji, J. Yamamoto, M. Ishino, N. Oku, *Development of New Propylene Oxide Process* **2006**.
- [102] R. A. Sheldon, *Chemical Communications* **2008**, 3352-3365.
- [103] S. B. Shin, D. Chadwick, *Industrial & Engineering Chemistry Research* **2010**, *49*, 8125-8134.
- [104] B. S. Lane, K. Burgess, *Chemical Reviews* **2003**, *103*, 2457-2474.
- [105] a) S. Huber, M. Cokoja, F. E. Kühn, *Journal of Organometallic Chemistry* **2014**, *751*, 25-32; b) Q. H. Xia, H. Q. Ge, C. P. Ye, Z. M. Liu, K. X. Su, *Chemical Reviews* **2005**, *105*, 1603-1662.
- [106] D. J. Cole-Hamilton, *Science* **2003**, *299*, 1702-1706.
- [107] a) M. J. Muldoon, *Dalton Transactions* **2010**, *39*, 337-348; b) W. Keim, *Green Chemistry* **2003**, *5*, 105-111; c) B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt, in *Multiphase Homogeneous Catalysis*, Wiley-VCH Verlag GmbH, **2008**.
- [108] C. M. Gordon, *Applied Catalysis A: General* **2001**, *222*, 101-117.
- [109] Q. Zhang, S. Zhang, Y. Deng, *Green Chemistry* **2011**, *13*, 2619-2637.
- [110] J. Muzart, *Advanced Synthesis & Catalysis* **2006**, *348*, 275-295.
- [111] R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792-793.
- [112] J. P. Hallett, T. Welton, *Chemical Reviews* **2011**, *111*, 3508-3576.
- [113] C. E. Song, E. J. Roh, *Chemical Communications* **2000**, 837-838.
- [114] K. A. Srinivas, A. Kumar, S. M. S. Chauhan, *Chemical Communications* **2002**, 2456-2457.
- [115] a) D. Betz, A. Raith, M. Cokoja, F. E. Kühn, *ChemSusChem* **2010**, *3*, 559-562; b) M. Herbert, A. Galindo, F. Montilla, *Catalysis Communications* **2007**, *8*, 987-990.
- [116] D. Betz, W. A. Herrmann, F. E. Kühn, *Journal of Organometallic Chemistry* **2009**, *694*, 3320-3324.
- [117] a) F. E. Kühn, J. Zhao, M. Abrantes, W. Sun, C. A. M. Afonso, L. C. Branco, I. S. Gonçalves, M. Pillinger, C. C. Romão, *Tetrahedron Letters* **2005**, *46*, 47-52;

- b) J. Dupont, J. Spencer, *Angewandte Chemie International Edition* **2004**, *43*, 5296-5297.
- [118] M. Małkosza, M. Fedoryński, *Catalysis Reviews* **2003**, *45*, 321-367.
- [119] M. Halpern, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, **2000**.
- [120] E. V. Dehmlow, M. Slopianka, *Chemische Berichte* **1979**, *112*, 2765-2768.
- [121] I. V. Kozhevnikov, *Chemical Reviews* **1998**, *98*, 171-198.
- [122] S.-S. Wang, G.-Y. Yang, *Chemical Reviews* **2015**.
- [123] R. Noyori, M. Aoki, K. Sato, *Chemical Communications* **2003**, 1977-1986.
- [124] X. Zuwei, Z. Ning, S. Yu, L. Kunlan, *Science* **2001**, *292*, 1139-1141.
- [125] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science* **2003**, *300*, 964-966.
- [126] a) A. Kumar, *Catalysis Communications* **2007**, *8*, 913-916; b) L. Liu, C. Chen, X. Hu, T. Mohamood, W. Ma, J. Lin, J. Zhao, *New Journal of Chemistry* **2008**, *32*, 283-289.
- [127] L. Hua, Y. Qiao, Y. Yu, W. Zhu, T. Cao, Y. Shi, H. Li, B. Feng, Z. Hou, *New Journal of Chemistry* **2011**, *35*, 1836-1841.
- [128] Y. Qiao, Z. Hou, H. Li, Y. Hu, B. Feng, X. Wang, L. Hua, Q. Huang, *Green Chemistry* **2009**, *11*, 1955-1960.
- [129] H. Li, Z. Hou, Y. Qiao, B. Feng, Y. Hu, X. Wang, X. Zhao, *Catalysis Communications* **2010**, *11*, 470-475.
- [130] J. Chen, L. Hua, W. Zhu, R. Zhang, L. Guo, C. Chen, H. Gan, B. Song, Z. Hou, *Catalysis Communications* **2014**, *47*, 18-21.
- [131] Y. Leng, J. Wang, D. Zhu, M. Zhang, P. Zhao, Z. Long, J. Huang, *Green Chemistry* **2011**, *13*, 1636-1639.
- [132] K. Yamaguchi, C. Yoshida, S. Uchida, N. Mizuno, *Journal of the American Chemical Society* **2005**, *127*, 530-531.
- [133] a) A. Pourjavadi, S. H. Hosseini, F. Matloubi Moghaddam, B. Koushki Foroushani, C. Bennett, *Green Chemistry* **2013**, *15*, 2913-2919; b) Y. Leng, W. Zhang, J. Wang, P. Jiang, *Applied Catalysis A: General* **2012**, *445-446*, 306-311.
- [134] M.-D. Zhou, M.-J. Liu, L.-L. Huang, J. Zhang, J.-Y. Wang, X.-B. Li, F. E. Kühn, S.-L. Zang, *Green Chemistry* **2015**, *17*, 1186-1193.
- [135] R. Graser Lilian, S. Jürgens, E. Wilhelm Michael, M. Cokoja, A. Herrmann Wolfgang, E. Kühn Fritz, in *Zeitschrift für Naturforschung B*, Vol. 68, **2013**, p. 1138.
- [136] K. Neimann, R. Neumann, *Organic Letters* **2000**, *2*, 2861-2863.
- [137] M. C. A. van Vliet, I. W. C. E. Arends, R. A. Sheldon, *Synlett* **2001**, *2001*, 0248-0250.
- [138] S. P. de Visser, J. Kaneti, R. Neumann, S. Shaik, *The Journal of Organic Chemistry* **2003**, *68*, 2903-2912.
- [139] A. Berkessel, J. A. Adrio, *Advanced Synthesis & Catalysis* **2004**, *346*, 275-280.
- [140] A. Berkessel, J. A. Adrio, D. Hüttenhain, J. M. Neudörfl, *Journal of the American Chemical Society* **2006**, *128*, 8421-8426.
- [141] A. Berkessel, J. A. Adrio, *Journal of the American Chemical Society* **2006**, *128*, 13412-13420.
- [142] A. Berkessel, J. Krämer, F. Mummy, J.-M. Neudörfl, R. Haag, *Angewandte Chemie International Edition* **2013**, *52*, 739-743.
- [143] B. Zhang, M.-D. Zhou, M. Cokoja, J. Mink, S.-L. Zang, F. E. Kühn, *RSC Advances* **2012**, *2*, 8416-8420.

- [144] I. I. E. Markovits, W. A. Eger, S. Yue, M. Cokoja, C. J. Münchmeyer, B. Zhang, M.-D. Zhou, A. Genest, J. Mink, S.-L. Zang, N. Rösch, F. E. Kühn, *Chemistry – A European Journal* **2013**, *19*, 5972-5979.
- [145] F. E. Kühn, A. M. Santos, I. S. Gonçalves, C. C. Romão, A. D. Lopes, *Applied Organometallic Chemistry* **2001**, *15*, 43-50.
- [146] a) F. Gu, H. Dong, Y. Li, Z. Si, F. Yan, *Macromolecules* **2014**, *47*, 208-216; b) H. Tian, Z. Yu, A. Hagfeldt, L. Kloo, L. Sun, *Journal of the American Chemical Society* **2011**, *133*, 9413-9422; c) I. Arellano, J. Guarino, F. Paredes, S. Arco, *J Therm Anal Calorim* **2011**, *103*, 725-730; d) A. Aupoix, B. Pégot, G. Vo-Thanh, *Tetrahedron* **2010**, *66*, 1352-1356; e) I. Dinares, C. Garcia de Miguel, A. Ibanez, N. Mesquida, E. Alcalde, *Green Chemistry* **2009**, *11*, 1507-1510; f) A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, *Angewandte Chemie International Edition* **2008**, *47*, 3210-3214; g) P. Lucas, N. E. Mehdi, H. A. Ho, D. Bélanger, L. Breau, *Synthesis* **2000**, *2000*, 1253-1258.

8 Curriculum Vitae and Publications

8.1 Curriculum Vitae



Surname	Wilhelm
First name	Michael
Date of Birth	October 25th 1985
Place of Birth	Memmingen, Germany

PhD/Education

- 07/2012 – 07/2015 **PhD in Chemistry**
 Technical University Munich (TUM)
 Catalysis Research Center (CRC)
 Supervisor: Prof. Dr. Dr. h.c. mult. W.A. Herrmann
“Ionic Catalysts for the Cycloaddition of Carbon Dioxide with Epoxides and the Oxidation of Olefins”
- Design, synthesis & characterization of novel catalysts
 - Investigation of catalytic properties & mechanisms
 - Optimization of reaction & catalysis parameters
 - Preparation of 12 publications & presentations
 - Supervision and education of students
 - Assistant for beginners and advanced students
- 10/2009 – 04/2012 **Master of Science Chemistry**
 Technical University Munich (TUM)
 Major subject: Organic chemistry
 Minor subject: Chemistry of macromolecules, colloids, interfaces
 Master's-Thesis: *“Copolymerization of CO₂ with Reactive Monomers”*
- 10/2006 – 09/2009 **Bachelor of Science Chemistry**
 Technical University Munich (TUM)
 Bachelor's-Thesis: *“ Sorption and Transport of Hydrocarbons in HZSM 5 Studied by Infrared Spectroscopy”*
- 09/1996 – 06/2006 **Allgemeine Hochschulreife**
 Allgäu-Gymnasium, Kempten

8.2 Journal and Book Contributions

- 1) "Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Organocatalysts"
M. Cokoja, **M. E. Wilhelm***, M. H. Anthofer*, W. A. Herrmann, Fritz E. Kühn, *ChemSusChem* **2015**, 7, 2436 – 2454.
- 2) "Hydroxy-Functionalized Imidazolium Bromides as Catalysts for the Cycloaddition of CO₂ and Epoxides to Cyclic Carbonates"
M. H. Anthofer*, **M. E. Wilhelm***, M. Cokoja, M. Drees, W. A. Herrmann, Fritz E. Kühn, *ChemCatChem* **2015**, 7, 94 – 98.
- 3) "Cycloaddition of Carbon Dioxide and Epoxides Using Pentaerythritol and Halides as Dual Catalyst System"
M. E. Wilhelm*, M. H. Anthofer*, M. Cokoja, I. I. E. Markovits, W. A. Herrmann, F. E. Kühn, *ChemSusChem* **2014**, 7, 1357 – 1360.
- 4) "Cycloaddition of CO₂ and Epoxides Catalyzed by Imidazolium Bromides at Mild Conditions: Influence of the Cation on Catalyst Activity"
M. H. Anthofer*, **M. E. Wilhelm***, M. Cokoja, I. I. E. Markovits, A. Pöthig, J. Mink, W. A. Herrmann, F. E. Kühn, *Catal. Sci. Technol.* **2014**, 4, 1749 – 1758.
- 5) "Niobium(V)chloride and Imidazolium Bromides as Efficient Dual Catalyst System for the Cycloaddition of Carbon Dioxide and Propylene Oxide"
M. E. Wilhelm*, M. H. Anthofer*, R. M. Reich, V. D'Elia, J.-M. Basset, W. A. Herrmann, M. Cokoja, F. E. Kühn, *Catal. Sci. Technol.* **2014**, 4, 1638 – 1643.
- 6) "Valorization of Carbon Dioxide to Organic Products with Organocatalysts"
M. H. Anthofer*, **M. E. Wilhelm***, M. Cokoja, F. E. Kühn, in *Transformation and Utilization of Carbon Dioxide* (Eds.: B.M. Bhanage, M. Arai), Springer Berlin Heidelberg, **2014**, 3 – 37.
- 7) "Epoxidation of Olefins Catalyzed by Polyoxomolybdates Formed in-situ in Ionic Liquids"
L. R. Graser, S. Jürgens, **M. E. Wilhelm**, M. Cokoja, W. A. Herrmann, F. E. Kühn, *Zeitschrift für Naturforschung B* **2013**, 68, 1138 – 1142.

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8.3 Talk and Poster Presentations

- 03/2015 **Poster** 48. Jahrestreffen Deutscher Katalytiker, Weimar
"Tailor-Made Dual Catalyst Systems for the Cycloaddition of CO₂ to Epoxides"
- 03/2015 **Poster**, 48. Jahrestreffen Deutscher Katalytiker, Weimar
"Perrhenathaltige ionische Flüssigkeiten als Katalysatoren in der Olefinepoxidierung: Löslichkeit, Stabilität und Kinetik"
- 10/2014 **Poster**, 7th Green Solvents Conference, Dresden
"Tandem Catalyst Systems for the Chemical Fixation of CO₂ with Epoxides to Cyclic Carbonates"
- 08/2014 **Talk**, 248th ACS National Meeting & Exposition, San Francisco
"Imidazolium and Dual Catalyst Systems for the Fixation of CO₂ as Cyclic Carbonates"
- 06/2013 **Poster**, 7th Forum of Molecular Catalysis, Heidelberg
"Recyclable Organocatalytic System for the Chemical Fixation of CO₂ at Mild Reaction Conditions"