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Olefin Epoxidation in Aqueous Phase Using Ionic Liquid Catalysts: Influence of the Cation on the Catalyst Activity and the Solubility of the Substrate in Water

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Abstract: Hydrophobic imidazolium-based ionic liquids (IL) act as catalysts for the epoxidation of unfunctionalized olefins in water using hydrogen peroxide as oxidant. Although the catalysts are insoluble in both the substrate and in water, surprisingly, they are very well soluble in aqueous H_2O_2 solution, owing to perrhenate-H_2O_2 interactions. Even more remarkably, the presence of the catalyst also boosts the solubility of substrate in water. This effect is crucially dependent on the cation design. Hence, the imidazolium perrhenates enable both the transfer of hydrophobic substrate into the aqueous phase, and serve as actual catalysts, which is so far unprecedented. At the end of the reaction and in absence of H_2O_2 the IL catalyst forms a third phase next to the lipophilic product and water and can easily be recycled.

For more than two decades, research on ionic liquids (IL) has been enjoying ever-growing academic and industrial interest.[1] ILs exhibit a high polarity and tunable hydrophobicity, which are going far beyond the physical and chemical properties of standard solvents in synthetic chemistry. The variation of cations and anions allows for an access to a huge library of compounds. Hence, ILs provide a versatile reaction medium, especially for multiphase chemical (catalytic) reactions where catalyst recycling and reusability play an important role.[2] The properties of ILs as reactants or catalysts are, on the other hand, comparatively underdeveloped. Beyond protic ILs for H^+-catalyzed reactions,[1b] and those containing halometalate[2b] or halide anions for catalytic cycloadditions of epoxides and CO_2 to carbonates,[3] there are few basic reactions that are catalyzed by ILs. For example, in the epoxidation of olefins[4] ILs currently only act as solvents with the aim of easier catalyst recycling and reusability.[5] The potential of ILs as catalysts is relatively unexplored. The most prominent examples in epoxidations involve polyoxometalates and other homogeneous metal complexes as catalysts for multiphase epoxidations in organic media using additional phase transfer or micellar reagents.[6,7,8,9] In this context, the phase transfer enables the catalyst to enter the organic phase containing the substrate in order to increase the activity. However, the product and the catalyst are in the same (organic) phase, so that efficient recycling is still a problem, particularly with respect to the epoxidation of lipophilic substrates. The transfer of a hydrophobic olefin substrate into the aqueous phase containing catalyst and oxidant would facilitate the catalyst separation, but has scarcely been reported on.[8] We have shown that imidazolium salts containing nucleophilic anions, such as the readily available perrhenate ($[ReO_4]^-$) anion, activate hydrogen peroxide via hydrogen bonding.[10] The activation of H_2O_2 by hydrogen bonds has been reported before,[11] however for compounds which have been regarded as notoriously inactive in epoxidation catalysis, this has been uncommon. Moreover, we recently reported on the extraction of $[ReO_4]^-$ by organic receptors from the aqueous phase into toluene, which leads to the 'switching on' of the catalytic activity of perrhenate for epoxidation and allows for a simple catalyst extraction and reusability.[12] This effect was originally ascribed to the hydrophobic character of ILs rendering hydrogen bonding between $[ReO_4]^-$ and H_2O_2 favorable, since compounds such as potassium or ammonium perrhenate do not show any activity. However, the exact role of the cation on the boost of catalytic activity of perrhenate is still unclear and warrants a deeper investigation.

To this end, in this work we have investigated the interplay between the degree of ion pairing, selectivity and solubility effects in the presence of IL catalysts and the consequences on their catalytic activity. Herein, we show that the substituents at the imidazolium ring have a dramatic effect on the solubility of the IL catalysts in aqueous H_2O_2, thus affecting the catalytic activity.

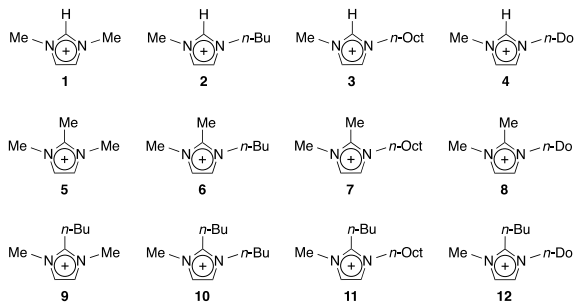

Figure 1. Illustration of IL catalyst cations used in this study (Me = methyl, *n*-Bu = *n*-butyl, *n*-Oct = *n*-octyl, *n*-Do = *n*-dodecyl). Anion: $[ReO_4]^-$.

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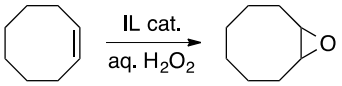
The cations of the used perrhenate catalysts are shown in Figure 1. Starting from 1,3-dimethylimidazolium perrhenate (**1**) we have modified the C2 position as well as the second *N*-wingtip substituent. Previous studies have shown that for imidazolium-based ILs containing nucleophilic anions, the ion contact strength can most efficiently be controlled by substituting the C2 proton by a methyl group, affecting both the physical properties (e.g. melting point)[13] and the catalytic properties of the anion.[14] Hence, the C2 proton in 1-alkyl-3-methyl imidazolium perrhenates has been substituted by Me and *n*-Bu moieties in order to change the nature of cation-anion contacts. It has been shown that introduction of a methyl substituent to the C2 position has an impact on the basicity of the anion.[15] Furthermore, in order to study the effect of the hydrophobicity of the ILs, alkyl chains with varying lengths, i.e. *n*-Bu, *n*-Oct, *n*-Do substituents, have been added to one of the *N*-wingtips. As typical test substrate, cyclooctene was subjected to epoxidation in a two-phase system with aq. H_2O_2 (50 wt.%) and 5 mol % catalyst at 70 °C (Table 1). It should be noted that after 4 h reaction time for all catalysts studied the selectivity of cyclooctene oxide was >99 %, i.e. possible by-products such as cyclooctane diol were not observed. After 24 h of reaction time in the cases of ILs **7** and **8** a slight decrease of the selectivity of epoxide was observed (<5 %), indicating ring opening of the product and formation of the respective diol.

Table 1. Conversion of cyclooctene after 4 and 24 h reaction time using catalysts **1**–**12**.[a]



Entry	Catalyst	Conv. after 4 h [%]	Conv. after 24 h [%]
1	**1**	3	22
2	**2**	7	55
3	**3**	44	98
4	**4**	64	96
5	**5**	4	60
6	**6**	8	70
7	**7**	88	100
8	**8**	85	100
9	**9**	5	60
10	**10**	24	100
11	**11**	21	34
12	**12**	2	8

[a] Reaction conditions: 10 mmol cyclooctene, 0.5 mmol catalyst (5 mol %), 25 mmol oxidant, T = 70 °C. The conversions and selectivities were analyzed by GC.

The results show that imidazolium cations with a proton in the C2 position and short *N*-alkyl chains lead to low conversion even after 24 h reaction time (Table 1, Entries 1 and 2). This may be a consequence of a strong cation-anion imidazolium-H–OReO_3 contact. On the other hand, substitution of a C2 proton by Me or *n*-Bu groups in these cases does not lead to a dramatic increase in activity, at least not within the first 4 h of reaction (Table 1, Entries 5, 6 and 9). This suggests that the anion activity is not primarily influenced by ion contacts, but that the catalyst hydrophobicity plays a more important role. This hypothesis is supported by the fact that ILs having a methyl group at the C2 position, as well as *n*-octyl and *n*-dodecyl *N*-groups exhibit the highest catalytic activities (catalysts **7** and **8**, Entries 7 and 8 in Table 1), yielding the product in 88 and 85 % yield, respectively (TOFs = 6 h^{-1}). Longer alkyl chains in the C2 position, such as an n-butyl substituent, however, have a detrimental effect on the activity (Table 1, Entries 9-12 and Figure S3 in the SI). While in the case of catalyst **9** the two *N*-Me groups most presumably still render the catalyst too hydrophilic to be as active as the benchmark catalysts **7** and **8**, in the case of catalysts **11** and **12** the *n*-Oct and *n*-Do wingtip groups are too hydrophobic forming a third phase next to aq. H_2O_2 and cyclooctene, suggesting that these ILs are too hydrophobic (Table 1, Entries 11 and 12). Figure S3 in the SI and Table 1, Entry 10 show that catalyst **10** exhibits a rather low activity during the first 4 h of reaction time before it reaches quantitative conversion of cyclooctene after 24 h. The generally low (initial) activities of catalysts **9**-**12** are most likely a consequence of a three-phase system substrate/aq. H_2O_2/catalyst, i.e. the low solubility of the catalyst in the aq. phase and/or the low solubility of the substrate in the aq. phase. Obviously, in this series catalyst **10** provides the relatively highest solubility in the aq. H_2O_2 phase, while exhibiting a sufficiently hydrophobic imidazolium cation bearing one Me group and two *n*-Bu groups to allow for a solubilization of the substrate in the aq. phase (see below). Hence, the activities of catalysts **9**-**12** reflect the subtlety of the influence of the ring substituents, most particularly the C2 position.

The hypothesis of the influence of the substituent at the C2 ring position of the IL cation on the solubility features of the catalyst and finally the catalytic activity is strengthened by a closer look at the series of 1-methyl-3-*n*-octyl imidazolium perrhenates, among which catalyst **7** is the most active (see Figure 2).

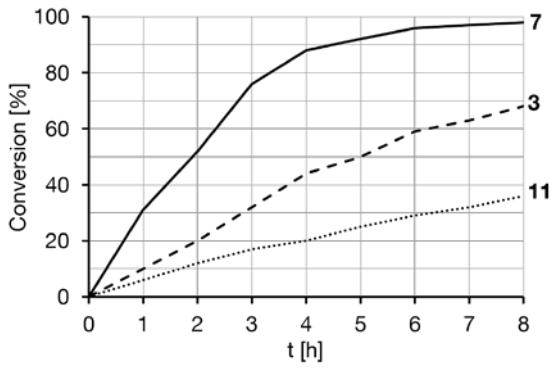


Figure 2. Kinetic plot of the conversion of cyclooctene to cyclooctene oxide with IL catalyst **7** (solid line), **3** (dashed line) and **11** (dotted line). Continuous samples (0.1 mL) were taken from the top phase (substrate + product), mixed with an internal standard (toluene, 1.0 mL) and analyzed by GC.

To gain a more thorough understanding of the effects underlying the difference in activity for catalysts **3**, **7** and **11**, we

focused on three aspects, namely the IL-catalyzed H_2O_2 decomposition (as a competing reaction to the desired epoxidation), catalyst solubility and substrate solubility. While catalysts **3** and **11** showed moderate conversions of H_2O_2 to O_2 without substrate, H_2O_2 conversion was below 1 % in 1 h in case of catalyst **3** when substrate was present. For catalyst **7**, activity toward H_2O_2 decomposition was below 1 % in either case. From these findings we infer that H_2O_2 decomposition is not decisive at least for explaining activity differences of catalysts **3** and **7**.

While the catalysts **3**, **7** and **11** show a solubility in water of less than 2 wt.%, surprisingly, catalysts **3** and **7** exhibit very good solubility (completely miscible and 25 wt.%, respectively) in aq. H_2O_2 (50 wt.%), which hints to a high degree of $[ReO_4]^-$–H_2O_2 H-bonding contacts. The most hydrophobic catalyst **11** is, on the other hand, insoluble in aq. H_2O_2 (50 wt.%), forming a third phase at the onset of reaction. Furthermore, the solubility of catalysts **3**, **7** and **11** was below 100 ppm in cyclooctene, which suggests that epoxidation occurs in the aqueous phase. To support this hypothesis, for the catalytic epoxidation of cyclooctene the molar catalyst:substrate:oxidant ratio was changed from 5:100:250 to 5:100:100. Using this ratio, catalyst **7** is no longer entirely soluble in the aqueous phase, which leads to a reduced activity (see the Supporting Information, SI, Figure S4). Catalyst **3**, which is completely miscible with aq. H_2O_2, does not show any change in activity within the first 4 h of reaction time. This finding rules out conventional phase transfer catalysis, i.e. transfer of reagents from the aqueous to the organic phase with the aid of a phase transfer agent.

Given that the different cation structures of IL catalysts **1**-**12** are not expected to exert a direct chemical influence on the reaction mechanism itself, we assumed that IL-mediated solubilization of cyclooctene into the aqueous phase may play a key role in explaining different activities. It has been reported before that water-soluble ILs can increase the solubility of hydrophobic compounds in the aqueous phase.[16] We determined the cyclooctene content in the aq. H_2O_2 phase containing catalytic amounts of IL catalyst **3**, **7** or **11**, respectively (catalyst:oxidant ratio of 5:250), by means of simple extraction of cyclooctene from the aqueous phase with heptane. Experiments were restricted to room temperature in order to avoid any catalytic conversion. In a blank sample without IL the cyclooctene solubility in aq. H_2O_2 (50 wt.%) was 50 ppm. It is noteworthy that catalysts **3** and **7** greatly promoted cyclooctene solubility in the aqueous phase by a factor of at least 50 (Figure 3, left), whereas for catalyst **11** no measurable effect was observed. It clearly shows transfer of cyclooctene into the aq. phase is around 30 % less efficient for catalyst **3** than for catalyst **7**. This finding qualitatively corroborates the dependence of the catalytic activity (see Figure 2) on the phase transfer ability of the IL catalyst. A probable reason for this finding might be micelle formation of the IL catalysts in aqueous environment, which has been discussed in the literature.[16, 17, 18, 19, 20] As the ILs only differ in their cation substitution pattern, minor differences in hydrophobicity could result in different modes and numbers of aggregation and hence in different capabilities of forming micelles and of solubilizing cyclooctene.

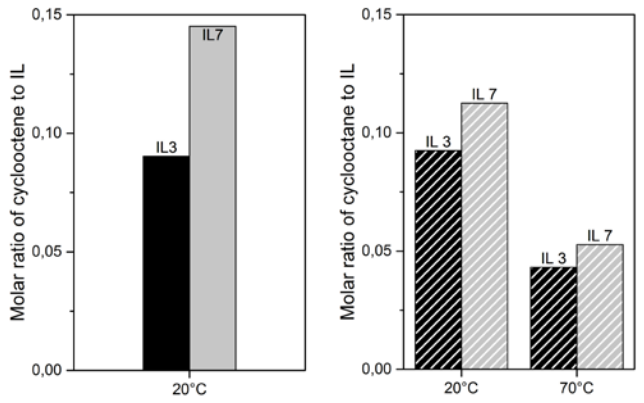


Figure 3. Left: Molar ratio of cyclooctene to IL **3** and **7** in aq. H_2O_2 (50 wt.%) at room temperature. Right: Comparison of molar ratio of cyclooctane to IL **3** and **7** in aq. H_2O_2 (50 wt.%) at room temperature and 70°C (molar composition as given in Table 1 [a]).

To further clarify if the trend of solubilization of cyclooctene by catalysts **3** and **7** also holds at reaction temperature (70 °C), analogous extraction experiments were performed using cyclooctane instead of cyclooctene at room temperature and at 70 °C (Fig. 3, right). By doing so, any bias originating from an ongoing reaction could be excluded. It is evident that the trend at room temperature is the same as with cyclooctene, yet less pronounced with IL **3** solubilizing only 20 % less cyclooctane than IL **7**. Surprisingly, the amount of solubilized cyclooctane decreases by a factor of 2 for either catalyst when temperature is increased to 70 °C. This means that qualitatively the results for cyclooctene at room temperature are expected to be valid also at reaction conditions.

The IL catalyst **7** can be recycled by extraction of the product with THF and subsequent IL extraction with CH_2Cl_2 (for details see the Supporting Information) for at least ten times without loss of activity, showing that this system can be recyclable without loss of the expensive metal. However, an even more convenient method of separating the catalyst from both the aqueous phase is to quench the excess of H_2O_2, which inevitably leads to separation of the catalyst from the aqueous phase.

Catalyst **7** was also used as catalyst for the epoxidation of 1-octene and propene. While 1-octene is converted to 70 % after 4 h (100 % after 24 h, epoxide selectivity >99 %) under the same conditions as for the epoxidation of cyclooctene (see Table 1), propene is converted to 40 % after 34 h with a propene oxide selectivity of 50 %. While lower activities could be rationalized by decreased IL-mediated solubilization of the substrates, in particular for the short-chain compound propene, we assume that the decrease in selectivity is due to high solubility (40 wt.% in water) of propene oxide in the aqueous phase and its subsequent conversion to the diol.

In summary, for the first time it is shown that imidazolium-based ILs bearing simple, nucleophilic anions act as epoxidation catalysts. Compared to the catalytic activity of classic molecular transition metal catalysts for epoxidations, the overall activity of the presented IL catalysts is average to good. Nevertheless, the

IL catalysts bear to striking advantages: they can easily be recycled and they can easily be modified for a broad spectrum of different substrates. The reaction takes place in the aqueous phase and the IL catalysts are able to deliver significant amounts of olefin to the aqueous phase. This is to the best of our knowledge the first time reported in literature that the catalytic compound itself acts both as catalyst and substrate-solubilizer in epoxidation catalysis in water. By designing the cation it is possible to fine-tune both the solubility properties, as well as the Coulomb-interactions between the cation and the anion, particularly in presence of aqueous hydrogen peroxide. As such, a good IL epoxidation catalyst must have a hydrophobic cation, which solubilizes the substrate into the aq. phase, and allow for a high degree of perrhenate-hydrogen peroxide interactions, which render the IL soluble in aq. H_2O_2. With this knowledge at hand, a library of ILs for different substrates can be screened with respect to their relative solubilities in the multiphase catalysis system. Formation of micelles of imidazolium perrhenates in aqueous hydrogen peroxide is a presumable scenario, which appears to be influenced by the structure of the ion pairs and the length of the *N*-alkyl chain. This is a central object of our further studies. This concept also opens the door to other IL catalysts with other nucleophilic metal- or metal-free oxo anions, which are less expensive and more abundant, yet as catalytically active as perrhenate.

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Keywords: Epoxidation • homogeneous catalysis • ionic liquids • solubility • two-phase catalysis

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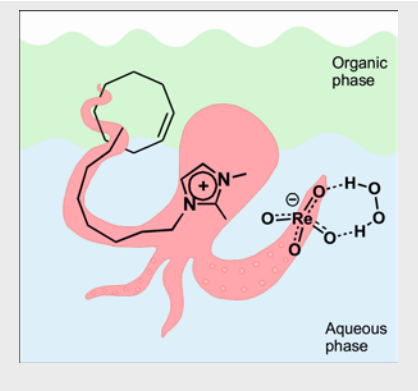
Entry for the Table of Contents

COMMUNICATION

Imidazolium perrhenate ionic liquids are effective catalysts for the epoxidation of unfunctionalized olefins using hydrogen peroxide as oxidant. The catalytic activity strongly depends on the the IL solubility in aq. H_2O_2, which is regulated by the nature of the cation. The IL catalysts significantly enhance the solubility of olefins into the aqueous phase, allowing for the reaction to take phase in water.



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