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Review

Recent advances in oxidation catalysis using ionic liquids as solvents

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ABSTRACT

Ionic liquids are an interesting alternative to classical solvents presenting several advantages. A variety of catalysts show good or even enhanced activities when applied in ionic liquids. Oxidation catalysis represents a large segment of industrial chemistry, providing both bulk chemicals and intermediates for high value added special products and pharmaceuticals. Particularly for the latter products organometallic and inorganic catalysts are being developed that can be applied in systems consisting of or containing ionic liquids. This work provides an overview on recent developments in this field.

1. Introduction

Ionic liquids (ILs) have been used in a variety of catalytic reactions during the last decade [1–3]. They attracted considerable attention due to their physical properties, such as thermal stability, low volatility, low flash point, and high polarity. Additionally, properties such as temperature-depending miscibility with water make them attractive alternatives to organic solvents [4–6]. Organometallic complexes, which are immiscible with hydrocarbons, are often soluble in ILs. Therefore they provide a non-aqueous alternative for two-phase catalysis, in which the catalyst is immobilised in the ionic liquid phase and can easily be separated from the product. ILs have been used for several types of reactions, such as hydrogenation, hydrosilylation and oligomerisation of olefins. Regarding oxidation reactions, Song reported the first manganese(III) (salen) complex, capable of catalysing an asymmetric epoxidation in an ionic liquid less than a decade ago [7]. Since then, ILs have been successfully applied in olefin

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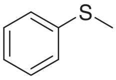
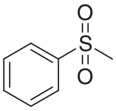
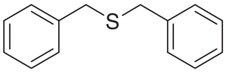
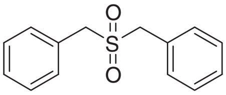
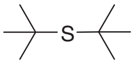
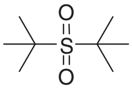
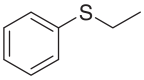
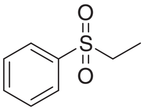
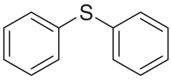
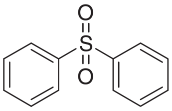
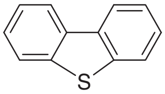
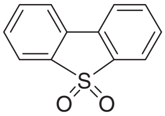
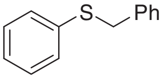
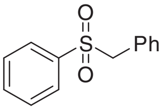
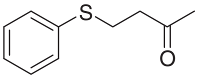
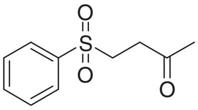
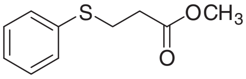
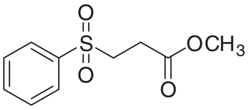
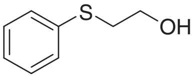
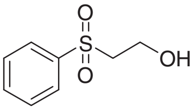
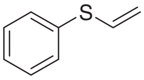
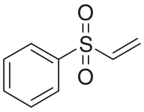
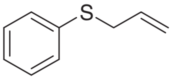
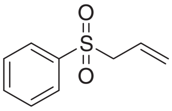
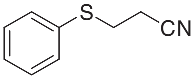
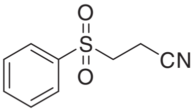
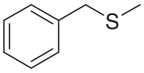
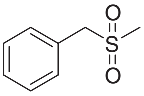
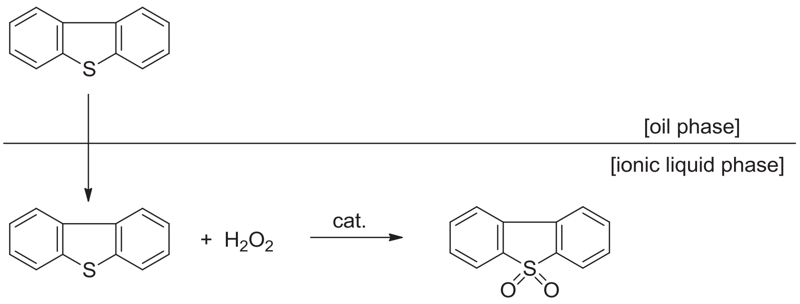
Table 1
Oxidation of sulfides with 5 mol% of $Ti_4[(OCH_2)_3CMe]_2(i\text{-}OPr)$ in $[bmim].BF_4$ at r.t.

Entry	Educt	Product	Time (h)	Yield (%)
1			10 min	95
2			2.5	93
3			1	93
4			2	98
5			2	91
6			2	89
7			2	90
8			1.5	90
9			2	91
10			3	91
11			2.5	87
12			2	91
13			2	91
14			1	94

epoxidations, e.g. utilising manganese(III) porphyrins as catalysts [8–11].

The ionic liquids described in this review are used either as solvents or as extractant. In some cases they are even catalytically active themselves and do not require an additional organometallic complex as catalyst. As a result of extensive studies on oxidation catalysis in ionic liquids, several reviews have been published during the past decade [12–14]. Therefore, this review highlights the most recent results. We also excluded the very well-known oxidation catalyst methyltrioxorhenium from this work since Saladino



Scheme 1. The general process of the oxidative desulfurisation in ILs.

Table 2
Oxidative desulfurisation of DBT in different ionic liquids at r.t.

Entry	IL	Yield (%)
1	[bmim].Cl/$FeCl_3$	99
2	[omim].Cl/$FeCl_3$	87
3	$Et_3NHCl/FeCl_3$	37

Reaction conditions: m(DBT)/m(IL) = 3:1, t = 10 min.

et al. described its activity in non-conventional solvents in 2010 [15].

2. Oxidation of sulfides

All systems described here the aim on the removal of sulfur-containing compounds in diesel fuel. The removal of sulfur containing compounds is an important process in the fuel industry. Hence, research focuses on cost efficient liquid phase processes, such as the oxidation of sulfides, to remove compounds from fuels, which are corrosive for car engines and potentially problematic for the environment. Several research teams have focused on the sulfide oxidation in ionic liquids. The involved ionic liquids were used both as reaction media and as extractants, which dissolve the formed sulfones. Scheme 1 shows the reaction principle.

The extraction of sulfur-containing compounds from diesel oil by ionic liquids could be an attractive alternative to common desulfurisation by hydrotreating. The efficiency of the extraction increases if the S-species are previously oxidised to the corresponding sulfoxides and sulfones [16]. Reddy and Verkade described the oxidation of organic sulfides into sulfones using $Ti_4[(OCH_2)_3CMe]_2(i\text{-}OPr)_{10}$. The reaction was investigated both in methanol (MeOH) and in three different RTILs ([emim].BF_4, [bmim].BF_4 and [bmim].PF_6) as solvents. H_2O_2 was used as oxidant and the reaction was performed at room temperature. Under these conditions, only sulfones but no sulfoxides were found. The activities in the different RTILs are very similar and the authors found for some substrates an acceleration of about 30% compared with MeOH as a solvent. Additionally, the catalyst could be recycled by simply extracting the product using diethyl ether. The catalytic system could be reused for six cycles without a loss of activity. Table 1 shows the product yields in [bmim].BF_4. The velocity of the oxidation reaction is in good accordance with the steric hindrance of the substituents at the sulfur atom [17].

Li et al. investigated three different ionic liquids based on iron chloride in the catalytic oxidation/desulfurisation (ODS) systems for removal of benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). The authors stated that the system [bmim].Cl/$FeCl_3/H_2O_2$ is able to remove 99% of DBT under mild reaction conditions. As can be seen in Table 2, [bmim].Cl/$FeCl_3$ and [omim].Cl/$FeCl_3$ ionic liquids show higher ability to remove sulfur than $Et_3NHCl/FeCl_3$ [18,19].

Table 3
Different investigated systems with their corresponding yields (%) in the desulfurisation of DBT.

Entry	Type of IL	IL	IL + H_2O_2	IL + Na_2MoO_4 + H_2O_2
1	[bmim].BF_4	16	32	99
2	[omim].BF_4	21	35	68
3	[bmim].PF_6	15	39	70
4	[omim].PF_6	20	45	78
5	[bmim].TA	15	31	49
6	[omim].TA	21	32	37

Reaction conditions: T = 70 °C, t = 3 h, 5 mol% catalyst.

Table 4
The reactivity of different Mo catalysts for desulfurisation.

Entry	Catalyst	Yield (%)
1	Na_2MoO_4	99
2	H_2MoO_4	94
3	$(NH_4)_6Mo_7O_{24}$	98
4	$H_3PMo_{12}O_{40}$	93
5	$(NH_4)_3PMo_{12}O_{40}$	98
6	$Na_3PMo_{12}O_{40}$	99

Reaction conditions: T = 70 °C, t = 3 h, 5 mol% catalyst in [bmim].BF_4.

In addition, the authors studied the recycling of the [bmim].Cl/$FeCl_3$ system. They observed only a small drop from 99 to 91% after six cycles. However, if the IL phase was extracted with CCl_4 after each run, no loss in activity could be found after nine cycles [18,19].

The same group investigated the desulfurisation with a catalytic system containing $Na_2MoO_4 \cdot 2H_2O$, H_2O_2, and [bmim].BF_4. When using DBT as a model compound, a sulfur removal of 99% was reached. The same reaction without the ionic liquid leads to a desulfurisation of 4%. The authors stated that without the IL, most of H_2O_2 decomposed at the applied temperature. Hence, the IL acts as an extractant, as reaction medium and as stabilising agent. Table 3 shows the different investigated systems with their corresponding oxidative desulfurisation yields [20,21].

Table 4 displays the oxidative desulfurisation with different Mo catalysts. Li et al. found that the reaction including molybdenum salts as catalysts was more efficient in polar ILs than in acidic ones, since they exhibit a lower electrolyte strength [20].

Leaching experiments were also performed and it was observed that in case of Na_2MoO_4 1.2 mg (0.9%) leach in 1 L of the substrate phase. This amount could be completely removed by extraction with water (2 × 10 mL).

Li et al. investigated the catalytic activity of V_2O_5 for the oxidative desulfurisation of fuels [22]. The best results were obtained when a combination of H_2O_2 and V_2O_5 in [bmim].BF_4 was used. In this case, the removal of sulfur was about 99%. The oxidation of methylphenylsulfide was performed at 35 °C using TBHP or UHP as an oxidising agent and 2.5 mol% of the catalyst. The authors stated that during the reaction, V_2O_5 was oxidised by H_2O_2 to the

Table 5
Different investigated systems with their corresponding yields (%) in the desulfurisation of DBT with phosphotungstic acid.

Entry	Type of IL	IL	IL + H_2O_2	IL + $H_3PW_{12}O_{40}$ + H_2O_2
1	[bmim].BF_4	14	26	98
2	[omim].BF_4	18	27	65
3	[bmim].PF_6	12	27	98
4	[omim].PF_6	18	35	64

Reaction conditions: $T = 30\,^\circ C$, $t = 1$ h, 1 mol% catalyst.

Table 6
Different decatungstate catalysts with their corresponding DBT desulfurisation yields (%).

Entry	Catalyst	Yield (%)
1	$[(C_4H_9)_4N]_4W_{10}O_{32}$	98
2	$[(CH_3)_4N]_4W_{10}O_{32}$	97
3	$[(C_2H_5)_3NC_7H_7]_4W_{10}O_{32}$	66
4	$Na_4W_{10}O_{32}$	95

Reaction conditions: $T = 60\,^\circ C$, $t = 0.5$ h, 1 mol% catalyst in [bmim].PF_6.

Table 7
Results of the recyclability.

Cycle	Yield (%)	Cycle	Yield (%)
1	100	7	100
2	100	8	98
3	99	9	95
4	99	10	97
5	100	11	95
6	100	12	93

Reaction conditions: $T = 60\,^\circ C$, $t = 2$ h, $V_{oil}/V_{IL} = 1{:}1$.

peroxovanadium compound which oxidises the sulfides to the corresponding sulfones. Without any ionic liquid the sulfur removal was lower than 3%.

The same group studied the oxidative desulfurisation of fuels by phosphotungstic acid ($H_3PW_{12}O_{40}$) and different decatungstates, respectively [23–25]. The reaction with phosphotungstic acid was performed in different ILs and H_2O_2 as an oxidant. The results are summarised in Tables 5 and 6, clearly pointing out the advantage of the [bmim].-type ILs in combination with the used catalysts.

Both investigated catalytic systems lead to almost quantitative yields at a catalyst concentration 1 mol%. By the same group $[WO(O_2)_2{\cdot}Phenanthroline{\cdot}H_2O]$, $[MoO(O_2)_2{\cdot}Phenanthroline]$ and Peroxophosphomolybdate catalysts were dissolved in ILs, e.g. [bmim].BF_4, [omim].BF_4, [bmim].PF_6, and [omim].PF_6 to oxidise DBT with hydrogen peroxide under moderate conditions. The sulfur removal of DBT-containing model oil reached 99% at 70 °C. The catalytic oxidation system containing $WO(O_2)_2{\cdot}Phen{\cdot}H_2O$, H_2O_2, and [bmim].BF_4 can be recycled four times without a significant decrease in activity [26,27].

Li et al. further investigated the desulfurisation of dibenzothiophene by a combination of both chemical oxidation and solvent extraction [28]. Benzyltrimethylammonium chloride·$2ZnCl_2$ is a low-cost ionic liquid and was used as an extractant for oxidative desulfurisation of DBT in *n*-octane. DBT was oxidised to the corresponding sulfone by peracetic acid, in situ prepared from H_2O_2 and acetic acid. With this system, the desulfurisation yield of DBT was 94% at 30 min and 99% after 50 min at room temperature. According to the authors, the metal-containing ionic liquid could be recycled six times without a significant decrease in activity.

In addition to the described systems there are several reports on the investigation of Brønsted acidic ionic liquids which are themselves acting as oxidative desulfurisation catalysts. Zhao et al. used the Brønsted acidic ionic liquid N-methyl-pyrrolidonium tetrafluoroborate ([hnmp].BF_4) as a catalyst for the oxidative desulfurisation of DBT in the presence of H_2O_2 as an oxidant [29,30]. It was found that a coordination compound was generated between hydrogen peroxide and the cation of the ionic liquid, which results in the formation of hydroxyl radicals. The sulfur-containing compounds were first dissolved in the IL and then oxidised by the radicals. Due to the high polarity the formed sulfones could only be detected in the IL phase. Table 7 shows the recyclability of the investigated system.

The same group studied the desulfurisation of thiophene with a non-fluorinated and environmentally benign IL $(C_4H_9)_4NBr{\cdot}2C_6H_{11}NO$ as an active catalyst [31,32]. A combination of hydrogen peroxide and acetic acid acts as an oxygen source for the reaction. After the oxidation the formed sulfoxide, sulfone and sulfate are more polar and could be extracted by the ionic liquid. A desulfurisation level of up to 99% was obtained after 30 min and 40 °C. An advanced oxidation process was studied by Zhao and coworkers as well [33]. In this case they used a combination of ozone and hydrogen peroxide leading to the formation of hydroxyl radicals. In contrast to applying ozone alone (64% yield), this combination led to an increased oxidation of DBT of 99% DBT at 50 °C after a reaction time of 150 min [bmim].BF_4 was investigated as a reaction medium and extractant. The authors stated that the reaction became faster with increasing temperature but a higher concentration of ozone was also required.

The same reaction was investigated by the group of Gao. In this case they used the Brønsted acidic ionic liquid [hmim].BF_4 as a catalyst for the oxidative desulfurisation of DBT in the presence of H_2O_2 as an oxidant [34].

The deep oxidative desulfurisation in the presence of H_2O_2 and UV irradiation without any catalyst at room temperature and atmospheric pressure was investigated by Zhao et al. The sulfur removal reached up to 99.5% within 8 h. Without UV irradiation the yield was around 52% after 12 h [bmim].PF_6 was used as the extraction media [35]. Gui et al. studied some task-specific ionic liquids which contain carboxyl groups in their cations. Fig. 1 shows the structure of the ionic liquids. In the following case the ILs act as both catalyst and extractant.

The oxidation potential of DBT with H_2O_2 as an oxidant decreases in the following order: E > F > C > A > B. The maximum yield was 97% with compound E as catalyst [36].

The group of Halligudi investigated a Ti–binol complex, supported on an ionic liquid-phase for enantioselective sulfide oxidation [37]. The principle of synthesising the "SILP"-type catalyst (SILP = supported ionic liquid-phase) is shown in Scheme 2.

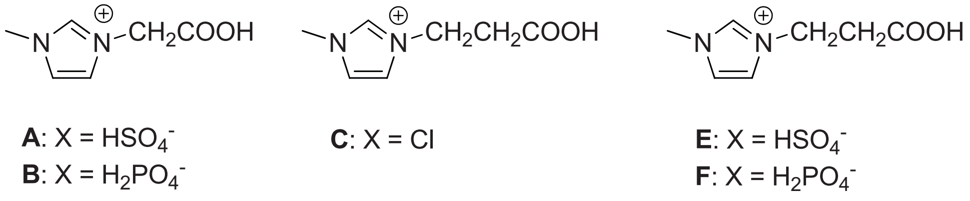
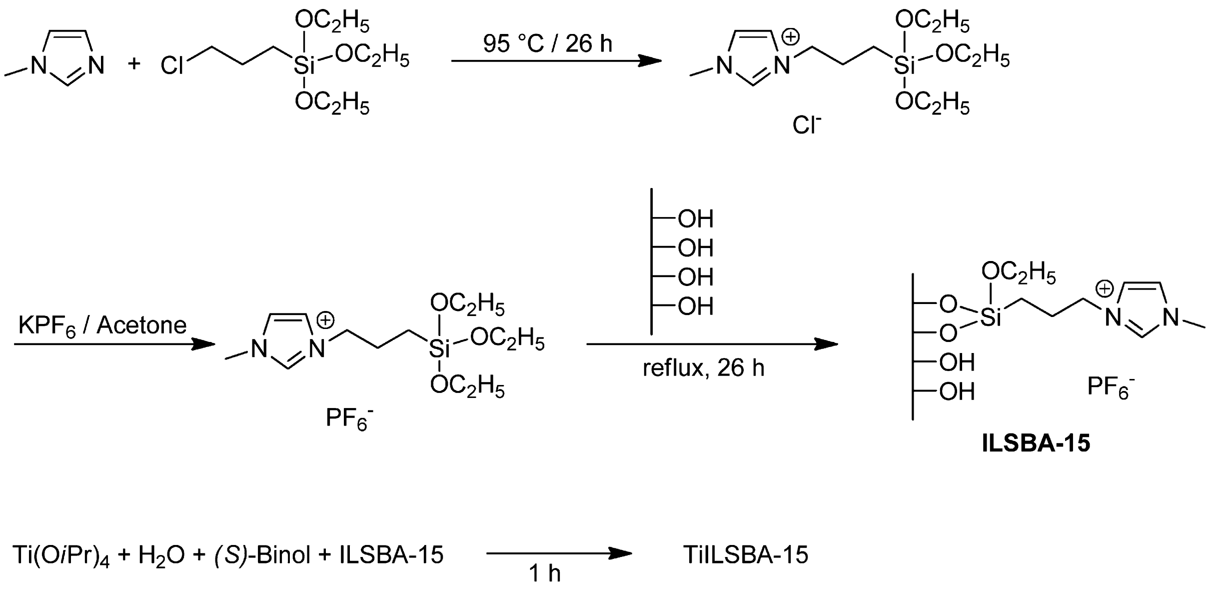
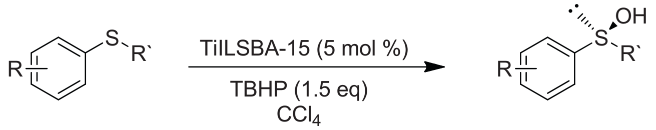


Fig. 1. Structure of the task-specific ionic liquids.



Scheme 2. Preparation of the TiILSBA-15 catalyst.



Scheme 3. Enantioselective oxidation of different sulfides.

Table 8
Catalytic results in the oxidation of different sulfur-containing compounds.

Entry	R	R′	Yield (%)	ee (%)
1	H	Me	59	99.9
2	4-Me	Me	62	99.5
3	4-Br	Me	58	99.2
4	4-Cl	Me	61	96.7
5	3-Br	Me	57	99.2
6	4-NO_2	Me	54	88.3
7	H	Et	63	77.2
8	4-OMe	Me	55	99.9
9	4-F	Me	59	98

TiILSBA-15 was synthesised and the XRD patterns of both SBA-15 and TiILSBA-15 could be associated with a *p6mm* hexagonal symmetry and the mesoporous structure of the support has not changed after the immobilisation. The activity in the enantioselective oxidation of sulfides (Scheme 3) with different substrates and aqueous TBHP as an oxidising agent was investigated (Table 8).

The authors used different solvents for this reaction and found out that CCl_4 gave the best enantiomeric excess. In order to test the stability of the catalytic system the authors recycled the catalyst eight times by simple filtration after each run. They found a decrease of both the yield from 62% to 56% and ee values from 99.2% to 98.2%. Less than 0.1 ppm of Ti leached into the organic phase.Xian-Ying and Jun-Fa investigated two different peroxotungstates immobilised on ionic liquid-modified silica, which are depicted in Scheme 4.

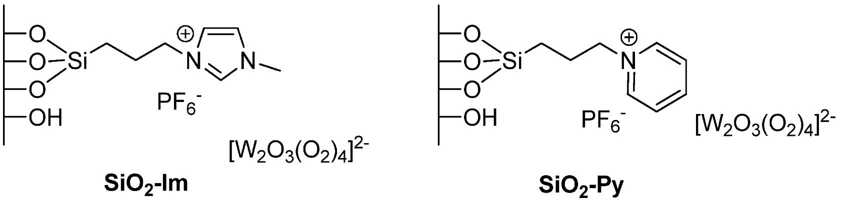
Depending on the ratio of catalyst, H_2O_2 and sulfide the authors could change the selectivity either to the formation of sulfoxides (1.5:110:100) or to the formation of sulfones (2:250:100). With both catalysts the sulfoxides could be prepared with yields between 80% and 95%, the sulfones between 79% and 99%, respectively [38].

In the work of Zhao et al., several pyridinium-based ionic liquids were employed as phase-transfer catalysts for the phase-transfer catalytic oxidation of dibenzothiophene. A mixture of H_2O_2 and formic acid was used as an oxidant. The best results were obtained with [bPy].HSO_4 at 60 °C. The desulfurisation reached a maximum of 93% within an hour. The [bPy].HSO_4 could be recycled for five cycles without a significant loss of activity [39]. A very similar system was studied recently by Liu and coworkers. They used [bmim].HSO_4 as a Brønsted acidic ionic liquid. This substitution leads to an increased activity in desulfurisation of 99.6% at room-temperature and after a reaction time of 90 min [40]. The group of Zhao optimized the oxidative desulfurisation using a quaternary ammonium coordinated ionic liquid $(C_4H_9)_4NBr{\cdot}2C_6H_{11}NO$ as a catalytic solution. The catalytic performance reached up to 99% in case of the oxidation and removal of DBT under the best conditions. The authors stated that with increasing temperature from 20 °C to 50 °C the yields also increased. This is caused by a reduced viscosity of the ionic liquid. With a further increase to 70 °C the yields decreased because of the decomposition of H_2O_2.

3. Oxidation of alcohols

In recent years many research efforts in field of the oxidation of alcohols in ionic liquids have been undertaken, for example the application of photooxidation or the reaction using reusable resins [41,42]. In 2007 Shen et al. were the first to investigate the copper-bisisoquinoline based selective oxidation of alcohols to the corresponding aldehydes and ketones using RTILs as solvent and O_2 as an oxidant [43]. The authors stated that the catalytic activity in ionic liquids was enhanced in comparison to conventional organic solvents. The oxidation of different alcohols has been studied, including primary, secondary, allylic, and benzylic alcohols. In all cases, both the selectivity and the yield were higher than 80%. The authors found that even air can be used instead of oxygen. Jiang and Ragauskas investigated the aerobic oxidation of alcohols to acids or aldehydes, respectively [44]. Following this method, it is possible to obtain the acid by the simple addition of Cu(II) 2-ethylhexanoate as a cocatalyst. Table 9 shows the results and the recyclability of the catalytic system.

In 2007 Liu et al. used $Cu(acac)_2$ for the oxidation of secondary alcohols with TBHP as an oxygen source [45]. They investigated different RTILs to find the ideal reaction conditions. The best results



Scheme 4. Different peroxotungstates investigated by Xian-Ying and Jun-Fa.

Table 9
Recyclability of the aerobic oxidation of benzyl alcohol under the two different conditions.

$$\underset{\textbf{X}}{PhCHO} \xleftarrow{A} PhCH_2OH \xrightarrow{B} \underset{\textbf{Y}}{PhCO_2H}$$

Cycle	Time (h)	Condition	Yield (%)	
			X	*Y*
1st	8	A	90	
	12	B		89
2nd	8	A	84	
	12	B		88
3rd	10	A	83	
	15	B		76

Reaction condition A: 2 mmol benzyl alcohol, 2 mol% $VO(acac)_2$, 6 mol% DABCO, 1 bar O_2, 0.3 g of $[bmim].PF_6$, 95 °C; reaction condition B: 2 mmol benzyl alcohol, 2 mol% $VO(acac)_2$, 2 mol% Cu(II) 2-ethylhexanoate, 6 mol% DABCO, 1 bar O_2, 0.3 g of [hmim].OTf, 95 °C for the specific time.

were achieved with imidazolium-type ionic liquids – especially with $[bmim].PF_6$. Subsequently, different substrates have been investigated in this RTIL (Table 10).

To prove the recyclability of the catalytic system, the oxidation of 1-phenylpropan-1-ol to the corresponding acetophenone was tested in five subsequent runs. The yield decreased from 91% in the first cycle to 84% in the fifth cycle. Later, Han and coworkers employed the same substrates for the oxidation with a novel copper Schiff-base complex (see Fig. 2) [45,46].

The authors found that in this case, the BF_4-type RTIL leads to the highest conversion. In addition, the selectivity of the formation of the corresponding acid reaches up to 98%. The authors also stated that with TBHP the reaction works best, instead of using H_2O_2 or NaClO as an oxidising agent. Finally, the reaction of the aromatic alcohols was faster than the aliphatic alcohols.

The catalytic oxidation with Ni(II)-Schiff-base catalysts in an [emim].-based IL and NaOCl as an oxidising agent was published by Bhat and coworkers [47]. They investigated different substrates and reached yields of >61% after 15 min at room temperature. The same group published analogous Co(II)-complexes (Scheme 5). A difference in the catalytic activity between the Ni(II) and the Co(II) catalysts could not be observed. The authors further stated that the activity is strongly influenced by the bulkiness of the substituent R in the ligand [47,48].

A. Shaabani et al. investigated the oxidation of alkyl arenes and alcohols to the corresponding carbonyl compounds in ionic liquids. A variety of metallo-phthalocyanines and ionic liquids were used and the best results were obtained using Co(II) phthalocyanine, [bmim].Br and an oxygen pressure of 0.1 atm. For the oxidation of alkyl arenes at 100 °C, yields between 74% and 93% were obtained, between 80% and 92% for the oxidation of alcohols, respectively [49]. The same catalyst was used in a tetrasulfonated type for the oxidative deprotection of trimethylsilyl ether to the corresponding carbonyl compound. In [bmim].Cl yields of up to 80% could be obtained [50]. The groups of Hajipour et al. worked on this reaction in the presence of a catalytic amount of [bmim].Br (10 mol%). They found an efficient method to obtain the carbonyl compounds under

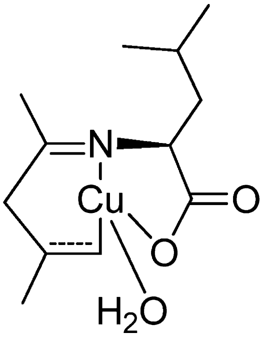
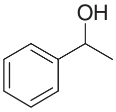
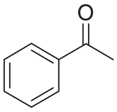
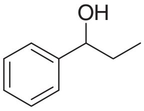
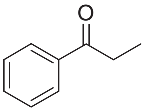
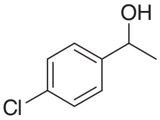
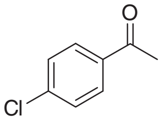
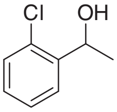
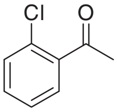
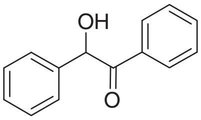
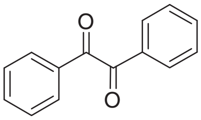
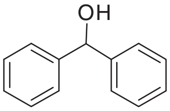
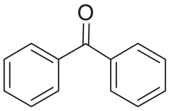
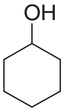
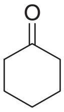
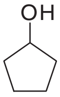
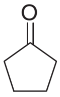
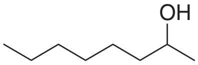
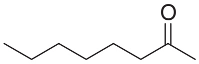
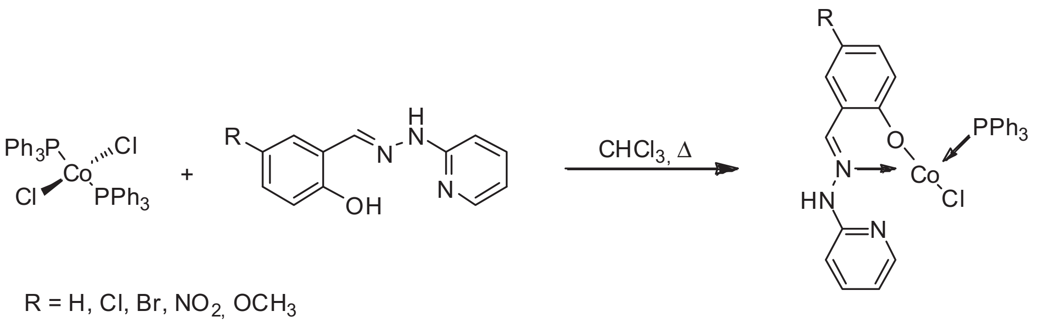


Fig. 2. Structure of the Cu-Schiff-base catalyst.

Table 10
Oxidation of secondary alcohols with 3 mol% $Cu(acac)_2$ as a catalyst.

Entry	Educt	Product	Time (h)	Yield (%)
1			5	91
2			5	91
3			5	93
4			5	41
5			5	94
6			5	93
7			5	65
8			15	66
9			15	58



Scheme 5. Synthesis of the Co(II) catalysts.

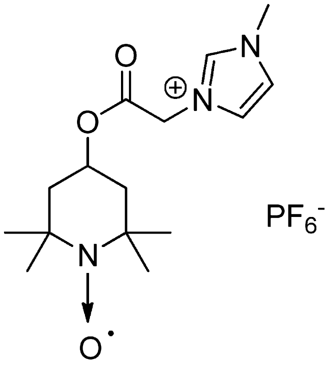


Fig. 3. Structure of a TEMPO-IL.

solvent-free conditions using potassium persulfate as an oxidant. After a reaction time of 15 min they got a maximum yield of 90% [51]. Fadini and coworkers studied the manganese(III) catalysed cleavage of vicinal diols. When applying ILs in this reaction, the yields increased between 10% and 60% compared to conventional solvents. With a concentration of [Mn(salen)(Py)].(OAc) of 5 mol% at a temperature of 60%, a quantitative oxidative C–C bond cleavage of 1,1,2,2-tetraphenyl-1,2-ethanediol could be obtained after 2 h and with oxygen as oxidant [52].

In 2008, Liu et al. studied the oxidation activity of different transition-metal salts by dissolving an equimolar amount of it in a *so-called* TEMPO-IL (TEMPO = 2,2,6,6-tetramethylpiperidine N-oxyl; Fig. 3) [53,54].

While $Co(OAc)_2$, $CoCl_2$, $FeCl_3$, $Mn(OAc)_2$ and $NiCl_2$ show no activities as catalysts of the oxidation of benzyl alcohol, CuCl exhibits a high catalytic activity, yielding benzaldehyde in 94%. Table 11 shows all the investigated substrates.

After the reaction, the IL phase was distilled and reused for five cycles without a loss of activity. In 2008, Liu et al. used the same catalytic system and found out that the addition of molecular sieve MS3A results in a remarkable faster reaction rate [55]. The authors stated that the acceleration results from the property of the MS3A to act as a Brønsted base and it is independent on the water content of the reaction mixture.

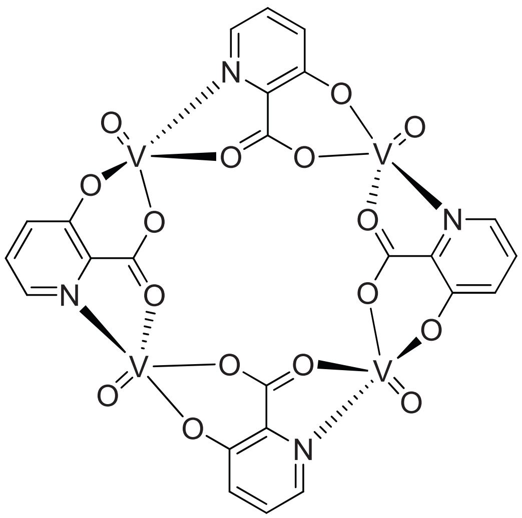
Table 11
TEMPO-IL/CuCl catalysed oxidation of alcohols.

Entry	Substrate	Temp. (°C)	Time (h)	Conversion (%)	Yield (%)
1	Benzyl alcohol	40	12	67	55
2	Benzyl alcohol	65	12	99	94
3	Cinnamyl alcohol	65	30	99	84
4	4-Nitrobenzyl alcohol	100	24	96	84
5	4-Chlorbenzyl alcohol	75	19	99	88
6	4-Methoxybenzyl alcohol	65	21	99	91
7	Diphenyl carbinol	65	21	94	85
8	2-Phenylethanol	65	30	54	30
9	Furfuryl alcohol	65	50	40	–
10	Cyclohexanol	65	40	–	–
11	Lauryl alcohol	65	40	23	–

Lei and coworkers studied a highly chemoselective oxidation of benzylic alcohols in the presence of aliphatic alcohols to the corresponding hydroxyl benzyl aldehydes and ketones in a [bmim].PF_6–H_2O-mixture. The reaction is an effective catalytic oxidation system, which leads to high yields using N-chlorosuccinimide (NCS)/NaBr/TEMPO-IL. The [bmim].PF_6, together with the catalyst TEMPO-IL could be recycled for ten subsequent runs without any loss of activity neither in terms of yield nor selectivity of the product [56]. Another effective system with a TEMPO functionalised imidazolium salt, a carboxylic acid substituted imidazolium salt and $NaNO_2$ for the aerobic oxidation of alcohols was established by He and coworkers [57].

Ogawa et al. compared the catalytic activity of tetranuclear vanadium(IV) complex bearing 3-hydroxypicolic acid (hpic) as ligand (Fig. 4) in organic solvents and [bmim].BF_4 [58].

The authors stated that commercially available vanadium complexes are not active in the oxidation of benzyl alcohol. However, with 0.5 mol% $[(VO)_4(hpic)_4]$. in acetonitrile (MeCN) a yield of 62% was reached with a selectivity of 100% to the corresponding aldehyde. In protic solvents (EtOH) the yields are even higher (up to 71%) but the selectivity is decreased because the aldehyde is further oxidised to the corresponding acid. The oxidation of benzhydrol to



$(VO)_4(hpic)_4$

Fig. 4. Structure of the vanadium(IV) catalyst.

Table 12
Oxidation of 1-(naphthylen-2-yl) ethanol under variable conditions.

Parameter	Yield (%)
Pressure (atm)	
2	60
2.7	93
3.4	99
Temp. (°C)	
80	79
90	92
100	99
Catalyst loading (%)	
20	26
30	58
40	99
50	99
60	91

benzophenone was also investigated under an atmosphere of oxygen and [bmim].BF_4 as solvent. Benzophenone was formed with a yield of 64%.

In 2008 Halligudi and coworkers investigated the selective oxidation of alcohols by a heteropoly molybdovanadophosphoric acid ($H_5PMo_{10}V_2O_{40}$) supported ionic liquid-phase catalyst [59]. The compound was immobilised on a mesoporous silica SBA-15. The authors obtained high activity in both primary and secondary alcohols to the corresponding aldehydes and ketones, respectively. The catalyst showed no activity with respect to the oxidation of the ketone and the aldehyde to the carboxylic acid. The authors performed the catalytic reactions in an autoclave under air pressure. Table 12 shows the results of the oxidation of 1-(naphthylen-2-yl) ethanol under different conditions.

The experiments were performed by dissolving the catalyst in MeCN and adding a radical initiator (AIBN or TBHP). At an oxygen pressure of 1 atm the yield was only 40% (increasing at higher pressure). With regard to the temperature the authors stated that no conversion was obtained at 50 °C. Under the best conditions the authors investigated the activity of different substrates which are depicted in the following Table 13.

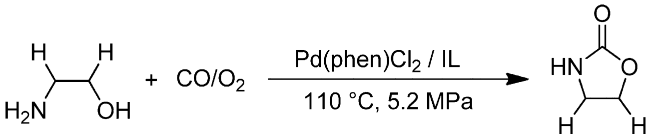
The authors were able to find the conditions ($T = 100\,^{\circ}C$, pressure: 3.4 atm and $c = 0.02$ mol%) which led to high yields of 83–99% in all investigated substrates.

Li and Xia studied the biphasic oxidative cyclocarbonylation of β-aminoalcohols and 2-aminophenol to their corresponding 2-oxazolidinones. Pd(phen)Cl_2 acts as the catalyst which is stabilised by [bmim].I. Scheme 6 shows the oxidation reaction.

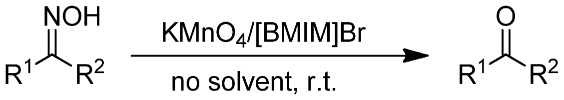
Table 13
Variation of the substrates.

Entry	Substrate	Time (h)	Yield (%)
1	1-(Naphthylen-2-yl) ethanol	7	99
2	Diphenylmethanol	7	99
3	Cyclohexanol	6	99
4	Phenylethanol	6	99
5	2-Hexanol	5	98
6	2-Phenylpropanol	7	93
7	4-Methoxy phenylethanol	6	98
8	4-Methyl phenylethanol	6	96
9	4-Chloro phenylethanol	6	98
10	4-Bromo phenylethanol	6	98
11	4-Nitro phenylethanol	6	94
12	Benzoin	7	95
13	Menthol	6	96
14	[1,7,7]Trimethylbicyclo [2,2,1]heptan-2-ol	8	95
15	3,5,5-Trimethylcyclohex-2-enol	7	94
16	Benzyl alcohol	12	98
17	1,3-Butanediol	8	83
18	Geraniol	10	97
19	Cinnamyl alcohol	13	98
20	Pyridin-2-methanol	11	96

Reaction conditions: $T = 100\,^{\circ}C$; air pressure: 3.4 atm; catalyst concentration: 0.02 mol%.



Scheme 6. Oxidative cyclocarbonylation of ethanolamine.



Scheme 7. The oxidation of various oximes with $KMnO_4$.

The best results were obtained using [bmim].I as an ionic liquid with a TOF of 3288 h^{-1} and a conversion of 94% [60]. The selective oxidation of alcohols in high conversion and selectivity using 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$)/MCM-41 in ionic liquids was studied by Shen et al. The best performance of the photocatalytic system was obtained with a catalyst loading of 30%, [omim].BF_4 as solvent and oxygen as oxidant. The yields were between 90% and 99%. The immobilisation resulted in an amorphous phase with a BET surface of 632 m^2/g, a pore volume of 0.53 cm^2/g with a pore diameter of 29.7 Å [61].

The immobilisation of perruthenate (RuO_4^-) on 1-vinyl-3-butyl imidazolium chloride leads to an active catalyst for the aerobic oxidation of benzyl alcohol to benzyl aldehyde. The catalytic reaction was done in supercritical CO_2, toluene and dichloromethane at 80 °C. Han et al. could demonstrate that the catalyst was very active and highly selective. The reaction rate in CO_2 depended strongly on pressure and reached a maximum at about 14 MPa [62].

4. Oxidation of oximes

Compounds such as aldoximes and ketoximes are derivatives of carbonyl compounds and are, for example, used for the characterisation and protection of carbonyl compounds. The regeneration of the carbonyl species is achieved by the oxidation of the corresponding oximes [63,64]. Safaei-Ghomi and Hajipour investigated the oxidation of oximes with $KMnO_4$ as an oxidising agent (Scheme 7) [65].

The best results could be obtained with a 1:0.7:0.4 ratio of oxime:IL:$KMnO_4$ at room temperature. The authors stated that the RTIL inhibits the further oxidation of the carbonyl compound to the respective carboxylic acid. In all the examined substrates

Table 14
Oxidation of oximes with $KMnO_4$ and [bmim].Br.

Entry	R^1	R^2	Time (min)	Yield (%)
1	C_6H_5	H	40	95
2	4-$O_2NC_6H_4$	H	9	>98
3	3-$O_2NC_6H_4$	H	18	95
4	4-$MeOC_6H_4$	H	53	91
5	3-$MeOC_6H_4$	H	42	94
6	2,4-$(MeO)_2NC_6H_3$	H	73	89
7	4-ClC_6H_4	H	12	94
8	4-BrC_6H_4	H	17	97
9	2,6-$Cl_2NC_6H_3$	H	23	91
10	2,4-$Cl_2NC_6H_3$	H	10	>98
11	4-MeC_6H_4	H	50	93
12	2-MeC_6H_4	H	41	95
13	3-MeC_6H_4	H	60	91
14	C_6H_5	C_6H_5	55	81
15	C_6H_5	CH_3	52	92
16	4-ClC_6H_4	CH_3	32	93
17	4-BrC_6H_4	CH_2Br	17	93
18	2-HOC_6H_4	CH_3	28	90

yields >81% are obtained. The results for various oximes are listed in Table 14.

In 2009, Shaabani and Farhangi investigated the aerobic cleavage of oximes in imidazole-based ionic liquids with phthalocyanin (Pc) catalysts [66]. The best results are obtained with Co-Pc catalysts and [bmim].Br as solvent. Table 15 gives an overview of the examined substrates.

In addition, it was shown that the catalyst can be reused after the extraction of the product with just a minor activity loss (see Table 15, Entry 1). Another advantage of using Co–Pc/RTIL in contrast to conventional methods is the performance under neutral conditions. Application of RTILs is also suitable for acid-sensitive functional groups.

5. Oxidation of olefins

In 2008 Welton et al. used a number of ionic liquids as co-solvents for the catalytic epoxidation of alkenes with Oxone® ($KHSO_5$) and *N*-alkyl-3,4-dihydroisoquinolinium salts [67]. Because of the possible oxidation of imidazolium based ILs, pyridinium cations were preferred. Welton et al. found that epoxidations carried out in water soluble ILs are not more efficient than those performed in MeCN. The results of the epoxidation of different substrates by 2-methyl-3,4-dihydroisoquinolinium tetrafluoroborate [mdhqm].NTf_2 catalysts are depicted in Table 16.

The 2-methyl-3,4-dihydroisoquinolinium cation is a compound which is able to catalyse the olefin epoxidation without an involved metal. The mechanism is shown in Scheme 8.

The authors tried a range of ILs as a co-solvent for the oxidation of 1-phenyl-cyclohexene at room temperature. Interestingly, in water immiscible ILs the epoxidation does not take place. With water miscible ILs the authors described the conversions of 63% in case of [bmim].OTf and 53% with [bmim].BF_4 to the corresponding epoxide. The authors explained this phenomenon with phase-transfer problems of the HSO_5^- in the case of the biphasic system. In recent years, there were some publications dealing with the catalytic epoxidation of olefins with different molybdenum compounds as catalysts. Valente et al. described dioxomolybdenum(VI) complex bearing an anionic N,O oxazoline ligand (Fig. 5) [68].

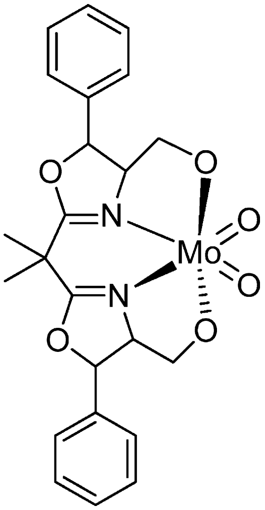


Fig. 5. The investigated dioxomolybdenum(VI) complex.

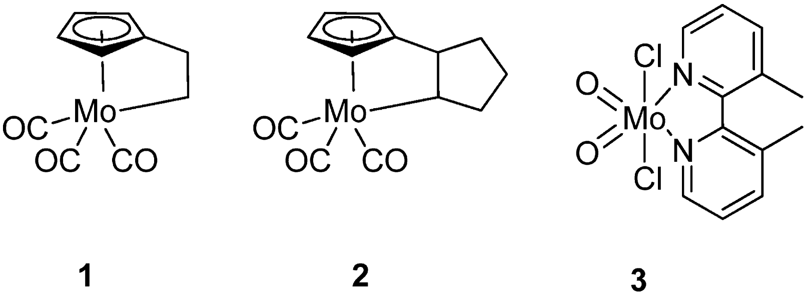
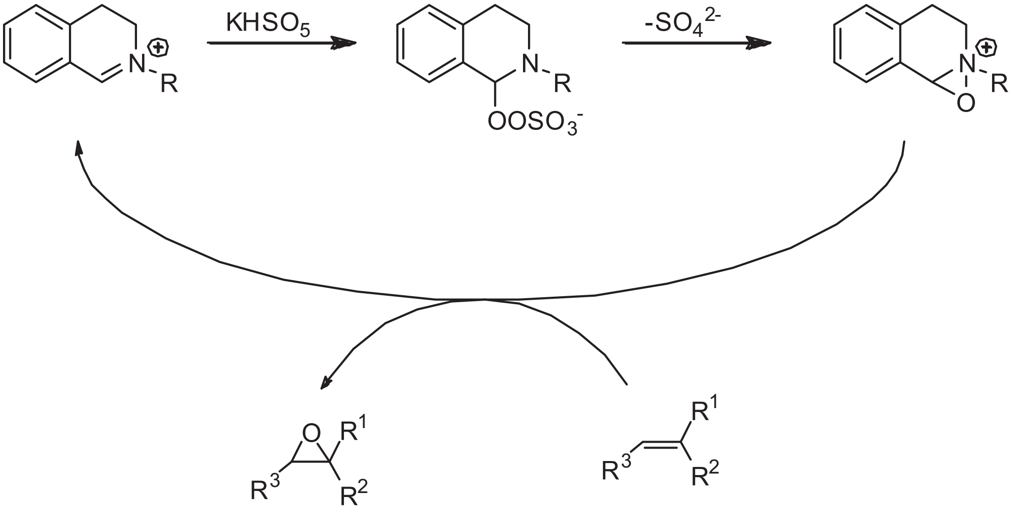


Fig. 6. The investigated Mo complexes.



Scheme 8. Olefin epoxidation without an involved metal-containing catalyst.

Table 15
Oxidation of oximes with Co-Pc/[bmim].Br at 70 °C.

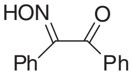
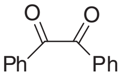
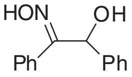
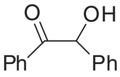
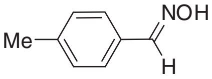
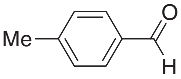
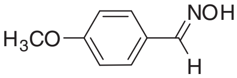
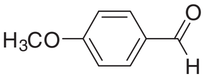
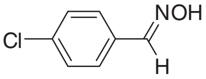
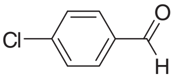
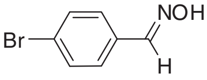
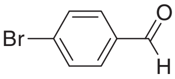
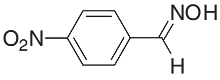
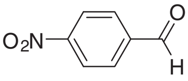
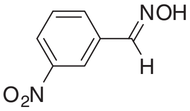
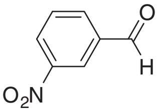
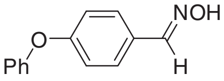
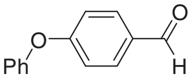
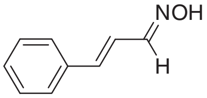
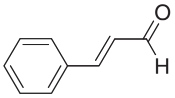
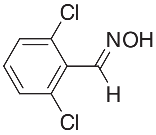
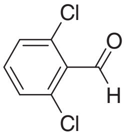
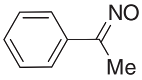
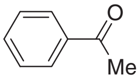
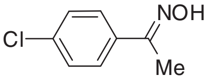
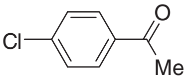
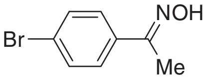
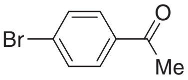
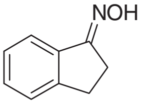
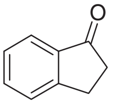
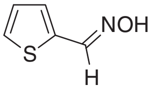
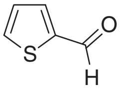
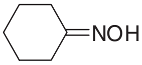
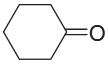
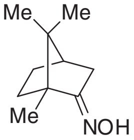
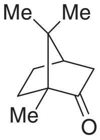
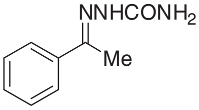
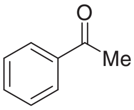
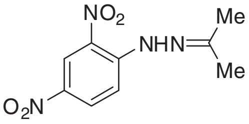
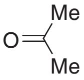
Entry	Educt	Product	Time (min)	Yield (%)
1			60	90, 88, 87
2			60	91
3			30	89
4			50	92
5			40	93
6			40	92
7			30	80
8			30	88
9			40	91
10			50	86
11			70	83
12			80	82
13			60	87
14			40	85
15			150	85
16			200	80
17			40	88

Table 15 (*Continued*)

Entry	Educt	Product	Time (min)	Yield (%)
18			180	70
19			4 days	87
20			4 days	70

The authors investigated different solvents, including ILs. They found a better solubility of the Mo(VI) complex in the more polar solvent [bmPy].BF_4 compared to [bmPy].PF_6 which led finally to a higher conversion of *trans*-β-methylstyrene in the polar solvent ([bmPy].BF_4: 31%; [bmPy].PF_6: 1% after 24 h). The selectivity was 100% when using an IL as solvent; only the desired epoxide was obtained. The recyclability of the systems containing [bmim].BF_4 or [bmPy].BF_4 was studied as well and they could find out that in contrast to [bmim].BF_4 the catalyst leaching out of the IL when using [bmPy].BF_4. Kühn et al. recently investigated three different Mo(VI) catalysts (Fig. 6) for the oxidation of cis-cyclooctene in ionic liquids [69,70].

In contrast to the most other studies, the catalytic test reactions were performed at room temperature. The best results were obtained using [bmim].NTf_2 as a solvent. With **1** and **2**, quantitative yields were obtained after 1 h and a concentration of 1 mol%. With a loading of catalyst **2** of 0.05 mol%, the turnover frequency reached an impressively high value of >44,000 h^{-1}. This is the highest value which has so far been reported for this type of reaction.

Recycling experiments led to only a minor loss of activity (80% at the 3rd run). Compound **3** gave a moderate yield of 43% after 24 h (1 mol%) and a TOF of around 110 h^{-1}. In addition a series of [$MoO_2X_2L_2$] (L = 4,4′-bis-methoxycarbonyl-2,2′-bipyridine, 5,5′-bis-methoxycarbonyl-2,2′-bipyridine, 4,4′-bis-ethoxycarbonyl-2,2′-bipyridine, 5,5′-bis-ethoxycarbonyl-2,2′-bipyridine; X = Cl) was investigated by the same group. The activity of the epoxidation of cis-cyclooctene with TBHP in different room-temperature ionic liquids was approximately four times higher compared with conventionally used dichloromethane [71].

Table 16
Catalytic epoxidation of olefins with [mdhqm].NTf_2.

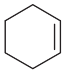
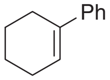
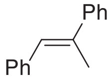
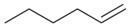
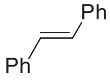
Entry	Educt	Conversion (%) (TON)	
		MeCN/H_2O (1:1)	[bmim].OTf/H_2O (1:1)
1		92 (19)	100 (20)
2		75 (15)	63 (13)
3		66 (13)	6 (1)
4		18 (4)	14 (3)
5		0	0

Table 17
Catalytic results of **4**–**6** in ILs.

Entry	Catalyst	Solvent	Selectivity (%)	Yield (%)	TOF (h^{-1})
1	**4** (1st run)	[bmPy].BF_4	54	67	97
2	**4** (2nd run)	[bmPy].BF_4	92	74	50
3	**5**	[bmPy].PF_6	50	22	52
4	**5** (1st run)	[bmPy].BF_4	83	74	57
5	**5** (2nd run)	[bmPy].BF_4	88	78	56
6	**6** (1st run)	[bmPy].BF_4	93	85	62
7	**6** (2nd run)	[bmPy].BF_4	94	86	31

Reaction conditions: substrate: cyclooctene, $T = 55\,^{\circ}C$, $t = 24$ h, oxidant: TBHP, 1 mol% catalyst.

Abrantes et al. used an amino acid-functionalised CpMo complex (Fig. 7) for the epoxidation of *trans*-β-methylstyrene in [bmim].BF_4 [72].The reaction was studied at room-temperature with a catalyst concentration of 1 mol%, TBHP as oxidant. The authors found that the catalyst was completely dissolved in the IL and the organic phase remained colorless during the whole reaction. However, they could not improve the ee, which was below 5% (independent from the solvent) and a quite low yield of 10% after 24 h was obtained, which is lower than in an aprotic solvent (77%). Pillinger and coworkers studied three different molybdenum compounds which are depicted in Fig. 8 [73].

The authors mentioned the poor solubility of complex **4** in the IL. This explains the lowest yield compared to catalysts **5** and **6** in the same solvent (see Table 17).

Interestingly, the authors stated that they found the same kinetic profile for **5** when using an aqueous TBHP solution. A comparison between the two runs reveals a loss in activity, which is probably due to the increasing concentration of *tert*-BuOH with time in the ionic liquid. In 2009, Wang and coworkers used $MoO(O_2)_2{\cdot}2QOH$ (QOH = 8-quinilinol) (Fig. 9) for the epoxidation of a technical mixture of methyl oleate and methyl linoleate in [bmim].BF_4, [Hydemim].BF_4, and [bmim].PF_6 [74].

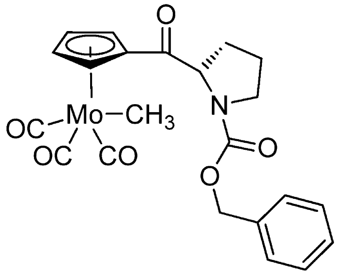
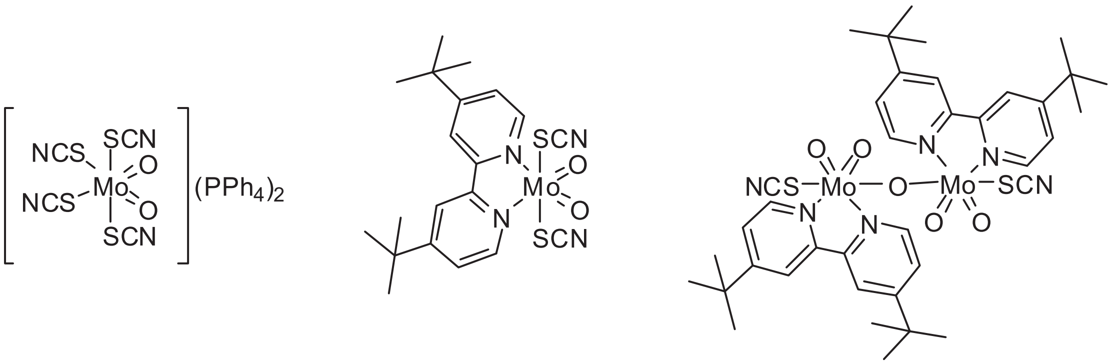


Fig. 7. Amino acid-functionalised CpMo complex.



4 **5** **6**

Fig. 8. Mo complexes used for the epoxidation of olefins by Pillinger et al.

Table 18
Epoxidation of methyl oleate and methyl linoleate catalysed by $MoO(O_2)_2 \cdot 2QOH$.

Entry	Solvent	Conversion (%)		Selectivity (%)	TON (TOF)
		Methyl oleate	Methyl linoleate		
1	No solvent	55	31	90	3690 (1845)
2	[bmim].BF_4	92	78	93	7812 (3906)
3	[bmim].PF_6	75	44	94	5358 (2679)
4	[Hydemim].BF_4	96	89	95	8740 (4370)
5	CH_3CN/30% CH_3CN	85	63	92	6624 (3312)
6	70% [Hydemim].BF_4	94	84	95	8360 (4180)
7	C_2H_5OH/30% C_2H_5OH	81	45	93	5580 (2790)
8	70% [Hydemim].BF_4	90	74	95	7695 (3848)

Reaction conditions: $T = 30\,^{\circ}C$, $t = 2$ h, oxidant: H_2O_2, 0.01 mol% catalyst, co-catalyst: $NaHCO_3$.

For the investigated substrate mixture, especially [bmim].BF_4 and [Hydemim].BF_4 showed high activities. Table 18 shows the conversions, selectivities and TOFs of the investigated ionic liquids.

The authors obtained the best results when using ILs with BF_4 counterions. The polar character of these species may play a key role in the epoxidation reaction. The positive effect concerning the activity of the catalyst was confirmed by the addition of [Hydemim].BF_4 to an organic solvent. Both the conversion and the selectivity to the corresponding epoxide increased. In addition, the catalytic system could be recycled for at least five runs (by washing with diethyl ether and drying) without any loss of selectivity and just a minor drop in conversion of methyl oleate (87%) and methyl linoleate (82%).

In 2010, Goncalves et al. described different cationic molybdenum(VI) dioxo complexes containing weakly coordinating anions for the cyclooctene epoxidation (Fig. 10) [75].

The catalysts were used at 55 °C in different solvents (DCE, [bmim].BF_4, [bmPy].BF_4, [bmim].PF_6 and [bmPy].PF_6). The performance with DCE as a solvent results in yields between 61% and 98% after 24 h with a selectivity of 100%. In all solvents complex **9** is less soluble than **7** and **8**, resulting in the lowest conversions.

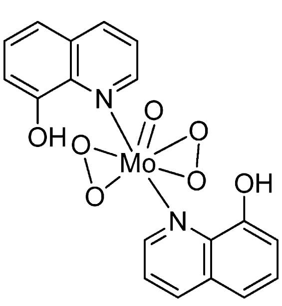
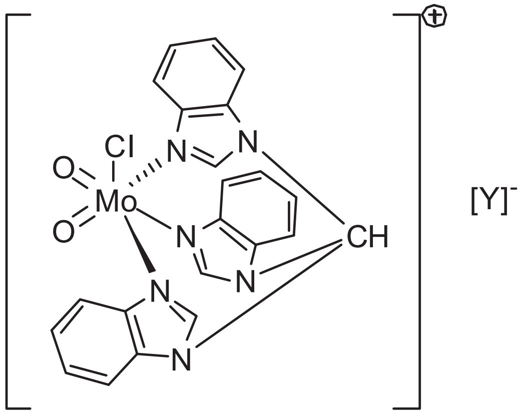


Fig. 9. Oxo-bisperoxo Mo catalyst.

In contrast to compound **9**, **7** could be completely dissolved in all ILs. Compound **8** was completely dissolved in the BF_4-type ILs, but was poorly soluble in PF_6-type ILs. The different solubility of the catalysts is obviously the most important factor concerning the activity. Table 19 shows the results of the catalytic reactions.

The authors stated that the reaction proceeds as a heterogeneous process, because the organic phase remained colorless, while the IL phase is yellow, because of the active species being formed. The authors additionally compared the results when using different oxidants in the oxidation of cyclooctene (Table 20).

In the case of water-free oxidants (TBHP in decane, UHP) the reactions are significantly faster, most presumably because of the coordinating properties of water which finally leads to a less active



Y = Cl (**7**), BF_4 (**8**), PF_6 (**9**)

Fig. 10. Cationic Mo-catalyst.

Table 19
Epoxidation of cyclooctene catalysed by **7**–**9**.

Solvent	Catalyst	Conversion (%)	TOF (h^{-1})
DCE	7	96	201
	8	98	168
	9	61	69
[bmim].BF_4	7	78	76
	8	75	91
	9	40	15
[bmPy].BF_4	7	80	64
	8	81	102
	9	40	15
[bmim].PF_6	7	91	142
	8	45	67
	9	42	22
[bmPy].PF_6	7	94	163
	8	51	73
	9	40	19

Table 20
Catalytic epoxidation of cyclooctene with **7** in [bmim].PF_6 using different oxidants.

Oxidant	Conversion (%)	TOF (h^{-1})
TBHP (decane)	91	142
TBHP (aq)	50	18
H_2O_2 (aq)	38	–
UHP	92	16

catalytic species. Interestingly, even when applying aqueous TBHP or H_2O_2 the authors did not observe any diol formation.

The catalytic system **7**/[bmim].PF_6/TBHP was finally used to investigate the epoxidation of different olefins. Cyclooctene gave the best results under the applied conditions (91%). It is followed by norbornene (55%), cyclohexene (37%) and styrene ≈α-pinene (15%).

Tsang et al. described the palladium-catalysed oxidation of styrene using different multicarboxylic acid appended imidazolium ILs (Fig. 11) as reaction medium [76].

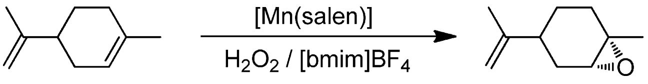
The treatment of the ionic liquids with the precatalyst $PdCl_2$, led to the formation of a species containing the $PdCl_4^{2-}$ or $PdCl_2Br_2^{2-}$ anion, which was shown to be an active catalyst of the selective catalytic oxidation of styrene to acetophenone with hydrogen peroxide as oxygen source. Compared with neat $PdCl_2$, the investigated system requires less $PdCl_2$ and is more active. The turnover frequency reached a maximum of 146 h^{-1}, a conversion of 100% with a selectivity of 93%. The same reaction without an IL led to a TOF of 21 h^{-1} with a conversion of 25% and a selectivity of 86% to acetophenone. Table 21 shows the results of the investigated systems.

After investigating all the possible combinations the authors found that the reaction temperature was the most important factor for the rate of the oxidation, independent of the nature of the cation and anions. A great advantage of the multicarboxylic acid containing ILs compared to [bmim].BF_4 is the possibility of reusing the catalytic system. With [bmim].BF_4, the selectivity decreased to <20% after the 3rd cycle. The catalyst could be recycled ten times without a loss of both activity and selectivity. The group of Lu studied an ionic manganese porphyrin catalyst, which is embedded in [bPy].BF_4 in the oxidation of different styrene derivatives. They found a good activity and recyclability compared to the neutral complex. The derivatives were converted into the corresponding epoxides in selectivities between 57% and 100% [77,78]. The asymmetric epoxidation of limonene was investigated by the group of Bernardo-Gusmão et al.. They used Jacobsens Mn(salen) catalyst and hydrogen peroxide as a oxygen source (Scheme 9).

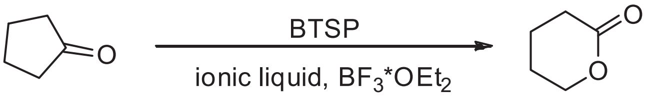
Table 21
Oxidation of styrene catalysed by $PdCl_2$/IL.

Entry	IL	Conversion (%)	Selectivity (%)	TOF (h^{-1})
1	–	25	86	21
2	10	100	93	146
3	11	84	92	116
4	12	80	92	92

Reaction conditions: $T = 55\,^{\circ}C$; catalyst concentration = 0.1 mol%.



Scheme 9. Oxidation of limonene catalysed by Jacobsens catalyst.



Scheme 10. Baeyer–Villiger reaction.

The catalytic procedure was performed in [bmim].BF_4 and resulted in a high diastereomeric excess of 74% to the respective 1,2-epoxi-*p*-ment-8-enes, while the conversion was 70% [79]. Also a Mn(salen) catalyst was used for the oxidation of styrene with molecular oxygen to benzaldehyde [80]. Besides studies of kinetics, reaction temperature and reaction pressure, three ionic liquids ([bmim].PF_6, [hmmim].CF_3COO and [bmim].BF_4) were tested as solvents in the oxidation [bmim].BF_4 turned out to be the best solvent in this reaction.

Another salen catalyst was investigated recently by Li and coworkers. They modified a Cu(salen) catalyst with an ionic pyridinium tag in the backbone of the salen-ligand. This complex was studied in the allylic oxidation of cyclohexene with molecular oxygen. The authors state that because of the highest nucleophilicity, Cu[salen-Py].X_2 with X = PF_4 showed the highest catalytic activity [81].

6. The Baeyer–Villiger reaction

In 2008 Slupska et al. reported the oxidation of various ketones with bis(trimethylsilyl)peroxide (BTSP) in ionic liquids (Scheme 10) [82]. The lactonisation of cyclopentanone was performed in an organic solvent (dichloromethane (DCM)) and in different ionic liquids to compare solvent influences (Table 22). These catalytic examinations were carried out with $BF_3{\cdot}OEt_2$ as acid catalyst (200 mol%), showing yields up to 20% higher yields in all used ionic liquids compared to dichloromethane. The lower yields of [bmim].HSO_4 and [bmim].BF_4 compared to the other ionic liquids were explained by the relatively fast decomposition of BTSP in these solvents. The necessity of adding an extra catalyst to the reaction mixture in order to obtain the desired product, together with the decomposition experiments, leads the authors to the conclusion

Table 22
Oxidation of cyclopentanone to δ-valerolactone.

Entry	Solvent	Catalyst	Yield (%)
1	[bmim].NTf_2	$BF_3{\cdot}OEt_2$	95
2	[bmim].HSO_4	$BF_3{\cdot}OEt_2$	80
3	[bmim].BF_4	$BF_3{\cdot}OEt_2$	78
4	[bmim].OTf	$BF_3{\cdot}OEt_2$	99
5	DCM	$BF_3{\cdot}OEt_2$	73
6	DCM	$AlCl_3$	55
7	DCM	$SnCl_3$	90
8	[bmim].NTf_2	$AlCl_3$	87
9	[bmim].NTf_2	$SnCl_3$	94

Reaction conditions: cyclopentanone (0.5 mmol), BTSP (1 mmol), catalyst (1 mmol), solvent (2 mL), reaction time: 5 h, r.t., yield determined by GC.

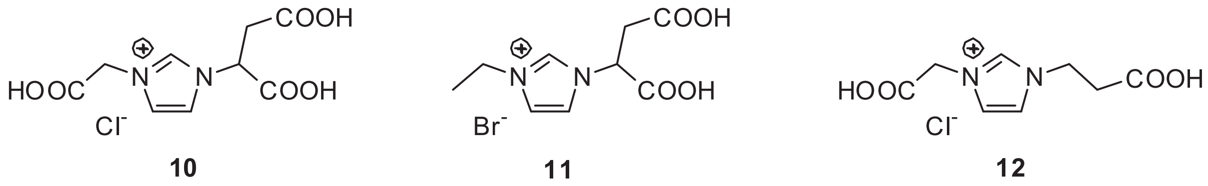


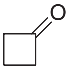
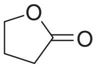
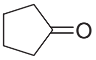
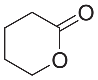
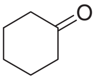
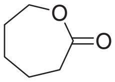
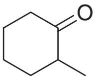
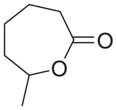
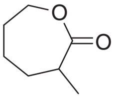
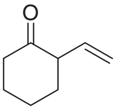
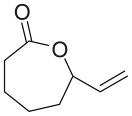
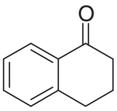
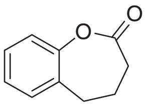
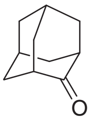
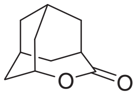
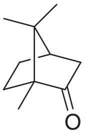
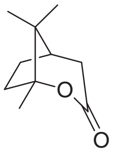
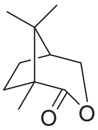
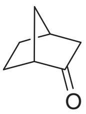
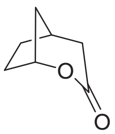
Fig. 11. Multicarboxylic acid containing ILs applied by Tsang et al.

that the rate of BTSP-decomposition is slower than the rate of the oxidation reaction only if a co-catalyst is present. The comparison of different catalysts ($BF_3{\cdot}OEt_2$, $AlCl_3$, $SnCl_3$) in [bmim].NTf_2 and dichloromethane leads to similar results for the ionic liquid, while the differences between the catalysts in dichloromethane are much more pronounced (Table 22).

The only catalyst free oxidation of cyclic ketones could be carried out in [bmim].OTf (Table 23). The reason for that is, due to the authors, the influence of the OTf^- anion. To proof their statement catalysis was successfully performed in dichloromethane together with NaOTf (Table 23). The proposed reaction mechanism is shown in Scheme 11.

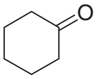
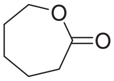
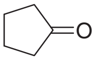
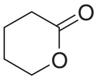
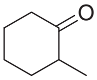
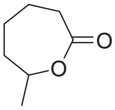
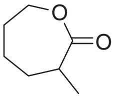
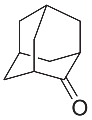
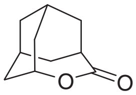
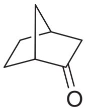
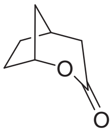
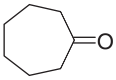
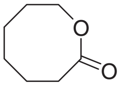
In further studies, Chrobok studied the Baeyer–Villiger reaction with molecular oxygen as an oxygen source in the presence of benzaldehyde [83], as this combination showed good results in previous examinations [84]. During this reaction benzaldehyde is converted to benzoic acid. The addition of a radial initiator such as 1,1′-azobis(cyclohexanecarbonitrile) (ACHN) increases the reaction rate of the lactonisation by a factor of four. The optimal concentration of ACHN was found to be 0.033 mol/L and the best substrate to benzaldehyde ratio was 1:2. The addition of Fe_2O_3 as a co-catalyst does not accelerate the reaction. The catalytic performance in different ionic liquids and with different substrates is summarised in Table 24.

Table 23
Oxidation of ketones in [bmim].OTf.

Entry	Ketone	Lactone	Time (h)	Temp. (°C)	Yield (%)
1			1	25	98
2			2	25	95
3			2	25	94
4		 	2	25	96
5			8	40	94
6			10	40	41
7			24	40	(87)
8		 	15	40	(89)
9			8	25	99

Reaction conditions: ketone (0.5 mmol), BTSP (1 mmol), [bmim].OTf (2 mL); yield determined by GC; isolated yields in parenthesis.

Table 24
Lactonisation of various ketones with oxygen.

Entry	Ketone	Lactone	Solvent	Time (h)	Conversion (%)	Yield lactone (%)
1			[bmp].NTf_2	2.5	95	89
2	:	:	[tmba].NTf_2	2.5	95	88
3	:	:	[bmim].BF_4	2.5	90	85
4	:	:	[emim].OSO_3Me	2.5	85	76
5	:	:	[bmim].CF_3COO	2.5	80	72
6	:	:	[bmim].OTf	2.5	62	55
7	:	:	[bmim].NTf_2	2.5	96	90
8			[bmim].NTf_2	2	99	85
9		 	[bmim].NTf_2	2	99	95
10			[bmim].NTf_2	4	100	96
11			[bmim].NTf_2	4	100	94
12			[bmim].NTf_2	10	49	40

Reaction conditions: ketone (3 mmol); benzaldehyde (6 mmol); ACHN (0.033 mol/L); solvent (2 mL); 90 °C; yields determined by GC.

The ionic liquids could be recovered via extraction methods after the reaction, this is possible, whether they are hydrophilic or hydrophobic. The same ionic liquids could be used for four runs without activity loss.

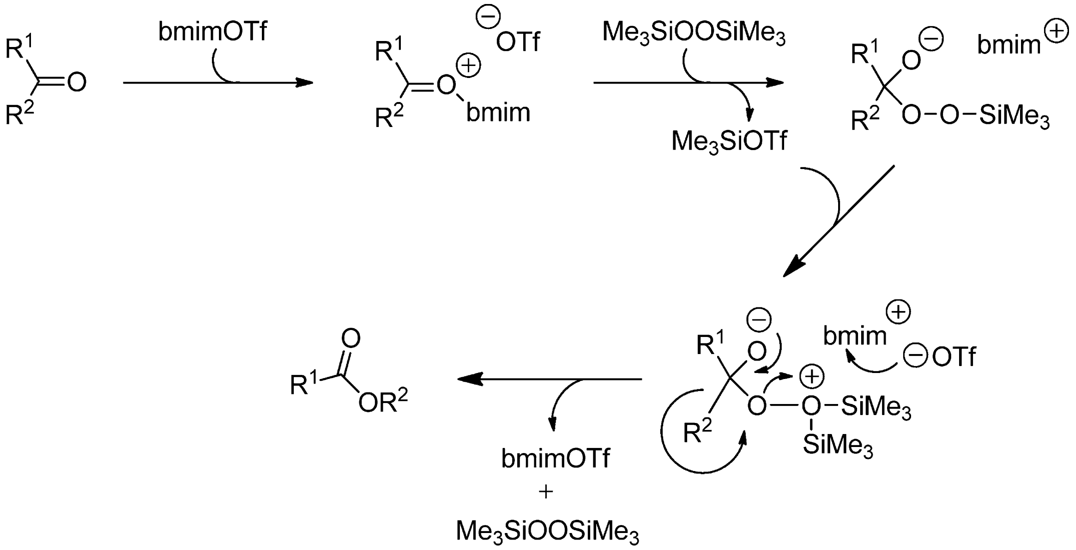
Another method to reuse ionic liquids is the heterogenisation of [pmim].HSO_4 on a silica support (Scheme 12) [85]. The tethering of the catalyst (HSO_4^-) is obtained via cation-anion interaction. The Baeyer–Villiger reaction was performed with H_2O_2 (68%) at 50 °C in dichloromethane as solvent, the data are given in Table 25.

Recycling experiments showed no loss of activity and 90% of the catalyst could be recovered after each of the four runs.

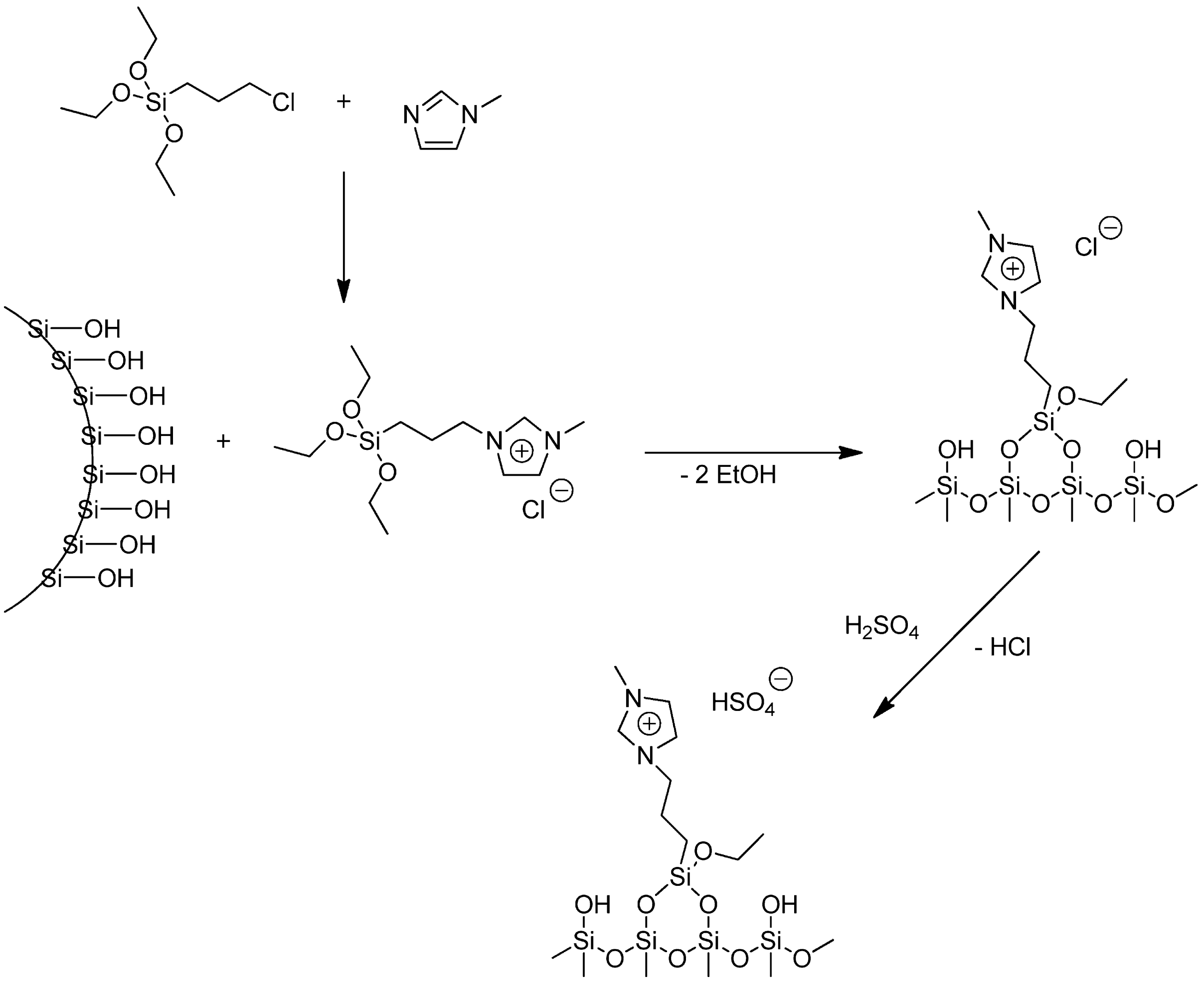
7. Special oxidations

7.1. Oxidation of nitrotoluene

The oxidation of nitrotoluene and derivatives to their corresponding nitrobenzoic acids with molecular oxygen in ionic liquids



Scheme 11. Proposed reaction mechanism of the Baeyer–Villiger oxidation of ketones by BTSP in the presence of [bmim].OTf.



Scheme 12. Heterogenisation of [pmim].HSO_4 on a silica support.

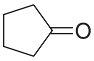
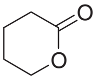
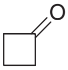
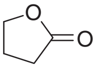
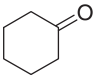
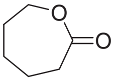
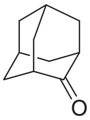
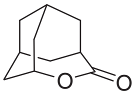
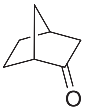
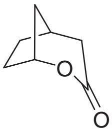
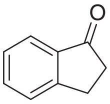
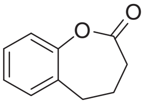
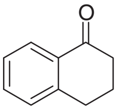
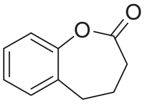
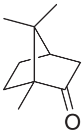
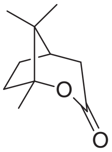
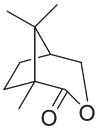
was first reported in 2009 [4]. Shan et al. performed the oxidation in a biphasic system containing an aqueous sodium hydroxide solution and different ionic liquids. As catalyst for the oxidation of *para*-nitrotoluene (PNT), different metallo-phthalocyanine complexes were tested (Table 26). The special behaviour of the chosen ionic liquid ([omim].BF_4), to be miscible with water at temperatures higher 70 °C and immiscible below, leads to an easy separation of product and catalyst. The reaction was performed at 90 °C in homogeneous phase. After cooling down the reaction mixture, the water and the ionic liquid phases separate, whereas the product is soluble only in the aqueous phase and catalyst and substrate in the ionic liquid. The catalyst was recycled by simple extraction methods and was reused for at least five more runs without loss of activity (Table 26, Entry 11: cat. used for 6 times). Other substrates used were *ortho*- (ONT), *meta*- (MNT), di-nitrotoluene (DNT) and toluene. As it can be seen from the data in Table 26, MNT and toluene show no activity due to their relatively low deprotonation ability in alkali aqueous solution which plays a major role in the reaction pathway towards benzoic acid [86]. The major role of NaOH can be seen in a decrease of the yield with decreasing NaOH concentration (compare Table 26, Entries 1 and 5).

7.2. Carbonylation

In 2008, ionic liquids were used as solvents for copper catalysed carbonylation of methanol to dimethyl carbonate (DMC) by Liu and coworkers [87]. Besides DMC, the main product, three other by-products were detected: dimethoxymethane (DMM), dimethylether (DME) and methylformate. Amongst these byproducts, DME reaches normally the highest yields. The different ionic liquids and catalysts as well as the space-time yield (STY), conversion and selectivities are listed in Table 27. The catalysis was usually performed with 1 mmol catalyst, 4 g MeOH, 2 g ionic liquid and 2.4 MPa CO and O_2 (ratio 2:1) at room temperature. A model system containing 1 mmol CuCl, 4 g MeOH, 2 g [bPy].BF_4 and 2.4 MPa CO/O_2 (ratio 2:1) at 120 °C was chosen to study different reaction parameters. After 4 h the conversion of MeOH stopped and no differences regarding selectivity were observed. Higher gas pressures (from 2.4 MPa to 6.0 MPa) of CO and O_2 lead to higher conversions of MeOH (from 19.8% to 37.1%) while the selectivity of DMC remained stable at nearly 100%. With temperatures higher than 120 °C, higher conversions could be reached, however, the selectivity of DMC also decreases. An increase of the ratio of CO to O_2 hampers the reaction more instead of increasing the selectivity of DMC.

In 2010, Stricker et al. inserted the copper catalyst directly into the ionic liquid [88]. They prepared three different types of catalysts, tetrakis(1-dodecylimidazole)copper(I)hexafluorophosphate $[Cu(Im^{12})_4][PF_6]$, bis(1-dodecylimidazole)cuproniumdihalogenocuprate $[Cu(Im^{12})_2][CuX_2]$ and $[dmim]._n[CuX_{2n}]$ for the carbonylation of methanol. With the applied conditions, the catalysis showed better conversions and similar selectivities compared to the results of Liu and coworkers (Table 28).

Table 25
Baeyer–Villiger reaction with different ketones and a heterogenised ionic liquid.

Entry	Ketone	Lactone	H_2O_2 (mol/mol ketone)	Catalyst (g)	Time (h)	Conversion (%)	Yield (%)
1			3	–	8	31	6
2	:	:	3	0.4 (silica support)	8	30	5
3	:	:	2	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	8	86	60
4	:	:	3	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	5	75	55
5	:	:	3	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	8	98	75
6	:	:	3	0.2 (pmimHSO$_{4\mathrm{SiO}_2}$)	8	60	45
7	:	:	3	0.6 (pmimHSO$_{4\mathrm{SiO}_2}$)	8	98	74
8	:	:	4	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	8	98	65
9	:	:	3	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	8	30	6
10	:	:	3	0.8 (tbapHSO$_{4\mathrm{SiO2}}$)	8	95	72
11			3	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	5	100	96
12			3	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	15	86	64
13			3	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	10	95	(89)
14			3	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	10	95	(88)
15			3	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	15	81	(75)
16			3	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	20	78	(74)
17		 	3	0.4 (pmimHSO$_{4\mathrm{SiO}_2}$)	20	64	60

Reaction conditions: ketone (1 mmol); H_2O_2 (68%); dry DCM (2 mL); 50 °C; yield determined by GC; isolated yields in parentheses.

Table 26
Oxidation of nitrotoluenes by molecular oxygen.

Entry	Substrate	Ionic liquid	Catalyst (mg)	NaOH (g)	P(O_2) (MPa)	Yield (%)
1	PNT	[omim].BF_4	Fe^{II}Pc; 10	1.5	2	92
2	PNT	[omim].BF_4	Fe^{III}Pc; 10	1.5	2	89
3	PNT	[omim].BF_4	Cu^{II}Pc; 10	1.5	2	70
4	PNT	[omim].BF_4	Fe^{II}Pc; 5	1.5	2	85
5	PNT	[omim].BF_4	Fe^{II}Pc; 10	1	2	70
6	PNT	[omim].BF_4	Fe^{II}Pc; 10	1.5	2.5	93
7	PNT	[omim].BF_4	Fe^{II}Pc; 10	1.5	1.5	84
8	PNT	[omim].Tf_2N	Fe^{II}Pc; 10	1.5	2	13
9	PNT	[dmim].BF_4	Fe^{II}Pc; 10	1.5	2	72
10	PNT	–	Fe^{II}Pc; 10	1.5	2	–
11	PNT	[omim].BF_4	Fe^{II}Pc; 10	1.5	2	92
12	ONT	[omim].BF_4	Fe^{II}Pc; 10	1.5	2	93
13	MNT	[omim].BF_4	Fe^{II}Pc; 10	1.5	2	–
14	DNT	[omim].BF_4	Fe^{II}Pc; 10	1.5	2	93
15	Toluene	[omim].BF_4	Fe^{II}Pc; 10	1.5	2	–

Reaction conditions: 0.2 mmol substrate; 10 mL ionic liquid; 5 mL water; 90 °C; 12 h.

Table 27
Oxidative carbonylation of methanol.

Entry	Catalyst	Ionic liquid	Conversion (%)	Selectivity of DMC (%)	Selectivity of DMM (%)	Selectivity of DME (%)	STY (g(DMC)/g(cat)h)
1	CuCl	–	9	97.3	2.8	–	2.3
2	CuCl	[bPy].BF_4	17	97.8	2.3	–	4.6
3	CuCl	[oPy].BF_4	17	98.3	1.8	–	4.6
4	CuCl	[bdmim].BF_4	14	99.2	0	–	3.8
5	CuCl	[bPy].Cl	14	87	0	9.7	3.5
6	CuCl	[bmim].Cl	4	70.3	5.3	25.8	0.8
7	CuCl	[emim].BF_4	7	81.2	5.3	14.5	1.5
8	CuCl	[omim].BF_4	9	93.5	2.4	4.5	2.3
9	CuCl	[bPy].PF_6	5	32.4	9.1	58.5	0.5
10	CuCl	[omim].PF_6	8	53.2	5.5	43	1.2
11	CuCl	[bdmim].PF_6	7	51.6	5	45	1
12	$CuCl_2 \cdot 2H_2O$	–	15	93.3	5.4	–	2.2
13	$CuCl_2 \cdot 2H_2O$	[bPy].BF_4	17	99.1	1	–	2.6
14	$CuBr_2$	–	11	90.1	9.2	1.3	1.2
15	$CuBr_2$	[bPy].BF_4	17	97.1	0.5	2.6	1.9
16	CuBr	–	9	96.9	3.4	–	1.6
17	CuBr	[bPy].BF_4	17	96.3	3.2	0.8	3.1
18	CuI	–	1	78.5	22.6	–	0.1
19	CuI	[bPy].BF_4	11	96.2	–	–	1.5

Reaction conditions: 1 mmol Cu catalyst; 4.0 g methanol; 2.0 g ionic liquid; 2.4 MPa; P(CO)/P(O_2) = 2:1; T = 120 °C; t = 2 h.

Table 28
Synthesis of DMC.

Entry	Catalyst	Conversion (%)	Selectivity (%)
1	$[Cu(Im^{12})_4][PF_6]$	31	58
2	$[Cu(Im^{12})_2][CuCl_2]$	60	83
3	$[Cu(Im^{12})_2][CuBr_2]$	62	89
4	$[CuCl + 4\,Im^{12}]$	48	78
5	$[CuCl + 4\,Im^{1}]$	45	73

Reaction conditions: 5 mol% Cu (total); MeOH (30 mmol); P(O_2) (3 bar); P(CO) (50 bar); 4 h; 120 °C.

Another carbonylation was carried out by Ma et al. who synthesised methyl phenyl carbamte (MPC) from aniline [89]. With an immobilised catalyst consisting of selenium and [bmim].BF_4 on mesoporous silica conversions higher than 74% were obtained. The selectivity was 99% and the catalyst could be reused for four times without loss in activity.

7.3. Oxidation of cysteine

In 2010, Shan et al. reported the catalytic oxidation of cysteine to cystine with iron-, and copper-phthalocyanine complexes in the presence of molecular oxygen in the ionic liquid [hmim].BF_4 (Scheme 13) [5].

The yields of cystine in dependence of different catalyst types and concentrations as well as of varying oxygen pressure are given in Table 29. The iron(II) catalyst showed the best performance and oxygen pressure above 2 MPa leads to increase of activity. This is presumably a consequence of a limited solubility of oxygen in ionic liquids. Without ionic liquids, the reaction gave only 13% yield, demonstrating the effect of this reaction medium.

Table 29
Oxidation of cysteine to cystine.

Entry	Ionic liquid (g)	Catalyst (mg)	P(O_2) (MPa)	Yield (%)
1	[hmim].BF_4 (1)	$Fe^{II}Pc$ (10)	2	98
2	[hmim].BF_4 (1)	$Fe^{III}Pc$ (10)	2	89
3	[hmim].BF_4 (1)	$Cu^{II}Pc$ (10)	2	82
4	[hmim].BF_4 (1)	$Fe^{II}Pc$ (15)	2	98
5	[hmim].BF_4 (1)	$Fe^{II}Pc$ (5)	2	70
6	[hmim].BF_4 (1)	$Fe^{II}Pc$ (10)	2.5	98
7	[hmim].BF_4 (1)	$Fe^{II}Pc$ (10)	1.5	84
8	[hmim].Tf_2N (1)	$Fe^{II}Pc$ (10)	2	23
9	[dmim].BF_4 (1)	$Fe^{II}Pc$ (10)	2	32
10	–	$Fe^{II}Pc$ (10)	2	14
11	[hmim].BF_4 (1)	$Fe^{II}Pc$ (10)	2	96

Reaction conditions: cysteine (2 mmol); water (4 mL); T = 80 °C; t = 12 h.

The catalysts were recycled by making use of the temperature dependent miscibility of ionic liquids with water (compare Section 7.1). The miscibility at temperatures higher 80 °C leads to a homogeneous phase of aqueous solution and ionic liquid in which the catalysis took place. After cooling down the phases separated and the educt remained in the water phase while the catalyst is in the ionic liquid phase. The solid product was filtered off. The sixth catalytic run (Table 29, Entry 11) showed almost the same activity as the first one (Table 29, Entry 1).

7.4. Oxidation of cyclohexane

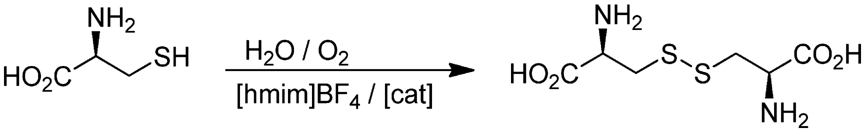
The oxidation of cyclohexane with metal-containing zeolits was studied by Wang et al. using TS-1 (titanium silicate) and various ZSM-5 zeolits [90,91].

The oxidation was carried out with TBHP as oxidant because H_2O_2 leads to low conversions (Table 30). The yield displays a

Table 30
Oxidation of cyclohexane.

Entry	Catalyst	Solvent	Time (h)	Conversion (%)	Yield (%)
1	TS-1	Acetone	24	3.62	2.81
2	TS-1	–	24	1.25	1.26
3	TS-1	[emim].BF_4	6	6.77	6.77
4	TS-1	[emim].BF_4	12	10.5	10.29
5	TS-1	[emim].BF_4	18	13.2	12.88
6	TS-1	[emim].BF_4	24	13.0	12.63
7	HZSM-5	–	12	0.98	0.98
8	HZSM-5	Acetone	12	3.29	2.46
9	FeZSM-5	Acetone	12	3.81	2.98
10	HZSM-5	[emim].BF_4	12	15.8	15.32
11	NiZSM-5	[emim].BF_4	12	15.9	15.44
12	CoZSM-5	[emim].BF_4	12	14.2	14.06
13	MnZSM-5	[emim].BF_4	12	15.5	15.13
14	FeZSM-5	[emim].BF_4	12	20.9	20.52
15	CuZSM-5	[emim].BF_4	12	9.5	9.5

Reaction conditions: 0.15 g catalyst; 27.8 mmol cyclohexane; 55.6 mmol TBHP (80% in H_2O); 5 mL ionic liquid; 90 °C.



Scheme 13. Oxidation of cysteine to cystine.

Table 31
Oxidation of halides in ionic liquids.

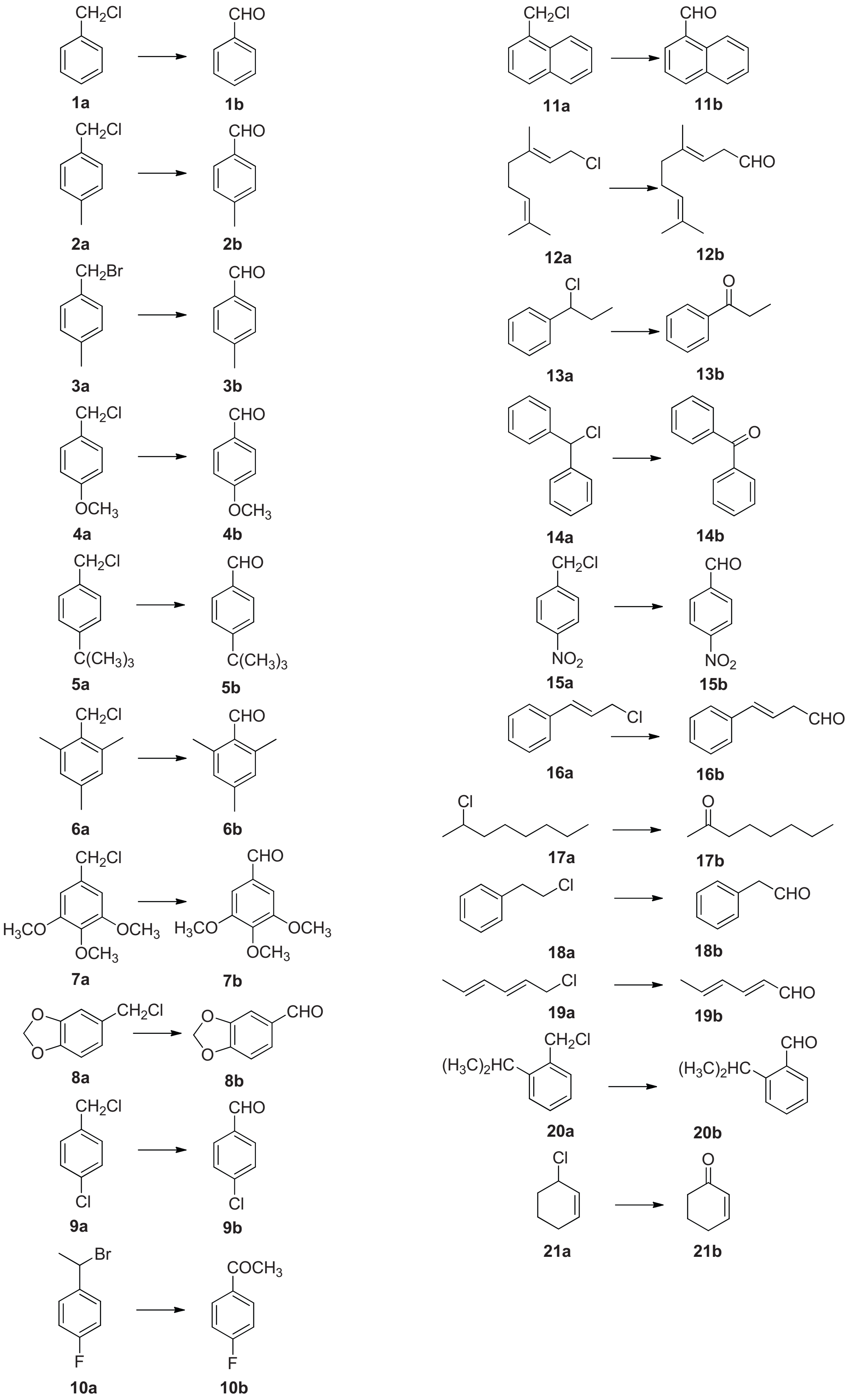
Entry	Ionic liquid	Product	Time (h)	Yield (%)
1	–	**1b**	4	42
2	[bmim][$FeCl_4$]	**1b**	2	75
3	[hmim][$FeCl_4$]	**1b**	2	78
4	[omim][$FeCl_4$]	**1b**	2	83
5	[dmim][$FeCl_4$]	**1b**	2	91
6	[C_{12}mim][$FeCl_4$]	**1b**	2	94
7	[C_{12}mim][$FeCl_4$]	**2b**	1.5	93
8	[C_{12}mim][$FeCl_4$]	**3b**	1.5	93
9	[C_{12}mim][$FeCl_4$]	**4b**	1.5	95
10	[C_{12}mim][$FeCl_4$]	**5b**	1.5	96
11	[C_{12}mim][$FeCl_4$]	**6b**	1.5	98
12	[C_{12}mim][$FeCl_4$]	**7b**	1.5	98
13	[C_{12}mim][$FeCl_4$]	**8b**	1.5	95
14	[C_{12}mim][$FeCl_4$]	**9b**	2	92
15	[C_{12}mim][$FeCl_4$]	**10b**	2.5	91
16	[C_{12}mim][$FeCl_4$]	**11b**	1.5	97
17	[C_{12}mim][$FeCl_4$]	**12b**	2	96
18	[C_{12}mim][$FeCl_4$]	**13b**	2	93
19	[C_{12}mim][$FeCl_4$]	**14b**	2.5	95
20	[C_{12}mim][$FeCl_4$]	**15b**	2.5	90
21	[C_{12}mim][$FeCl_4$]	**16b**	2	94
22	[C_{12}mim][$FeCl_4$]	**17b**	3	88
23	[C_{12}mim][$FeCl_4$]	**18b**	3	90

Reaction conditions: organic halide (10 mmol); H_5IO_6 (11 mmol); 30 °C; ionic liquid (0.4 mmol).

Table 32
Oxidation of organic halides with H_5IO_6/V_2O_5.

Entry	Catalyst	Ionic liquid	Product	Time (h)	Yield (%)
1	V_2O_5	–	**2b**	10	53
2	–	[bmpy].PF_6	**2b**	6	48
3	V_2O_5	[bmim].BF_4	**2b**	7	74
4	V_2O_5	[bmim].Cl	**2b**	8	68
5	V_2O_5	[hmim].OTf	**2b**	6	76
6	V_2O_5	[hmim].PF_6	**2b**	6	83
7	V_2O_5	[bpy].PF_6	**2b**	3	89
8	V_2O_5	[bmpy].PF_6	**2b**	3	97
9	V_2O_5	[bmpy].PF_6	**1b**	3	92
10	V_2O_5	[bmpy].PF_6	**3b**	5	93
11	V_2O_5	[bmpy].PF_6	**4b**	3	98
12	V_2O_5	[bmpy].PF_6	**5b**	3	96
13	V_2O_5	[bmpy].PF_6	**6b**	3	98
14	V_2O_5	[bmpy].PF_6	**7b**	3	99
15	V_2O_5	[bmpy].PF_6	**8b**	3	96
16	V_2O_5	[bmpy].PF_6	**9b**	6	89
17	V_2O_5	[bmpy].PF_6	**10b**	8	87
18	V_2O_5	[bmpy].PF_6	**11b**	3	96
19	V_2O_5	[bmpy].PF_6	**12b**	3	93
20	V_2O_5	[bmpy].PF_6	**13b**	6	91
21	V_2O_5	[bmpy].PF_6	**14b**	6	94
22	V_2O_5	[bmpy].PF_6	**15b**	10	87
23	V_2O_5	[bmpy].PF_6	**16b**	3	92
24	V_2O_5	[bmpy].PF_6	**17b**	24	63
25	V_2O_5	[bmpy].PF_6	**18b**	24	75
26	V_2O_5	[bmpy].PF_6	**19b**	3	90
27	V_2O_5	[bmpy].PF_6	**20b**	3	95
28	V_2O_5	[bmpy].PF_6	**21b**	6	89

Reaction conditions: organic halide (10 mmol); V_2O_5 (0.3 mmol); H_5IO_6 (12 mmol); ionic liquid (5 mL); 50 °C.



Scheme 14. Oxidation of various halides.

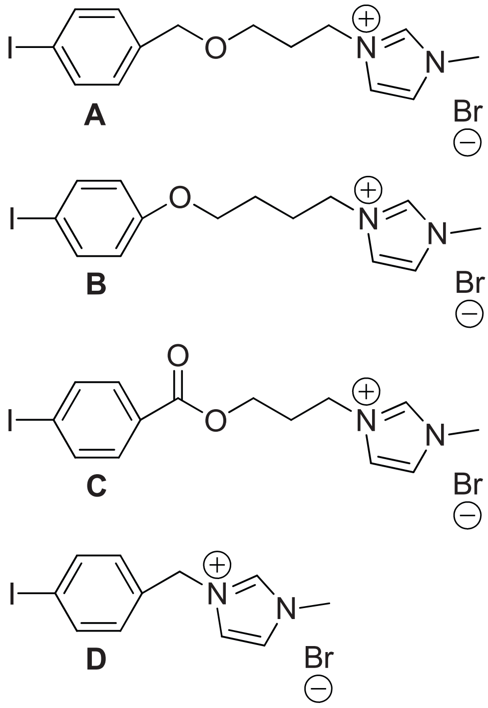


Fig. 12. IL-supported PhI **A**–**D**.

mixture of cyclohexanol, cyclohexanone and with ZSM-5 catalysts cyclohexyl hydroperoxide (CHHP). Temperature screenings revealed 90 °C as the optimal temperature and the best ratio of substrate and oxidant was found to be 1:2. Iron turned out to be the most active metal for the oxidation of cyclohexane and recycling of the catalyst by decantation lead to no decrease in activity after four runs.

7.5. Oxidation of halides

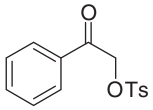
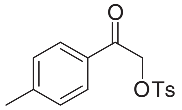
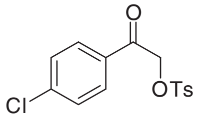
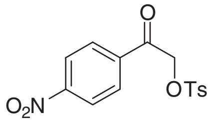
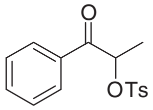
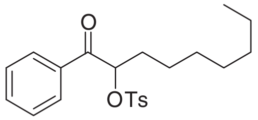
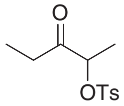
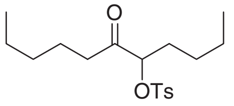
The oxidation of halides to ketones and aldehydes with H_5IO_6 proceeded better if ionic liquids were doted to the reaction mixture (Table 31) [92]. Further studies dealt with V_2O_5 as catalyst in ionic liquids (Table 32) [93]. The different oxidised species for both ways are shown in Scheme 14.

7.6. α-Tosyloxilation of ketones

The oxidation of various ketones was carried out in [emim].OTs as solvent as well as small amounts of IL-supported PhI **A**–**D** (Fig. 12) together with *m*-chloroperbenzoic acid (MCPBA) and *p*-toluenesulfonic acid (PTSA·H_2O) [94].

The different products and yields are summarised in Table 33. After extraction of the products and oxidants the ionic liquids were reused twice with small losses in activity.

Table 33
Tosyloxidation of ketones.

Entry	Product	Yields (%)			
		A	B	C	D
1		82	83	80	70
2		60	58	39	48
3		77	76	67	67
4		65	70	72	71
5[a]		83	75	63	70
6[a]		81	75	52	56
7		57	64	61	69
8		57	66	62	53

Reaction conditions: substrate (1 mmol); MCPBA (1.3 equiv.); PTSA·H_2O (1.1 equiv.); A, B, C or D (0.1 equiv.); [emim].OTs (2 mL); 50 °C; 5 h.

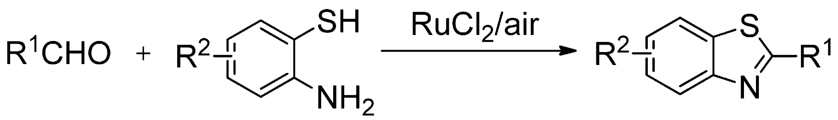
[a] PTSA·H_2O (0.5 equiv.).

7.7. Synthesis of thiazoles

Additionally to tosyloxylation the condensation of acetophenone and thioamides to thiazoles was studied by Akiike et al. Applying the same conditions as used in the tosyloxilation, yields between 37% and 72% were reached [94].

Wang et al. studied the oxidative reaction of 2-aminothiophenol and aldehydes to thiazoles with air as oxidant (Scheme 15) [95].

The experimental data is summarised in Table 34. Extraction of the ionic liquid with diethyl ether and reuse of the IL for three times lead only to a slight decrease of yield. Moreover, the authors applied their catalytic procedure to synthesise 5-heteroaryl-substituted-2′-deoxyuridines.



Scheme 15. Oxidative condensation towards thiazoles.

Table 34
Thiazole formation.

Entry	R^1	R^2	Solvent	Catalyst (0.05 equiv.)	Time (h)	Temp. (°C)	Yield (%)
1	C_6H_5	H	THF	$RuCl_3$	3	Reflux	68
2	C_6H_5	H	CH_3CN	$RuCl_3$	3	Reflux	62
3	C_6H_5	H	Toluene	$RuCl_3$	3	80	50
4	C_6H_5	H	dichloromethane	$RuCl_3$	3	Reflux	61
5	C_6H_5	H	[bmim].PF_6	–	3	80	Trace
6	C_6H_5	H	:	$InCl_3$	2	80	Trace
7	C_6H_5	H	:	$CeCl_3$	2	80	Trace
8	C_6H_5	H	[bmim].BF_4	$RuCl_3$	0.5	80	75
9	C_6H_5	H	[bmmim].PF_6	:	:	80	63
10	C_6H_5	H	[bmim].PF_6	:	:	60	78
11	C_6H_5	H	:	:	:	80	83
12	4-BrC_6H_4	H	:	:	:	:	85
13	4-CH_3 OC_6H_4	H	:	:	:	:	80
14	4-CNC_6H_4	H	:	:	:	:	85
15	2-BrC_6H_4	H	:	:	1	:	81
16	2-$NO_2C_6H_4$	H	:	:	0.5	:	82
17	2-ClC_6H_4	H	:	:	1	:	81
18	3-$NO_2C_6H_4$	H	:	:	0.5	:	86
19	3-BrC_6H_4	H	:	:	:	:	84
20	3-$CH_3C_6H_4$	H	:	:	:	:	79
21	C_6H_5	4-Cl	:	:	:	:	83
22	4-$NO_2C_6H_4$	4-Cl	:	:	:	:	88
23	4-BrC_6H_4	4-Cl	:	:	:	:	83
24	4-CH_3 OC_6H_4	4-Cl	:	:	:	:	82
25	3-ClC_6H_4	4-Cl	:	:	:	:	83
26	3-BrC_6H_4	4-Cl	:	:	:	:	80
27	2-$NO_2C_6H_4$	4-Cl	:	:	:	:	80
28	2-ClC_6H_4	4-Cl	:	:	1	:	80
29	2-BrC_6H_4	4-Cl	:	:	1	:	79
30	N-propyl	H	:	:	2	:	75
31	N-propyl	4-Cl	:	:	2	:	76
32	C_6H_5	3-Cl	:	:	4	:	62
33	4-$NO_2C_6H_4$	3-Cl	:	:	3	:	75
34	3-$CH_3C_6H_4$	3-Cl	:	:	4	:	60
35	2-$NO_2C_6H_4$	3-Cl	:	:	6	:	43
36	4-BrC_6H_4	4-CH_3	:	:	2	:	80
37	3-$CH_3C_6H_4$	4-CH_3	:	:	2	:	78

Reaction conditions: starting materials (1 mmol); solvent (1 mL).

8. Conclusion and perspective

Clearly, ionic liquids attract more and more attention in many fields of catalytic applications. This broadening attractivity ranges from well examined reactions, like the oxidative desulfurisation of organic compounds, to more uncommon reactions, e.g. the oxidation of oximes. In any case, ionic liquids are usually able to improve the performance of the catalytic reaction. They could therefore certainly act as substitutes for conventional organic solvents, in some cases even as “catalysts” themselves or as extraction media for the separation of products. The transfer of ionic liquids from lab-scale application to industrial processes would be desirable especially from the “green” chemical point of view and will probably happen in the future due to their significant advantages as well. Particularly the recycling of the catalytic system might play a key role with regard to sustainability, provided IL are environmentally neutral or benign.

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Glossary of ionic liquids

[emim].: 1-Ethyl-3-methylimidazolium.
[bmim].: 1-Butyl-3-methylimidazolium.
[omim].: 1-Octyl-3-methylimidazolium.
[dmim].: 1-n-Decyl-3-methylimidazolium.
[C_{12}mim].: 1-n-Dodecyl-3-methylimidazolium.
[pmim].: 1-Methyl-3-(triethoxysilylpropyl)imidazolium.
[hmim].: 1-n-Hexyl-3-methylimidazolium.
[bdmim].: 1-Butyl-2,3-dimethylimidazolium.
[Hydemim].: 1-(2-Hydroxy-ethyl)-3-methylimidazolium.
[bPy].: N-butyl-pyridinium.
[bmPy].: N-butyl-3-methylpyridinium.
[oPy].: 1-Octyl-pyridinium.
[hnmp].: N-methyl-pyrrolidonium.
[mdhqm].: 2-Methyl-3,4-dihydroisoquinolinium.
[tbap].: Tributylpropylammonium.
[tmba].: Trimethylbutylammonium.