Ionic liquid assisted olefin reactions

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ABSTRACT

In this review article the authors studied the ionic liquid assisted various alkene reactions with various metal complex catalysts such as Isomerization, Hydrogenation, Hydroformylation, Metathesis-Oligomerization, Dimerization, Arylation, Cyclization, Polymerization, Epoxidation, Michael addition and Tandem Cross-coupling reactions.

Keywords: Ionic liquids, alkene reactions, Metal complexes, Nano catalysts, olefin reactions

1. INTRODUCTION

Ionic liquids are ionic compounds (salts) which are exists liquid state below 100 °C. Generally, ionic liquids melts below room temperature. They contain cation, anionic components and possess coulomb interactions. In 1914, the first ionic liquid was introduced [EtNH₃][NO₃], melts at 12 °C.

Then huge developments reported about the ionic liquids and Now-a-days this is most important in green synthesis. They possess stability and functionality. The physical properties such as viscosity, surface tension and melting points are associated with cations and the oxygen
balance, density and high energy content ion are depends on the anion. Some ionic liquids are immiscible with water and organic reagents.

They possess characteristic properties such as Thermal and chemical stability, low melting point, high ionic conductivity, affinity-solubility with many compounds, negligible volatility, flame retardancy, moderate viscosity and high polarity. A small variation of ion structure is favorable to ion conductive materials for electrochemical devices, solvents for chemical reaction and bioscience. The melting points of the ionic liquids are depending upon the size of the ions. They exist as irreversible proportions.

If the cation and anion size are small, the melting points of the ionic liquid is high on the other hand large size of the ions possess low melting points. Based on the above characters this is very useful for conducting the various chemical reactions especially greener methods. In bio science, they are used as extraction and dissolution of polysaccharides from biomass, hydrolysis of polysaccharides into mono-, di-, or oligo-saccharide and Conversion of chemical energy, involving the resulting sugars, into electric energy. Supported Ionic Liquid Phase (SILP) also useful for conducting the chemical reactions.

They are supported by combines the homogeneous or heterogeneous catalyst and proceed the reaction. The Homogeneity is difficulty, expensive, poor and excellent. On the other hand, the heterogeneity is easy cheap and good. Since the last decades, chemists and scientists paid much more attention in the ionic liquids assisted organic synthesis. Ionic liquid plays an important role in green synthesis instead of organic volatile solvents due to its infinite level vapour pressure and better solubility for other substances. Numerous reactions such as additions, substitutions, condensation and polymerization were successfully performed with good yields in ionic media. In this chapter the author desalts the reactions of alkenes performed in ionic liquids.

The reactions are Isomerization, Hydrogenation, Hydroformylation, Metathesis-Oligomerization, Dimerization, Arylation, Cyclization, Polymerization, Epoxidation, Michael addition and Tandem Cross-coupling reactions.

2. DISCUSSION
2.1. Alkene Isomerization in ionic liquids

Bo et al., have successfully carried out the alkene isomerization in ionic liquid with Ruthenium catalyst, RuCl₃⋅3H₂O:[Bmim]PF₆. They demonstrated [1-4] that the isomerization of various 3-aryl substituted-1-preopenes by the stirring of the alkenes, catalyst and ionic liquid in methanol medium at 80 °C for 8 or 12 h (Scheme 1). The conversion rate is up to 100% and the obtained yield was up to 94%.

2.2. Hydrogenation

Palladium nano catalyst [5-7] assisted hydrogenation of multiple bonds was performed in ionic liquid. This reaction is used for conversion of olefin to be saturated, diene to ene, acetylenic to ethylene and an α, β-unsaturated carbonyl compounds into carbonyl compounds with good yields (Scheme 2). The catalyst was recyclable.
Scheme 1. Ruthenium catalyst assisted isomerization of ally systems in presence of ionic liquid.

Scheme 2. Hydrogenation of alkenes by palladium nano scale catalyst under ionic liquid medium.
2. 3. Hydroformylation

Transformation of ethylene to proanaldehyde by Pt-catalyzed hydroformylation (Scheme 3) in [Et₄N][SnCl₃] ionic liquid medium was reported by Parshall et al. [10].

\[
\begin{align*}
&\text{PtCl}_2 \\
&[\text{NEt}_4][\text{SnCl}_3] \\
&90 \, ^\circ \text{C}, 400 \text{ bar CO/H}_2
\end{align*}
\]

Scheme 3. Hydroformylation of alkenes by stannic chloride catalyst under ionic liquid medium.

Knifton [11] used [Bu₄P]Br ionic liquid for hydroformylation of different olefins with ruthenium- and cobalt-catalyst. The cobalt catalyst [Co(Py₆)²⁺][Co(CO)₄]²⁻ and [PyH⁺][Co(CO)₄]⁻ with ionic liquids assisted hydroformylation of alkenes (Scheme 4) were reported by Magna et al. [12].

![Scheme 4. Rhodium catalyzed hydroformylation of alkenes in presence of ionic liquid.](image)

2. 4. Metathesis of olefins

The ring opening metathesis polymerization (ROMP) under biphasic conditions using a nonpolar organic solvent (toluene) and the ionic liquid (IL) 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [BDMIM⁺][BF₄⁻] in the presence of novel dicationic catalyst [(RuCl₂(H₂ITapMe₂) (=CH–2(2-PrO)-C₆H₄))²⁺ (OTf⁻)₂] (Ru-2, H₂ITapMe₂ = 1,3-bis(2',6'-dimethyl-4’-trimethylammoniumphenyl)-4,5-dihydroimidazol-2-ylidene, OTf⁻ = CF₃SO₃⁻) based on a dicationic N-heterocyclic carbene was studied by Koy et al. [13].

The quantum chemical calculations to establish the factors favoring the metathesis of olefin in ionic liquid. From the calculations the effects of conventional and ionic liquids on the metathesis of olefin have been investigated.

The results of the quantum chemical calculations suggested that ionic liquids stabilizes olefin and the catalyst better than the conventional solvents. The activation energy is lowered and alkyledene intermediate was fastly formed. The equilibrium constant is lower for ionic liquids and it suggests that somewhat less product yields.

Ring closure metathesis reaction was important for cyclic ester synthesis. Thomas et al. have synthesized some cyclic bister using Hoveyda-type catalyst in 1-isopentyl-3-methylimidazole hexafluorophosphate [Mipolmecuimles] ionic liquid. Dimethyl diallyl malonate was subjected to RCM in [bmim][NTf₂] under mild reaction conditions (Scheme 5) gave cyclic biester [14].
Scheme 5. Ring closure metathesis of dimethyl diallyl malonate in [bmim][NTf₂].

Ruthenium imidazolium tagged catalyst also shows excellent activity for the ring closure metathesis of N, N-diallyltosylamide (Scheme 6) in the presence of [bdmim][PF₆] resulting in the formation of cyclic olefin [15]. But the catalyst was not cyclable. The same was reported by Audic et al. [16].

Scheme 6. Ring closure metathesis of N, N-diallyltosylamide in [bdmim][PF₆].

Oligomerization is important reaction in petroleum product industries. It is used for enhancing the quantity of gasoline contents of hydrogenated species from butane and isobutene. They are used as additives for gasoline and diesels. This oligomerization of unsaturated compounds was carried out with Imidazolium ionic liquids immobilized with silica gel [17] (IL 1-4) as illustrated in Fig. 1. These ionic liquids assist the selectivity of the oligomerization reaction products of C₈ or C₁₂⁺ species. And the yields are more than 90%.

Figure 1. Imidazolium silica immobilized ionic liquids.
An alkene 1-pentene was oligomerized using Lewis acidic chlorogallate(III) ionic liquid, 1-ethyl-3-methylimidazolium heptachlorodigallate(III), \([\text{C}_2\text{mim}][\text{Ga}_2\text{Cl}_7]\) in chemometric conditions [18]. This process was employed for lubricant based oils production species having C\(_{20}\)-C\(_{50}\).

2.5. Olefin to dimerization reactions

Dimerization of butene over the \([\text{Ni(MeCN)}_6][\text{BF}_4]_2\) catalyst [19], yields the dimers usually contain dimethyl hexene (39 ±1%), monomethylheptene (56 ±2%), and \(n\)-octene (6 ±1%) and the process, does not depend on the addition of phosphine ligands (Scheme 7). But-1- and 2-enes gave the same distribution of the dimer fraction, and the linear dimer always is formed only in an amount of no more than 6%:

![Scheme 7. Olefin dimerization](image)

Propylene dimerization in the chloroaluminate IL medium based on 1-buthyl-3-methylimidazolium chloride ([bmim][AlCl_4]), the so-called nickel process [20-24], has been developed (Scheme 8). In this reaction the obtained mixture of dimers contains 2,3-dimethylbutenes as the main component (83%) [25].

![Scheme 8. Olefine dimerization to propylene](image)

2.6. Arylation of alkenes in ionic liquid media

Ionic liquid 1-Butyl-3-methylimidizolium tetrafluoroborate, ([bmim][BF_4]) is a good media for Palladium catalysed regioselective Heck arylation of electron rich alkenes, enamides and aryl methyl silanes. This reaction performed with remarkable regioselective efficiency without need for any other toxic halide scavengers for substitution of aryl group to the carbon-carbon double bond systems. This experiment provides a simple, effective for synthesis of branched arylated olefins to the extension of Heck arylation. This ionic liquid reaction offers more than 80% yields. The Palladium catalyzed Heck arylation of butyl vinyl ethers using...
various aryl bromides in [bmim][BF₄] ionic liquid followed by acidification gave aryl methyl ketones [26-31]. These are summarized in the Scheme 9.

![Scheme 9](image)

<table>
<thead>
<tr>
<th>R</th>
<th>Yield (%)</th>
<th>R</th>
<th>Yield (%)</th>
<th>R</th>
<th>Yield (%)</th>
</tr>
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<td>4-Me</td>
<td>88</td>
<td>3-Me</td>
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</tr>
<tr>
<td>4-F</td>
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<td>3-CHO</td>
<td>81</td>
<td>1-Naphthyl</td>
<td>95</td>
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<tr>
<td>4-H</td>
<td>97</td>
<td>3-F</td>
<td>83</td>
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</tbody>
</table>


The Palladium catalyzed Heck arylation of butyl vinyl ethers using various aryl iodides in [bmim][BF₄] ionic liquid and on acidification gave more than 90% yield of aryl methyl ketones [32-36] were summarized in the Scheme 10.

![Scheme 10](image)

<table>
<thead>
<tr>
<th>R</th>
<th>Yield (%)</th>
<th>R</th>
<th>Yield (%)</th>
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<tr>
<td>4-CHO</td>
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<td>4-Me</td>
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<td>4-OMe</td>
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<td>91</td>
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<tr>
<td>4-COMe</td>
<td>96</td>
<td>1-Naphthyl</td>
<td>94</td>
</tr>
</tbody>
</table>

The Palladium catalyzed Heck arylation of butyl vinyl ethers using various aryl halides [31, 37-39] in [bmim][BF₄] ionic liquid followed by acidification gave more than 90% yield of substituted aryl methyl ketones and are summarized in the Scheme 11. In this reaction 100% conversion observed.

\[
\text{[bmim][BF}_4\text{]} \quad \text{115°C}
\]

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>Yield (%)</th>
<th>R</th>
<th>X</th>
<th>Yield (%)</th>
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<td>4-CN</td>
<td>Br</td>
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<td>Br</td>
<td>94</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

**Scheme 11.** The palladium catalyzed Heck arylation of vinyl ethers with aryl halides in [bmim][BF₄] ionic liquid medium.

The above said palladium Heck arylation methodology was applicable for enamides with aryl bromides [31, 40, 41] followed the same conditions, they yield more than 70% of aryl substituted enamines and are given in the Scheme 12.

\[
\text{DMSO} \quad \text{115°C}
\]

<table>
<thead>
<tr>
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<th>R₂</th>
<th>Yield (%)</th>
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<td>83</td>
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<td>Me</td>
<td>80</td>
<td>4-Me</td>
<td></td>
<td></td>
<td>73</td>
</tr>
</tbody>
</table>
The same ionic liquid [bmim][BF₄] media was applied for Palladium catalyzed Heck arylation of allyltrimethylsilane [33, 44] by aryl halides gave various aryl substituted allyl trimethyl silanes. The observed yield is more than 65% and are summarized as Scheme 13.

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>Yield (%)</th>
<th>R</th>
<th>X</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-CHO</td>
<td>Br</td>
<td>82</td>
<td>4-I</td>
<td>Br</td>
<td>89</td>
</tr>
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<td>93</td>
<td>4-Me</td>
<td>I</td>
<td>89</td>
</tr>
<tr>
<td>4-COOME</td>
<td>Br</td>
<td>85</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Scheme 12.** Heck arylation of some olefins.

<table>
<thead>
<tr>
<th>4-H</th>
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<th>Me</th>
<th>82</th>
<th>2-Naphthyl</th>
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<tbody>
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<td>2-F</td>
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<td>Me</td>
<td>74</td>
<td>4-H</td>
<td>76</td>
</tr>
<tr>
<td>1-Naphthyl</td>
<td>Me</td>
<td>Me</td>
<td>86</td>
<td>2-Naphthyl</td>
<td>71</td>
</tr>
<tr>
<td>4-COCH₃</td>
<td></td>
<td></td>
<td>83</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Scheme 13.** Palladium catalysed Heck arylation of allyltrimethylsilane by aryl halides in [bmim][BF₄] ionic liquid media.
Deshmukh et al. [43] have studied the Heck arylation of olefins by the reaction of iodobenzenes and alkenes in the presence of Palladium nano-scale catalyst under ultrasonication in ionic liquid media (Scheme 14). In this method, the observed yields of the arylated alkenes are more than 73%.

Scheme 14. Heck reaction of substituted iodo benzenes and alkenes in imidazolium-based ionic liquids at 30 ºC under ultrasonic conditions.

Zhao and his co-workers [44-46], Calo, et al. [47, 48] Cui et al. [49] utilized the Stille reaction for the synthesis of aryl styrene’s. They have synthesized up to 65% yields of some arylated olefins from the reactions of aryl halides and tributylvinylstannane (Scheme 15) in the presence of Pd-nanoscale catalyst in ionic liquid at 80 ºC.

Scheme 15. Stille reaction of aryl halides with tributylvinylstannane catalyzed by Pd-NPs in ionic liquid media.

The application of Sonogashira reaction in ionic liquid media is useful for the synthesis of arylated alkenes. Gao et al. [50] and Croma et al. [51, 52] have synthesized up to 99% yields of some olefinated acetophenones (Scheme 16) from the reactions of halogenated acetophenones and phenyl acetylene in the presence of Pd-nano wire catalyst in ionic liquid media at high temperatures.

The Mizoroki–Heck protocol is important for synthesis of arylated alkenes [53]. Aryl and alkenyl sulfonyl chlorides can be used in Heck–Mizoroki type couplings with mono- and disubstituted olefins in a nitrile-functionalized ionic liquid, viz. [C3CNpy][Tf2N]. Dubbaka et al. [53] have synthesized some arylated olefins using Heck–Mizoroki protocol by the reaction
of alkenes and aryl sulfonyl chlorides (Scheme 17) in the presence of Pd catalyst in ionic liquid media at high temperature. In this reaction they observed yields are 35-90%.

Scheme 16. Sonogashira reaction catalyzed by Pd-nanowires catalyzed olefins in imidazolium ionic liquids (BMI.PF$_6$ and BM$_2$I·PF$_6$).

Scheme 17. Palladium-Catalyzed Desulfitative Mizoroki–Heck-Type Reactions of substituted Sulfonyl Chlorides with Alkenes in ionic liquid.

2. 7. Cyclization reaction of alkenes

Ethanol buffered chloroaluminate ionic liquid used for cyclization [54] of 1-dodecene to cyclododecane with high selectivity, especially under moderate pressure. In this reaction, easy separation of product due to the immiscibility with ionic liquids (Scheme 17)
2.8. Alkene polymerization in ionic liquids

The carbon monoxide and olefin co-polymerization process [55, 56] was carried out in presence of Palladium catalyst under ionic liquid medium. This polymerization was important, and the resulting polymers have many advantages such as new high density, industrial engineering polymers, including Carilon and Kadel, high thermal and wear resistance, and excellent mechanical properties. This co-polymerization was performed with olefin and CO in solution under moderate pressure of CO, using homogeneous cationic transition metal catalyst [Pd(dppp)2][PF6]2 [dppp = 1,3-bis(diphenyl-phosphino)propane]. Styrene and CO were subjected to copolymerization gave the copolymer in ionic liquid media (Scheme 18).

![Scheme 18. Polymerization of styrene and CO in presence of ionic liquid.](image)

2.9. Epoxidation and oxidation

Ionic liquids are also useful for conducting the epoxidation of alkenes. Lentini and his co-workers [5] reported the regioselective epoxidation of styrenes with hydrogen peroxide and the catalyst as bioinspired ion complex with a pyridyl triazacyclononane ligand (Fig. 2) in the various ionic liquids (Fig. 3) medium instead of acetonitrile. In this study they used various Imidazolium, pyrimidine based ionic liquids. In this reaction they observed 0-100% product depends on the nature of ionic liquid.
The epoxidation reaction was shown in Scheme 19.

![Scheme 19](image)

\( R = H \ (2a), \ Me \ (2b) \)

**Figure 2.** Bioinspired manganese and iron complexes with a pyridyl triazacyclononane ligand.

![Image](image)

**Figure 3.** Imidazolium and Pyrimidine based ionic liquids.

**Scheme 19.** Epoxidation of styrene with hydrogen peroxide in ionic liquid.

These catalysts were insoluble in both the substrate, water and soluble in aqueous H\(_2\)O\(_2\) solution, performed to perrhenate-H\(_2\)O\(_2\) interactions. Remarkable, solubility of substrate in water also enhances the reactions and it is dependent on the cation design.
Hence, the Imidazolium perrhenates enable both the transfer of hydrophobic substrate into the aqueous phase, and serve as actual catalysts, which is unprecedented. At the end of the reaction and in absence of H$_2$O$_2$ the ionic liquids catalyst forms a third phase next to the lipophilic product and water and can easily be recycled. Based on the above facts cyclooctene was converted to cyclooctane epoxide in the presence of above ionic liquid catalysts from 4 to after 24 h (Scheme 20).

Scheme 20. Conversion of cyclooctene after 4 and 24 h reaction time using catalysts 1–12.

Radical mechanism was excluded for the ionic liquid involved epoxidation in CH$_3$CN solvent. Holbrey et al. [55] studied the catalytic activity of [$\gamma$-SiW$_{10}$O$_{36}$(PhPO)$_2$] 4-polyanions in Ionic Liquids: This catalyst was used the oxidation of cyclooctene by the “Green” Solvent Catalytic Oxidations with Hydrogen Peroxide with the hydrophobic ionic liquid ([bmim][PF$_6$] or hydrophilic IL [bmim][(CF$_3$SO$_2$)$_2$N]).

The catalyst activity is high due to the high yield and selectivity for epoxidation of olefins under microwave irradiation in the hydrophilic ionic liquid (Scheme 21).

Liu et al. [56] investigated the role of [bmim][PF$_6$] ionic liquid as an activator for efficient olefin epoxidation with H$_2$O$_2$ catalyzed by Keggin polyoxometalate [bmim]$_3$PW$_{12}$O$_{40}$ (Scheme 22). In the ionic liquid, the interaction of ions created a special microenvironment, speeding up the generation of the active peroxytungstate ([PO$_4$WO(O$_2$)$_2$$_4$]$_3$ species from
[bmim]$_3$PW$_{12}$O$_{40}$ and H$_2$O$_2$. In some sense, the [bmim] [PF$_6$] ionic liquid could be a co-catalyst and it promote the formation of active species for epoxidation.

\[ \text{[\gamma-SiW_{10}O_{36}(PhPO)_2]}^{4-} \stackrel{\text{aq. H}_2\text{O}_2, \text{ionic liquid}}{\longrightarrow} \]

$[X^\cdot] = [\text{BF}_4^-][\text{CF}_3\text{SO}_3^-]$ and $[\text{PF}_6^-][(\text{CFSO})\text{N}^-]$

**Scheme 21.** Epoxidation of cis-Cyclooctene with H$_2$O$_2$ and polyoxometalates in both hydrophilic and hydrophobic ionic liquids.

\[ \text{[bmim]}_3\text{PW}_{12}\text{O}_{40}/[\text{bmim}][\text{PF}_6^-] \]

**Scheme 22.** Epoxidation of olefins with H$_2$O$_2$ and polyoxometalates in [bmim] [PF$_6^-$] ionic liquid.

Liu and Xia [57] describes the epoxidation of some alkenes in ionic liquids using manganese(III) porphyrin 1, (meso-tetrakis(pentafluoro phenyl) porphinato) manganese(III) chloride, for the epoxidation of alkenes such as styrene, cyclohexene, cyclooctene, heptane, indene and 1,2-dihydro naphthalene’s with PhI(OAc)$_2$ in a [bmim]PF$_6$/CH$_2$Cl$_2$ mixture at room temperature (Scheme 23). In these reactions they observed more than 80% conversion and up to 95% of products.

Liu [56, 57] synthesized novel Ni$^{2+}$ containing 1-methyl-3-[(triethoxysilyl)propyl] imidazolium chloride (TMICl) ionic liquid immobilized on silica and it is applied for catalytic oxidation of styrene to benzaldehyde with H$_2$O$_2$ under solvent-free condition (Scheme 24).

With the assist ed. of ionic liquid, water attractants and repellent reactant were accessible to the active sites of hydrophobic natured imidazolium-based ionic liquids. This catalyzed the epoxidation of unfunctionalized olefins in water using hydrogen peroxide as oxidant.
Scheme 23. Epoxidation of alkenes by Mn(III) porphyrin (meso-tetrakis(pentafluoro phenyl) porphinato) manganese(III) chloride, with PhI(OAc)₂ in a [bmim]PF₆/CH₂Cl₂ mixture.

Scheme 24. Oxidation of styrene to benzaldehyde with H₂O₂ under solvent-free condition in the presence of IMM-TMICl-Ni (II) catalyst by grafting Ni²⁺ on ionic liquid in Silica. [53]

Epoxidation reactions of C=C double bonds are of very much interest for the synthesis of bio organic substrates such as pharmaceuticals, flavor & fragrance molecules [58]. Many metal complexes were utilized as catalysts for epoxidation. Chemists found the highly active methyltrioxorhenium (MTO), several other Re (VII), Ti (IV), V(III), Mo(VI) and Mn(III) complexes are suitable catalysts for olefin epoxidations [59]. Numerous catalysts based on molybdenum and tungsten have been extensively studied and employed in asymmetric epoxidation catalysis [60]. Complexes of the type [MoO₂X₂L₂] (L = Lewis base) and [Cp'Mo(CO)₃Cl] can easily be transformed to catalytically active oxo-peroxo species for olefin epoxidation with tert-butyl hydroperoxide (TBHP) [61]. [Cp'Mo(CO)₃R] (R = alkyl) complexes show a catalytic activity comparable to their chloro analogues [62].
Among this class of compounds, Bets et al. exploring ansa complexes of the general type \([\text{Mo}(\eta^5-C_5H_4(CH(CH_2)n)-\eta^1-\text{CH})(\text{CO})_3]\) as epoxidation catalysts [63-66]. The tungsten ansa-complexes with cyclopentyl moieties and exceptionally stable bridging units and performed first studies of these compounds as epoxidation catalysts [63f]. Bets et al. report the remarkable activity of ansa-bridged Mo(VI) complexes for the epoxidation of different olefins in room temperature ionic liquids (RTIL) as solvents. Due to their high stability towards oxidation, imidazolium salt type RTILs are employed [67, 68]. In the last decade, a plethora of catalytic reactions has been performed in RTILs as reaction media [69].

The unique physical properties of RTILs such as low volatility, low flash point, thermal stability and high polarity are an attractive alternative to organic solvents [67]. Inorganic or organometallic complexes which are insoluble in hydrocarbons are often soluble in RTILs. Ionic liquids therefore provide a non-aqueous version of two-phase catalysis, in which the catalyst is dissolved in the ionic liquid phase and can be easily separated from the product. Less than a decade ago, Song and Roh were the first to report the asymmetric epoxidation in an ionic liquid catalyzed by a manganese (III) salen complex [70]. Ever since, RTILs have been successfully applied as reaction media for olefin epoxidation, e.g. with Fe(III) porphyrin complexes, inorganic dioxo molybdenum (VI) systems, or methyltrioxorhenium (MTO) as catalyst, where the activity in RTILs is also higher than in conventional solvents or under solvent-free conditions [71].

The catalytic activities of \([\text{Cp'Mo(CO)}_3R]\) compounds (Cp’ = Cp, Cp*; R = Cl, Me) have as well been investigated in RTILs. Among all examined catalysts, the best epoxide yields are obtained with \([\text{bmim}]\text{NTf}_2\) as the RTIL (bmim = 1-butyl-3-methylimidazolium), as shown by both Valente et al. and our group [71f, 72]. The RTILs \([\text{bmim}]\text{PF}_6\), \([\text{omim}]\text{PF}_6\), \([\text{bmim}]\text{NTf}_2\) and \([\text{bmim}]\text{BF}_4\) were prepared and purified as described in the literature [67, 68].

2. 9. 1. Olefin epoxidation with perrhenate catalysts

For a long time, it was believed that methyltrioxorhenium is only catalytically active in olefin epoxidation when hydrogen peroxide was used as oxidant. In 1993, Herrmann et al. reported that organic peroxides, such as tert-butyl hydroperoxide (TBHP), lead to deactivation of MTO [73]. In this work, this study was revisited. First, the reaction of MTO and TBHP was investigated by means of \(^{17}\text{O}\) labeling experiments, B\(_3\)LYP calculations and extensive catalytic studies. Besides the well-known MTO/H\(_2\)O\(_2\) system, the activity of MTO using TBHP as an oxidizing agent was investigated. The catalysis was performed at room temperature with an MTO: \(\text{cis}\)-cyclooctene: TBHP ratio of 1:100:200 and different ionic liquids as solvents. They are; \([\text{bmim}]\text{BF}_4\), \([\text{bmim}]\text{PF}_6\), \([\text{omim}]\text{PF}_6\), \([\text{bmim}]\text{NTf}_2\) and \([\text{bmim}]\text{BF}_4\). Highly soluble dichloro, dibromo and dimethyl dioxo molybdenum(VI)-bipyridine complexes as catalysts for the epoxidation of olefins.

2. 9. 2. Catalytic epoxidation of \(\text{cis}\)-cyclooctene

The epoxidation of cyclooctene using TBHP as oxidant in the presence of complexes 1-11 at 55 ℃ yields cyclooctene oxide as the only product. Two series of experiments with different molar ratio of catalyst: substrate: oxidant (1:100:150 and 1:1000:1500) were undertaken in order to compare the catalytic potential of the systems. The details of the catalytic reactions are given in the experimental section. Control experiments confirm that epoxidation does not take place in the absence of catalyst. The time-dependent curves obtained for
compounds 1-11 are typical for [MoO₂X₂L₂]-type complexes used as epoxidation catalysts with TBHP. [74, 75] Initially the reaction is fast, indicating that the active oxidizing species are formed rapidly after addition of the peroxide to the reaction medium. Progressively, the reaction rate decreases, when the reaction is nearly complete, due to an increasing lack of substrate (Figure 4).

![Complexes](image)

**Figure 4.** Complexes used for epoxidation.

All examined compounds show high catalytic activity. Only complexes 5 and 6 show an induction period. Compounds 5 and 6 dissolves very slowly after addition of TBHP leading to a slow reaction in the beginning, whereas the other complexes dissolve immediately. After the catalyst has totally dissolved, the reaction is fast in all cases. The activities of the examined catalysts are in the range of 1600-2000 and yields 95 % within 30 min. These results differ from literature data where the halide complexes, particularly the –Cl compounds, were found to be significantly more active (for cyclooctene epoxidation) than the methyl derivatives under reaction conditions identical to those used in the present work [74c, 75, 76]. In the light of the results presented here it can be assumed that these lower activities of the -CH₃ complexes are mainly due to solubility problems. Furthermore, in some cases the TOFs have been calculated differently (not at the steepest slope of the olefin epoxide formation curves), the reported numbers can therefore be regarded as ‘lower limits’ not as realistic turnover frequencies. When changing the catalyst: substrate: oxidant ratio from 1:100:150 to 1:1000:1500, the activities lower except for complex 8. In the latter case the TOF increases slightly from 1970 h⁻¹ to 2310 h⁻¹. It appears that optimal activities for the system have been reached when applying a 1:100:150 catalyst:substrate:oxidant ratio. Lowering the reaction temperature to 25 ºC also lowers the
activity. In the case of compound 3, the TOF decreases from ca. 1884 h⁻¹ (at 55 °C) to ca. 230 h⁻¹ (at 25 °C)

2.9.3. Catalytic epoxidation of cis-cyclooctene with RTILs as solvents

The chloride-containing complexes are investigated additionally in RTILs ([bmim]PF₆, [omim]PF₆, [bmim]NTf₂ and [bmim]BF₄) as solvents. In contrast to the catalysis without an additional solvent this catalysis was performed at room temperature and with a catalyst: substrate: oxidant ratio from 1:1000:1500. The catalyst was dissolved in the RTIL and this solution was added to the reaction solution. Since the catalytically active Mo(VI) species are water-sensitive, the activity of the system depends on the water-content of the ionic liquid. [bmim]NTf₂ has the lowest water-content of all the investigated RTILs [76, 77], leading to the highest activity in this solvent. The TOFs in [bmim]NTf₂ are considerably higher than the TOF under solvent free conditions.

2.9.4. Epoxidation of Alkenes MTO

The use of aromatic N-donor ligands in significant excess (ca.10–12:1) together with MTO leads to higher activities and selectivity’s in epoxidation catalysis than with MTO alone [78]. This behavior is displayed both with mono- and bidentate aromatic Lewis bases with N-donor ligands [79]. In the meantime, many N-ligand adducts of MTO have been isolated, characterized and applied for the epoxidation of olefins as catalysts [80]. Other donor adducts of MTO, despite being mentioned sporadically in the literature, have never been examined to the same extent with respect to their applicability as epoxidation catalysts [81]. Rhenium complexes with Schiff-base ligands derived from salicylaldehyde and mono- or diamines have received attention due to their applications in catalysis and nuclear medicine. Re(V) oxo complexes bearing Schiff-base ligands have been investigated extensively. [82] Kühn et al. described the following Schiff-base adducts of MTO (Scheme 25) and applied them as epoxidation catalysts [83].

Scheme 25. Schiff’s base adducts of MTO.

2.9.5. Epoxidation of α-pinene in ionic liquids

MTO (0.024 mmol) and t-butylpyridine (5 equiv.) were dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆) (0.2 mL). In a separate flask, mesitylene (100 µL), ethylbenzene (100 µL) and α-pinene (100 equiv.) were mixed together and a blank sample was taken from this solution. UHP or aqueous H₂O₂ (300 equiv.) was then
added to the ionic liquid followed by the solution of α-pinene. The sampling time is the same as for conventional solvents. At defined times, 41 μL of the organic phase was poured in a vial containing MnO₂ in order to destroy excess oxidant, dried over MgSO₄ and filtered. 2 mL of CH₂Cl₂ were then added and the sample was analyzed by GC. This condition was applied to the epoxidation of α-pinene. However, the formation of α-pinene diol was observed. From this observation it was deduced that α-pinene oxide appears to be more acid sensitive than cyclooctene oxide, being easily transformed to α-pinene diol in the presence of MTO and water (Scheme 26).

Scheme 26. Reaction from α-pinene to α-pinene diol in presence of MTO/H₂O₂ and water.

2. 9. 6. Oxidation of olefins

In 2008, Welton et al. used several ionic liquids as co-solvents for the catalytic epoxidation of alkenes with Oxone (KHSO₅) 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. A great advantage of the multicarboxylic acid containing ILs compared to [bmim]BF₄ is the possibility of reusing the catalytic system. With [bmim]BF₄, 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]BF₄ 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 selectivity’s between 57 % and 100 % [77, 78]. The asymmetric epoxidation of limonene was investigated by the group of Bernardo-Gusmão. They used Jacobsens Mn(salen) catalyst and hydrogen peroxide as an oxygen source (Scheme 27).

Scheme 27. Oxidation of limonene catalyzed by Jacobsens catalyst
3. CONCLUSIONS

The study of ionic liquid assisted reactions of olefins were reached to the chemical community as evident by many reactions reported. The authors also believed that there are many interesting ionic liquids assisted reactions are very useful to the chemical community for future synthetic work. Also, there is enormous of interest to support a great deal of further research. The literature survey regarding ionic liquid assisted reactions shows that we are only at the beginnings of understanding how the nature of ionic liquids can affect the chemical reactions that occur in them. This is the basic for the utilization, manipulated and to develop the applications of ionic liquids in a sophisticated manner. This detailed study was useful for the green chemistry beginners through the literature, evidence of kinetic investigations, stereochemical, complexes and systematic comparisons-correlations of different ionic liquids. By gaining and engaging the reactions thorough understanding of these fascinating ionic liquids that their true potential will be comprehended.

List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>ROMP</td>
<td>Opening metathesis polymerization</td>
</tr>
<tr>
<td>(MTO)</td>
<td>Methyltrioxorhenium</td>
</tr>
<tr>
<td>(TBHP)</td>
<td>Tertiary butyl hydroperoxide</td>
</tr>
<tr>
<td>RTIL</td>
<td>Room temperature ionic liquid</td>
</tr>
<tr>
<td>[bmim]</td>
<td>1-butyl-3-methylimidazolium</td>
</tr>
<tr>
<td>[omim]</td>
<td>1-octyl-3-methylimidazolium</td>
</tr>
<tr>
<td>[dmim]</td>
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<tr>
<td>[tmba]</td>
<td>trimethylbutylammonium</td>
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References


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