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Review

Ionic liquids in catalysis

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Contents

Abstract

The current state of the art of the application of ionic liquids in catalysis is reviewed. The review selects examples of the different ways in which ionic liquids have been applied in catalysis, i.e. as the catalyst itself, as a co-catalyst or catalyst activator, as the source of a new ligand for a catalytic metal centre, or just as the solvent for the reaction. Where possible, examples have been selected that elucidate the behavior of the ionic liquids in the process being described.

Keywords: Ionic liquids; Catalysis; Hydrogenation; Hydroformylation; Dimerization; Organocatalyst; Oxidation; Electrocatalysis; Supported ionic liquid; Solvent properties

1. Introduction

Ionic liquids have been generating increasing interest over the last decade [1]. It is a testament to the speed with which ionic liquids have caught the popular chemical imagination that in 1999 a monograph titled “Modern Solvents in Organic Synthesis” [2], could be published in which ionic liquids received no mention at all; a situation that would be unimaginable now. Much of this interest is centered on their possible use as “greener” alternatives to volatile organic solvents (see below). There is, however, also a more fundamental

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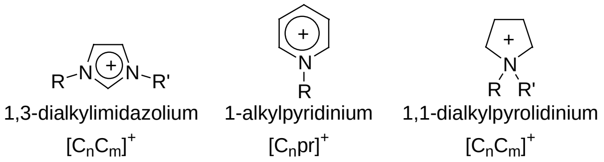

Fig. 1. Some common cations used for ionic liquids.

interest in how the unusual solvent environment that they provide for solute species might affect reactions conducted in them. There have been a number of excellent ionic liquid reviews concerning their chemical and physical properties [3], and applications in synthesis and catalysis [1,4].

This review does not attempt to be comprehensive; with modern search engines the literature of ionic liquids in catalysis can be accessed easily. Rather it attempts to show how ionic liquids might be useful in catalysis and, where possible, to report on the chemistry underlying any observed effects of the ionic liquids. I will limit examples as far as possible to those that inform the readers' understanding of the ionic liquid systems and their chemistries. This means that a great deal of fine work is not covered and no slight is intended in any of these cases. For what it is worth, I have tried to give my opinion throughout the review. I am sure that there will be points on which I am quite wrong and I apologize if I have misunderstood your results, but I hope that this will lead to more stimulating discussion in the future. The basic construction of the review is to briefly introduce the ionic liquids themselves and then to select examples of how they have been used in catalysis, that is as the catalyst itself, as a co-catalyst or catalyst activator, as the source of a new ligand for a catalytic metal centre, or just as the solvent for the reaction. The review will not cover catalysis by enzymes, a subject in which I have no expertise [1,5]. The review covers the literature up to the end of 2003.

1.1. Introduction to ionic liquids

Although it is only an arbitrary divide, ionic liquids are generally defined as salts that melt at or below 100 °C to afford liquids composed solely of cations and anions. In some cases, the ionic liquids are free-flowing liquids at room temperature, in which case they can be called *ambient temperature ionic liquids*. Of course, these latter liquids have real advantages over higher melting salts in terms of the practicalities of handling.

The list of ionic liquids grows daily, but the cations are generally bulky, asymmetric ammonium or phosphonium salts, or heteroaromatics, with low symmetry, weak intermolecular interactions and low charge densities (Fig. 1). The 1,3-dialkylimidazolium salts[1] remain the most intensively investigated, although this could well change in the future as more affordable alternatives arrive on the scene. However, if you wish to generate a low-melting salt of any particular anion, an unsymmetrical 1,3-dialkylimidazolium still appears to be the best place to start. Typically, the anions are inorganic and include $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, and $[(CF_3SO_2)_2N]^-$ although more recently, organic anions (e.g. $[RCO_2]^-$) have also been introduced. The physical and chemical properties of the ionic liquid, including their melting points, are dependent on both the nature of the cation and the anion.

Ionic liquids are attractive as potential solvents for a number of reasons:

- They are generally colorless liquids with relatively low viscosities.
- They exhibit very low vapor pressures under ambient conditions and thus are effectively non-volatile.
- Ionic liquids can be found that are good solvents for a broad spectrum of inorganic, organic and polymeric materials and are immiscible with numerous organic solvents. Thus, applications in process intensification and as non-aqueous polar alternatives in biphasic systems are possible.
- Being composed of two parts, there is a synthetic flexibility that is not available for single component molecular solvents.

In addition to these properties, they are also readily prepared from commercially available reagents. It is also now possible to source ionic liquids commercially from a number of suppliers in a range of different qualities. This is particularly important in catalysis, where trace impurities can make a huge difference to the outcome of a reaction.

1.2. Ionic liquid solvent properties

The study of solvent effects on reactions is one of the longest established areas of chemical research [6], and catalytic reactions are just as sensitive to changes in solvents as any other, if not more so. Usually we think of solvents in terms of their polarity as expressed by the dielectric constant. However, it is not possible to measure the dielectric constant of an ionic liquid directly, so this cannot help us.

In catalysis, we are generally interested in two things: the solubilities of the reaction components (starting materials, products, catalyst, co-solvents) and any specific interaction that may take place between the solvent and solutes to enhance or reduce the reactivity of any of the solute species.

Clearly, the miscibility of any given substance with an ionic liquid is dependent on the particular ions of which it is composed as well as the properties of the solute. This idea, of the need for the solvent and solute to have complimentary properties in order to mix, forms the basis of the Abraham solvation model [7], which has been used by Anderson et al., to measure the solvent properties of ionic liquids [8]. Using the GC retention times of a range of probe solutes (36) on a variety of columns using ionic liquids (14)

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[1] Note on nomenclature, 1-alkyl-3-alkylimidazolium cations will be abbreviated throughout this article as $[C_nC_m\text{im}]^+$, where n and m are the lengths of the alkyl chains.

as the stationary phases, they were able to make some general statements as to how the ionic liquids were behaving. The ionic liquids were interacting with solute via high dipolar and dispersion forces and also acting as strong hydrogen bond bases. The dipolar forces and hydrogen bond basicity varied with the different ionic liquids, whereas the dispersion forces were nearly constant for all of the ionic liquids studied. The hydrogen bond basicity was dominated by the choice of anion. When hydrogen bond acidity was observed it arose from the cation of the ionic liquid, although the anion also greatly influenced this property. Not surprisingly, ionic liquids with aromatic ions were more capable of π–π and n–π type interactions with solutes.

A number of more specific studies of miscibilities have been reported, such as those of various gases in $[C_4C_1im][PF_6]$ [9], of a variety of $[C_nC_1im][PF_6]$ ($n = 4$–8) ionic liquids in butanol [10], or $[C_nC_1im][PF_6]$ ($n = 2$ or 4) in both aromatic and cyclo-aliphatic hydrocarbons [11] have also been conducted.

Ionic liquids form biphasic mixtures with supercritical CO_2 ($scCO_2$), with the ionic liquid showing very low solubility in the CO_2 layer, but the CO_2 having significant solubility in the ionic liquid [12]. This has excited a great deal of attention as a way of producing a ‘green’ biphasic reaction system, in which the catalyst is trapped in the ionic liquid layer and the reagent and products can be added and removed in the CO_2 layer [13].

The miscibility of ionic liquids with water is particularly interesting. All ionic liquids described to date are hygroscopic. Some will mix with water in all compositions, whereas others eventually saturate and then form two layers [14]. This behavior is principally controlled by the anion of the ionic liquid, with the cation having a secondary effect. The reason for this is that strong hydrogen bonds can form between the water and the anion of the ionic liquid [15]. The solubility of water in ionic liquids can be manipulated by adding short chain alcohols to biphasic systems to increase mixing [16], or adding salts to separate otherwise water miscible ionic liquids [17]. The $[C_nC_1im][BF_4]$ ionic liquids provide borderline cases in this behavior such that their miscibility with water can be controlled thermally [18]. This behavior has been used to generate a thermally controlled reaction system, where the reaction mixture is monophasic at the temperature of reaction, allowing maximum mixing of the starting materials, but biphasic at room temperature, allowing facile separation of the products and catalyst [19].

The ways in which solvents interact with solutes can also be studied by analyzing the effect of changing the solvent on the spectra of probe dyes. This forms the basis of the Kamlet-Taft system [20], which is seen as a measure of interactions between solute species and their immediate solvent environment. It gives complimentary scales of hydrogen bond acidity (α), hydrogen bond basicity (β) and dipolarity/polarizability effects (π^*) and has been used recently to describe a variety of ionic liquids [21]. π^* is the value that most resembles our qualitative notions of ‘polarity’ in the absence of hydrogen bonding effects. All of the π^* values for the ionic liquids are high in comparison with most non-aqueous molecular solvents. However, there is no way in which the ionic liquids could be thought of as ‘super polar’.

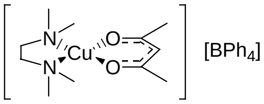


Fig. 2. $[Cu(acac)(tmen)][BPh_4]$.

The α-values are largely determined by the nature of the cation, with a smaller anion effect. It is interesting to note that some of ionic liquids that showed moderately high values here, showed no hydrogen bond donor characteristics in the GC experiment described above. As the conjugate bases of strong acids, the anions of the ionic liquids might be expected to have low β-values in comparison to other solvents. However, although those found in this study are not as high as for acetone, they are comparable to acetonitrile, which is thought of as an electron pair donor solvent.

In catalysis, there is the particular concern of how the solvent can interact with the metal centre itself and interfere with the reactivity of the active site. The λ_{max} for the d → d band of the square planar cation of $[Cu(acac)(tmen)][BPh_4]$ (Fig. 2), which correlates well with solvent donor numbers [22], has been used to measure this for ionic liquids [21,23]. This value is dominated by the nature of the anion of the ionic liquid and correlates well with the β-values described above.

It might seem surprising, since the anions that are used to make ionic liquids are usually described as non-coordinating, that any great difference between the ionic liquids is seen. The fact that these so-called non-coordinating ions very clearly do coordinate to the metal centre reveals something about the nature of coordination in an ionic liquid in comparison to a molecular solvent that can have profound effects in catalytic chemistry. If we consider a cationic metal centre that is coordinatively unsaturated with vacant orbitals dissolved in a molecular solvent; the possibilities are: (i) an anion can directly coordinate to the metal centre; (ii) the anion and the cation may be well separated in the solvent, with the cation coordinated to molecules of the solvent, or the cation and anion can exist as either; (iii) an intimate; or (iv) a solvent separated ion-pair. In a pure ionic liquid there are no molecules available to separate the ions and the cations of the ionic liquid will be repelled by the charge on the metal complex. Hence, in an ionic liquid options (i) and (iii) are the only ones available. The cationic centre will always be closely associated with the anions. Since the anions are in the neighborhood and there is no other source of potential electron pairs (until deliberately added as a reagent) and being the solvent and therefore in vast excess, they will interact with the metal centre to some extent. Hence, anions of ionic liquids are more likely to coordinate to a transition metal centre than the same anions in a molecular solvent.

2. Ionic liquids as catalysts

Perhaps the potentially most powerful way in which an ionic liquid can be used in catalysis is as a combination of solvent and catalyst. Whenever changing solvent leads to a faster reaction the new solvent can be viewed as being a catalyst. After all, the reaction has been accelerated and the solvent has remained unchanged by the process. However, I think that for the purposes of this review it is best to separate those processes in which changes in rate occur due to generalized ‘polarity’ effects and will not be covered and those where a specific reaction or interaction is responsible for the observed behavior. In these latter examples, the ionic liquid is deliberately prepared with one of the ions being the catalyst for a reaction.

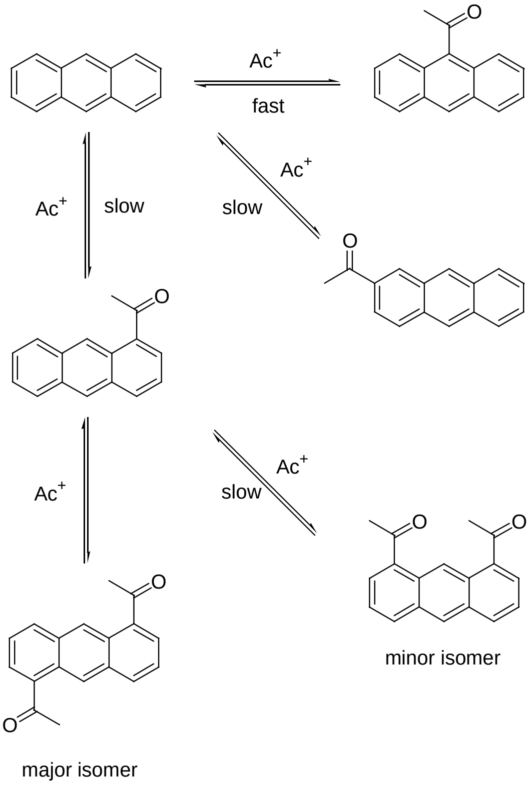
2.1. Electrophilic substitutions in chloroaluminate(III) ionic liquids

The high concentration of $[Al_2Cl_7]^-$ in acidic (mole fraction of $AlCl_3 > 0.5$) chloroaluminate(III) ionic liquids coupled with the good solubility of simple arenes makes them ideal solvents for electrophilic aromatic substitutions. Basic (mole fraction of $AlCl_3 < 0.5$) chloroaluminate(III) ionic liquids do not supply sufficiently acidic chloroalumiante(III) ions for reaction to occur.

For alkylation reactions of benzene with 1-chloropropane in acidic $[C_2C_1im]Cl–AlCl_3$ polyalkylation was observed, as with conventional systems [24]. As usual in this situation, use of a large excess of the arene reduced, but did not entirely eliminate this. Mixing benzene and hexamethylbenzene in the acidic ionic liquid did not lead to the formation of toluene, xylenes, mesitylenes, etc. showing that there is no dissociation of the methyl substituents under these conditions. However, in an investigation of the electrochemical oxidation of hexamethylbenzene in mixtures of an acidic (mole fraction of $AlCl_3 = 0.67$) ethylpyridinium bromide–aluminium(III) chloride ionic liquid with benzene [25], it was found that a product mixture containing penta-, tetra-, and tri-methylbenzene and diphenylmethane was formed. The authors postulated that the mixture was formed by a series of Friedel–Crafts reactions initiated by a two-electron oxidation of hexamethylbenzene, but it may also have arisen from the presence of proton impurities, which are very difficult to remove completely.

In a study of the alkylation of benzene with benzyl chloride in acidic $[C_2C_1im]Cl–AlCl_3$ the ionic liquid system was found to be highly active and selective [26]. This was maintained in a second run, but the activity dramatically decreased on the third run. The activity of the system was found to be highly dependent upon the stirring rate, suggesting that mass transfer limitations were coming into play.

The alkylation/depolymerisation of coal has been investigated in a pyridinium chloride based ionic liquid (mole fraction of $AlCl_3 = 0.65$) [27], using 2-propanol as the alkylating agent. Although the reaction was successful and no alkylated pyridines, from reaction with the ionic liquid itself, were formed, autoalkylation of 2-propanol yielded a series of high molecular weight polymers.



Scheme 1. The acylation of anthracene in $[C_2C_1im]Cl–AlCl_3$.

Friedel–Crafts acylation reactions of benzene have also been carried out in the $[C_2C_1im]Cl–AlCl_3$ ionic liquids [24]. For the reaction of acetyl chloride with benzene, it was determined that the rate at which acetophenone was produced was dependent on the Lewis acidity of the ionic liquid, which is, in turn, dependent on the ionic liquid composition. Acylation of anthracene gave diacylated products (Scheme 1) [28]. It was shown that after initial monoacylation, disproportionation to diacetylanthracenes and anthracene occurred. The simplest possible explanation for this is the presence of a Brønsted superacid in the system.

The range of substrates was further extended when the acylation of a variety of substituted indoles were reported [29]. For some of the products formed, it was claimed that acylation in the chloroaluminate(III) ionic liquid provided the best available synthesis. Although all of acylations described here succeeded in generating the products in moderate to high yields, their isolation still requires aqueous work-up and destruction of the ionic liquid. Extraction of the products from the ionic liquid without its destruction would make these systems very much more attractive and requires further investigation.

In order for the Friedel–Crafts reactions to occur, it is necessary to be able to form an electrophile in the ionic liquid. In the reactions with 1-chloropropane products resulting from

$$Ph_3CCl + [Al_2Cl_7]^- \longrightarrow [Ph_3C]^+ + 2[AlCl_4]^-$$

Scheme 2. The formation of the triphenylmethyl cation in a moderately acidic ionic liquid.

$$CH_3COCl + [Al_2Cl_7]^- \longrightarrow [CH_3CO]^+ + 2[AlCl_4]^-$$

Scheme 3. The formation of the acylium ion in acidic $[C_2C_1im]Cl–AlCh_3$.

secondary carbonium ions were formed [24]. This implies that alkylation occurs, at least to some extent, via the dissociated carbonium ions. Luer and Bartak [30] demonstrated that even in a moderately acidic (mole fraction of $AlCl_3 = 0.52$) ionic liquid, dissolution of chlorotriphenylmethane leads to the formation of the triphenylmethyl carbonium ion (Scheme 2).

The reaction between acetyl chloride and the acidic ionic liquid has been followed by ^1H NMR [24]. The results suggested a stoichiometric reaction between CH_3COCl and $[Al_2Cl_7]^-$ (Scheme 3). This has been confirmed by subsequent infrared spectroscopic investigations [31]. Indeed, it is possible to isolate solid $[CH_3CO][AlCl_4]$ from the acidic chloroaluminate(III) ionic liquids.

An alternative way of producing a reactive carbocation for alkylation is by the protonation of an alkene [32]. This, of course, requires the presence of protons, which can be added deliberately or arise adventitiously through the reaction of the chloroaluminate(III) ions with water. When protons are present in these ionic liquids they can be superacidic [33]. The Brønsted acidity varies as both a function of proton concentration and precise composition of the ionic liquid, with Hammett acidities of up to -18 for the most acidic ionic liquids. Some evidence points towards HCl as the only proton containing species present in acidic chloroaluminate(III) ionic liquids [34], but the formation of the hydrogen-bonded species $[AlCl_4–HCl]^-$ and $[Al_2Cl_7–HCl]^-$ has also been suggested [35]. It is likely, since it has been shown that $[AlCl_4]^-$ and $[Al_2Cl_7]^-$ are only poor hydrogen-bond acceptors [36], that the bond is relatively weak. Hence, the situation is likely to be highly dynamic, with the HCl being solvated by the best hydrogen-bond acceptor ions available in the ionic liquid.

Protons in acidic chloroaluminate(III) ionic liquids have been known to catalyze the formation of oligomers, with molecular weights characteristic of a cationic reaction, from olefins [37]. This chemistry has led to a number of patents for the polymerization of raffinate gas (mixtures of butenes) [38] and the preparation of branched oligomeric fatty acids from linear fatty acids [39].

Isobutane alkylation has also been investigated in ionic liquids. Again, it was the adjustable nature of the Lewis acidity of the systems that made them attractive [40]. The process involved a reaction mixture consisting of isobutane, butane, and but-2-ene (mixture of *cis*- and *trans*-) in a $[C_4C_1im]Cl–AlCl_3$ ionic liquid. The products of the reaction included included 2,2,4-trimethylpentane, 2,5-dimethylhexane, light ends (C_5–C_7 isoparaffins), and heavy ends (C_{9+} isoparaffins). The rate and selectivity of the alkylation reaction was found to be dependent on the precise composition of the ionic liquid, reaction temperature, feed rate into the reactor, and residence time of the mixture in the ionic liquid.

There are a number of electrophilic aromatic substitutions, closely related to the Friedel–Crafts reaction. Chlorination occurs in both acidic and basic chloroaluminate(III) ionic liquids [41], but is only an electrophilic aromatic substitution in the acidic ionic liquids. In both reactions, the primary product was chlorobenzene, but in acidic compositions, large amounts of at least two dichlorobenzene isomers were synthesized, as well as some trichlorobenzene products. This suggests that a very reactive electrophile is produced, probably Cl^+, formed by the reaction of Cl_2 with $[Al_2Cl_7]^-$.

Nitration of aromatic compounds in $[C_2C_1im]Cl–AlCl_3$ ionic liquids used KNO_3 as the source of $NO_2{}^+$, which acts as the electrophile and resulted in a 55% yield of nitrobenzene [41]. NH_4NO_3 and NO_2BF_4 were also tried as nitrating agents but gave much lower yields.

Sulfonylation has also received some attention. The reaction of a variety of substituted benzenes with 4-methylbenzenesulfonyl chloride in acidic $[C_4C_1im]Cl–AlCl_3$ gave almost quantitative yields under ambient conditions, representing an increased reactivity of the substrates in comparison to conventional conditions [42]. The product sulfones were found to act as Brønsted bases and to interact strongly enough with the by-product HCl to liberate its Cl^- ion, which reacted with the $[Al_2Cl_7]^-$ to generate $[AlCl_4]^-$, so reducing the Lewis acidity of the system (Scheme 4). The consequence of this on the reactions was that the rates of the reaction dropped off from the initially high rates seen at low conversion of substrate. Hence, as in conventional systems, the reaction is effectively stoichiometric in Lewis acid $\{[Al_2Cl_7]^-$ in this case$\}$. It can be inferred from this that the same is true of Friedel–Crafts acylations in the ionic liquids. Notwithstanding these problems, the same authors have gone on to use acidic $[C_4C_1im]Cl–AlCl_3$ to prepare diaryl sulfoxides from arenes and thionyl chloride [43]. Again aqueous work-up and concurrent destruction of the ionic liquid was used in these reactions.

2.2. *Condensation reactions in chloroaluminate(III) ionic liquids*

Condensation reactions are a useful way of making C–C bonds, with the elimination of a small molecule by-product. A number of Lewis acid condensation reactions have been tried in chloroaluminate(III) ionic liquids. These are the

$$[Al_2Cl_7]^- + HCl + Ar_2SO_2 \longrightarrow 2[AlCl_4]^- + [H(Ar_2SO_2)]^+$$

Scheme 4. The reaction of aryl sulfones with HCl in acidic chloroaluminate(III) ionic liquids.

Pechmann reaction [44], the Knoevenagel reaction [45], the Ficher Indole synthesis [46], and the Baeyer condensation [47]. While these have all given high conversions of starting materials under the best conditions, they suffer from having water as a principle by-product. Any water generated by the reaction reacts with the chloroaluminate(III) species in the ionic liquid, so reducing its acidity and eventually destroying the ionic liquid.

Other Lewis acid mediated reactions that have been conducted in chloroaluminate(III) ionic liquids include the cleavage of aromatic methyl ethers [48], acylative cleavage of ethers [49], esterifications [50], Diels–Alder cycloadditions [51], and the formation of 4-chloropyrans during an attempted Prins reaction [52] but, once again, the ionic liquid is consumed in the reaction or during product isolation.

This problem, that the ionic liquid is consumed and cannot be considered to be a true catalyst for the reactions has arisen repeatedly with the use of chloroaluminate(III) ionic liquids. Even when the ionic liquid is not being destroyed by a product or by-product of the reaction, product separation has been a problem and the reactions have used aqueous work-up and, therefore, destruction of the ionic liquid. This presents a challenge to their use on a large scale. However, where tested, the ionic liquids have in several of the examples above shown themselves to be superior to solid $AlCl_3$ itself, which is also destroyed by the same mechanisms. This is presumably largely due to better mixing of the substrates with the ionic liquid, which can be thought of as a liquid form of aluminium chloride, and may be sufficient to warrant their use on the laboratory scale.

2.3. Ionic liquids as organocatalysts

In the last few years a renewed interest in the use of organic compounds as catalysts has begun to emerge—organocatalysis [53]. Ionic liquids have the potential to have a huge impact in this area. One of the promising approaches to organocatalysis is through hydrogen bonding interactions, and the reactions to which this has been most often applied are Diels–Alder cycloadditions and their derivatives [54].

The Diels–Alder cycloaddition was one of the first reactions to be investigated in the new, non-chloroaluminate(III) ionic liquids [55–58]. Both rate and selectivity improvements were seen in comparison to many molecular solvents. Rate enhancements were also seen for, the closely related, 1,3-dipolar cycloaddition reactions in ionic liquids [59]. In a careful investigation of the effects of changing both the cations and anions of the ionic liquids on the reaction of methyl acrylate and cyclopentadiene, it was demonstrated that the rate and selectivity enhancements seen were due to an explicit hydrogen bond between the cation of the ionic liquids and the carbonyl group of the methyl acrylate (Fig. 3) [60]. It has been demonstrated that the ionic liquids are capable of being stronger hydrogen bond donors than uncharged equivalents [21], opening the way for their exploitation in this new field.

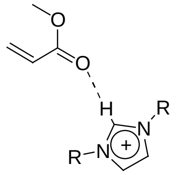
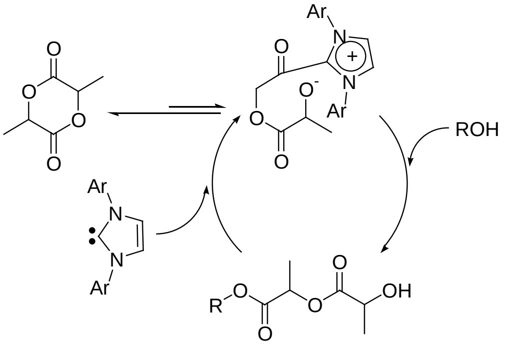


Fig. 3. The hydrogen bond between methyl acrylate and the $[C_4C_1im]^+$ cation.

Subsequently, Srinivasan et al. proposed the formation of a hydrogen bond between an ionic liquid's cation and the carbonyl group of an anhydride to explain the acetylation of alcohols [61]. However, although this effect may be playing a role, it does not fully explain all of the results presented, particularly the role of the anions in the process. MacFarlane et al. have also studied the acetylation of alcohols and proposed that the anion of their ionic liquids is acting as a base catalyst in the acetylation of alcohols, but have not studied the effect of the cations [62]. What is exciting about these reactions is not that there is an apparent disagreement here, but that both could be interpretations correct. That is, the cation is acting as a Lewis acid and activating the acetic anhydride and the anion is acting as a Lewis base and activating the alcohol. If this interpretation is correct, the simple fact that all ionic liquids are necessarily composed of two parts will provide a new way of approaching this type of catalysis.

There are some other reactions that have been successfully conducted in ionic liquids in which I believe that these hydrogen bonding effects may also be playing a role, e.g. Michael [63] and other conjugate additions with no added catalyst [64,65]. However, insufficient data is currently available to be sure that this is the case.

Although not strictly speaking catalysis by the ionic liquid itself, a particularly interesting way of using them has recently arisen. Imidazolylidenes, often referred to as *N*-heterocyclic carbenes (NHC's) can act as nucleophilic catalysts [66]. Hedrick and co-workers [66] have used ionic liquids as the source of the NHC as well as one of the solvents in a biphasic ring opening polymerization of lactide and lactones. $[C_2C_1im][BF_4]$ with THF provided an excellent medium for the reaction (Scheme 5), which was



Scheme 5. The NHC catalyzed ring opening polymerization of lactide.

initiated by the addition of a small amount of potassium *tert*-butoxide that deprotonates the imidazolium ring to generate the NHC. The now neutral NHC transfers to the THF layer, where the reaction occurs. The reaction is terminated by addition of a protic ammonium salt, which regenerates the imidazolium cation by proton transfer.

3. Ionic liquids as co-catalysts

Another way in which an ionic liquid can be useful is if one of the ions of the ionic liquid can act as a catalyst activator, or co-catalyst for a reaction. Again, chloroaluminate(III) derived ionic liquids have been the main focus for attention in this area.

3.1. Olefin dimerization

Acidic chloroaluminate(III) ionic liquids were the first to be used as a combination of solvent and co-catalyst for the dimerization of propene to hexenes with nickel(II) catalysts [67]. Basic compositions of the ionic liquid failed to give catalytically active solutions. The product hexenes separated from the ionic liquid phase and were easily removed by decantating. Since a nickel–carbon bond is required to facilitate the reaction, only those catalysts with one were active. The desired products were contaminated with the products of a fast cationic side reaction, arising from the superacidity of proton contamination of the ionic liquid. This side reaction has been confirmed as the culprit by conducting oligomerisations of olefins in ionic liquids without the added nickel complexes [37].

Alkylaluminum(III) compounds react vigorously with protons, to give the respective alkane. Hence, using ionic liquids derived from ethylaluminium(III) dichloride prevented the cationic side reaction. Alkylaluminum(III) compounds can also act as alkylating agents, so this alteration also allowed a greater number of potential catalysts to be used, e.g., nickel phosphine dihalides, which are then activated by the ionic liquid itself.

A number of air-stable NiL_2C_2 complexes (L: $P(Bu)_3$, $P(^iPr)_3$, $P(cyclohexyl)_3$, and pyridine) have been successfully used as catalysts for the regioselective dimerization of propene in chloroaluminate(III) and ethylchloroaluminate(III) ionic liquids [68]. A co-solvent of heptane was used to improve product separation giving an upper organic layer containing the products that can be removed easily, leaving the catalyst in the ionic phase to be reused. The system slowly deactivates if pure ethylchloroaluminate(III) ionic liquids are used as the solvent, because of the extraction of the dimeric $[Et_4Al_2Cl_2]$ into the organic layer. This was avoided by using $[C_4C_1im]Cl–AlCl_3$ as the solvent with a small amount of dichloroethylaluminum(III) added.

This work has been extended to the oligomerization of butenes [69,70], which has been developed by the Institut Français du Pétrole into the Difasol process [71], and to the selective dimerization of ethene [72]. In this latter example, quantitative analysis of the nickel content of the two phases indicated that over 98% of the Ni remained in the ionic layer. Optimum dimerization activity and selectivity is achieved when toluene is used as the cosolvent for the reactions [68,72]. When other organic solvents such as heptane are used or a cosolvent was omitted, a mixture of high molecular weight ethene oligomers was synthesized. It is feasible that this occurs as a result of coordination of $AlCl_3$ to the aromatic ring [73]. This would reduce the acidity of the ionic liquid, perhaps attenuating the activity of the catalyst. Alternatively, it could be that toluene provides the best extraction of the dimers from the ionic liquid, so preventing their continued reaction with the catalyst.

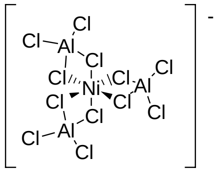


Fig. 4. $[Ni(AlCl_4)_3]^-$.

The active nickel catalyst is formed in situ in the ionic liquid by reaction of the precursor with the alkylaluminate(III) species in the ionic liquid. de Souza and co-workers used a variety of $[Ni(MeCN)_6][MX_4]_2$ (where M: B, Al or Zn and X: F or Cl) salts, $[Ni(PhCN)_6][BF_4]_2$ and $(PBu_3)_2NiCl_2$ as the catalyst precursors in a $[C_4C_1im]Cl–EtAlCl_2$ ionic liquid to dimerize 1-butene [74]. They showed that the product selectivity was independent of the catalyst precursor used, but that the TOF for the reaction was very sensitive to it. They proposed that a single active nickel hydride was formed in the ionic liquid, regardless of the precursor used, but in varying amounts depending on the counter ion for the different salts.

It is known that tetrachloroaluminate(III) ions in ionic liquids can coordinate Ni(II) centres (Fig. 4) [75]. However, unpublished EXAFS work from my own group shows that when $(PPh_3)_2NiCl_2$, $(PMe_3)_2NiCl_2$ or $(dppe)_2NiCl_2$ are dissolved in acidic $[bmim]Cl–AlCl_3$ ionic liquids, the phosphines remain coordinated to the metal centre [76]. It is likely that an initial coordination of the alkylaluminate(III) species, probably through a chloride ion, to the nickel centre followed by alkylation and β-elimination yields the active nickel hydride catalyst [77], which will also be coordinated by other available ligands, or in their absence $[AlCl_4]^-$.

An alternative approach to preventing the problem of cationic side reactions, is to reduce the acidity of protons in the ionic liquid by buffering it to its neutral composition with a suitable base [78]. The buffered ionic liquid can then be used as the solvent for the catalyst. This methodology has been applied to butene dimerisation, catalyzed by [Ni(COD)(hfacac)] (where COD: cyclooctadiene and hfacac: 1,1,1,5,5,5-hexafluoropropan-2,4-dione) in $[C_4C_1im]Cl–AlCl_3$ [79]. It was found that metal halide buffers poisoned the catalyst, but that aromatic amine bases prevented the cationic side reactions without preventing the nickel catalyst from operating. As stated above, in the absence of a nickel–carbon bond an activator is usually needed for the catalyst. This notwithstanding, it was found that the ionic liquid solution was active at −10 °C, whereas in toluene temperatures over 50 °C were required, so some unidentified activating mechanism is operating [80].

4. Ionic liquids as a ligand source

Even when the solvent is not being used as a catalyst activator, one of the first questions that should be asked when conducting catalysis in solution is: is the species that is actually present in solution the same as the one that was originally dissolved in the liquid? In spite of the fact that ionic liquids were initially thought of as entirely innocent, non-coordinating solvents, there have been examples of reactions in ionic liquids where the answer was a resounding ‘No’.

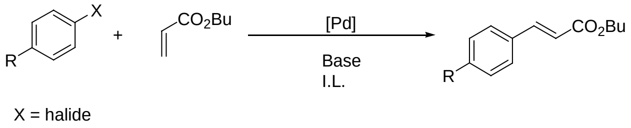
4.1. Hydrogenation and hydroformylation in chlorostannate(II) ionic liquids

The use of $[Et_4N][SnCl_3]$ as a solvent for hydrogenation and hydroformylation is now widely recognized as the first use of an ionic liquid in transition metal catalysis [81]. Solutions of $PtCl_2$ in $[Et_4N][SnCl_3]$ effectively catalyze the hydrogenation of olefins with no apparent decomposition of the catalyst to metal, allowing the catalyst solutions to be used repeatedly without loss of activity, so long as contact with the air was avoided. Even at this early stage, before the introduction of the *Green Chemistry* concept, the ability to isolate the products by decanting or distillation was noted as an advantage of the system. $PtCl_2$ led to a more reactive catalyst solution than $(PPh_3)_2PtCl_2$. It was proposed that in the ionic liquid $PtCl_2$ formed $[Pt(SnCl_3)_5]^{3-}$ and $[HPt(SnCl_3)_4]^{3-}$, which was isolated from the ionic liquid after a reaction, during the hydrogenation.

It took 28 years for this work to be followed up, when Wasserscheid used the room-temperature ionic liquid $[C_4C_1im][SnCl_3]$ as a solvent for platinum catalyzed hydroformylation [82]. This ionic liquid provided the advantage that it allowed lower operating temperatures, which favored the desired hydroformylation over the competing hydrogenation.

4.2. The in situ formation of palladium NHC complexes in imidazolium based ionic liquids

Ionic liquids have been used as solvents for quite a range of palladium catalyzed reactions. During these investigations it became clear that some interesting chemistry was occurring. This area is controversial and no general consensus has yet been reached. Both the formation of NHC complexes and of nanoparticles has been suggested. In this section, I will concentrate on the work where the formation of NHC complexes is possible and the form of the palladium was part of the discussion, or where an observation raises the possibility of their formation. I will address the systems where the formation of NHC complexes is not possible in the following section.

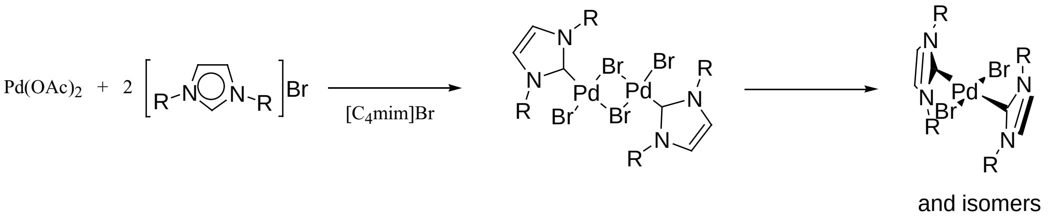


Scheme 6. A simple Heck reaction in ionic liquid.

Seddon reported the Heck reactions of bromo- and iodo-arenes (Scheme 6) in a series of *N*-hexylpyridinium $\{[C_6py]^+\}$ and *N*,*N*′-dialkylimidazolium based liquids with $[PF_6]^-$ and $[BF_4]^-$ anions [83]. The imidazolium ionic liquids were found to be the least effective solvents in terms of catalyst reactivity. The addition of PPh_3 was found to inhibit the reaction in $[C_6py]Cl$ such that higher temperatures were required to afford comparable yields, but to increase the catalytic activity of the imidazolium ionic liquids. So, although the imidazolium based ionic liquids had the poorest reactivities on their own, once a phosphine was added they gave the highest reactivities. Clearly this requires some explanation.

Herrmann also investigated the use of a variety of ionic liquids as solvents for the Heck reaction [84,85]. He too noted that, regardless of the conditions used, all of the imidazolium based ionic liquids gave poor results in comparison to simple tetraalkylammonium salts. Again, this suggests that something different is occurring in the imidazolium based ionic liquids than in the other classes of ionic liquids.

The first evidence that the imidazolium based ionic liquids could be generating an entirely new catalyst in situ, came from the observation that the Heck reaction proceeds more efficiently in $[C_4C_1im]Br$ than $[C_4C_1im][BF_4]$ [86]. Also, ‘palladium black’ was seen to precipitate during reactions performed in $[C_4C_1im][BF_4]$, but not $[C_4C_1im]Br$. Xiao and co-workers [86] found that the complexes $[PdBr_2(C_4C_1imy)_2]$ and $[Pd_2(\mu\text{-}Br)_2Br_2(C_4C_1imy)_2]$ (C_4C_1imy: 1-butyl-3-methylimidazolylidene) could be isolated from the $[C_4C_1im]Br$ solution (Scheme 7) but not from the far less active $[C_4C_1im][BF_4]$ solution. These *N*-heterocyclic carbene (NHC’s) ligands have been used in other solvents to prepare catalysts for a wide variety of reactions, many palladium catalyzed [87]. Synthesis of $[PdX_2(C_nC_{n'}imy)_2]$ (X: Br, I) complexes from the imidazolium halide and $Pd(OAc)_2$ is particularly facile [88]. However, when the imidazolium chloride salt is used, the reaction does not proceed at all. This strong anion effect probably explains why the complexes form in $[C_4C_1im]Br$, but not in $[C_4C_1im][BF_4]$. However, when independently prepared $[PdBr_2(C_4C_1imy)_2]$ was dissolved in $[C_4C_1im][BF_4]$ the yield of the reaction was the same as



Scheme 7. The formation of [PdBr$_2$(C$_4$C$_1$imy)$_2$] in [C$_4$C$_1$im][BF$_4$].

that when palladium acetate was used. This suggests that, if the [PdBr$_2$(C$_4$C$_1$imy)$_2$] complex is responsible for the improved yields in [C$_4$C$_1$im]Br, it must rapidly form another species when dissolved in [C$_4$C$_1$im][BF$_4$]. Unfortunately, the actual species present in the [C$_4$C$_1$im][BF$_4$] solution could not be identified.

An EXAFS study of palladium acetate dissolved in [C$_4$C$_1$im][BF$_4$], [C$_4$C$_1$im][PF$_6$], [C$_4$Py][BF$_4$] and [C$_4$py][PF$_6$] showed that a gradual change to palladium metal occurred [89]. However, the use of [C$_6$C$_1$im]Cl led to the formation of [PdCl$_2$(C$_6$C$_1$imy)$_2$]. This is entirely consistent with Xiao and co-workers's observations above [86]. Interestingly, when [C$_6$C$_1$C$_1$im]Cl {where [C$_6$C$_1$C$_1$im]$^+$ is the 1-hexyl-2,3-dimethylimidazolium cation}, which has its C-2 position blocked, is used to prevent NHC complex formation, [PdCl$_4$]$^{2-}$ is formed rather than the metal. This is clearly the result of the relative coordinating strengths of the Cl$^-$ anion in comparison to [BF$_4$]$^-$ and [PF$_6$]$^-$. At no time was the palladium acetate itself stable in solution in the ionic liquid. When the experiment was repeated in the presence of PPh$_3$, [C$_6$C$_1$C$_1$im]Cl yielded [PdCl$_2$(PPh$_3$)$_2$] while [C$_6$C$_1$im]Cl still gave [PdCl$_2$(C$_4$C$_1$imy)$_2$]. However, when the [BF$_4$]$^-$ and [PF$_6$]$^-$ ionic liquids were studied under these conditions, nanoparticulate palladium (0.8–1.6 nm diameter) was seen. The addition of the Heck reagents did not change the palladium speciation. Unfortunately, [C$_6$C$_1$im]Cl does not give a catalytically active solution for the Heck reaction and no Br$^-$ based ionic liquids were studied. So, it remains possible that although [PdBr$_2$(C$_4$C$_1$imy)$_2$] is formed in [C$_4$C$_1$im]Br, nanoparticles are also formed and that these are responsible for the catalysis with the coordination complex itself being catalytically inactive [86]. However, this is not consistent with Xiao's observation that the [C$_4$C$_1$im]Br gives the most active solution. It is also possible that the inactivity of the chloride ionic liquids arises from the high coordinating ability of the Cl$^-$ ion itself, and is completely unrelated to the formation of NHC complexes.

In an ultrasound experiment the in situ formation of [PdY$_2$(C$_4$C$_4$imy)$_2$] (Y: Br$^-$, [BF$_4$]$^-$) was proposed, but as an intermediate en route to palladium nanoparticles [90]. Considering the poorly coordinating nature of the [BF$_4$]$^-$ ion, it seems unlikely that [Pd(BF$_4$)$_2$(C$_4$C$_4$imy)$_2$] is an appropriate formulation of this compound, which would probably be better described as [Pd(C$_4$C$_4$imy)$_2$][BF$_4$]$_2$. This [Pd(C$_4$C$_4$imy)$_2$]$^{2+}$ complex would be expected to be quite unstable and decomposition to palladium metal is a distinct possibility. This alone may be enough to explain the results, but it should also be noted that the environment of a collapsing cavitation bubble is very extreme in terms of both temperature and pressure and may lead to the decomposition of complexes that would be stable under thermal conditions.

In 1999, Xiao and co-workers reported the Pd(OAc)$_2$/4PPh$_3$ catalyzed allylation of 1,3-diphenylallyl acetate with a wider range of stabilized carbanions in [C$_4$C$_1$im][BF$_4$] under various conditions [91]. Outstanding reactivities were observed, even at room temperature. The reaction was later found to be dependent on the nature of the phosphine ligands employed [92], with strongly electron donating phosphine ligands giving enhanced reactivity relative to PPh$_3$, while weakly σ-electron donating and strongly π-electron accepting phosphines exhibited a decrease in activity. This strongly suggests that the active catalyst is a palladium phosphine species. The use of TPPTS as a ligand prevented catalyst leaching into the product layer during recycling, which had been a problem when using PPh$_3$, again also indicating that the catalyst is a phosphine containing complex and militating against the formation of nanoparticles.

The closely related cross-coupling reaction the Suzuki reaction [93], the coupling reaction of a halogenoarene with an arylboronic acid or ester, has also been successfully performed in ionic liquids [94]. A stable solution could be formed in [C$_4$C$_1$im][BF$_4$] from Pd(PPh$_3$)$_4$ that catalyzed the reaction of a range of bromo- and iodo-arenes with phenylboronic acid, more effectively than under the usual conditions in molecular solvents. It is particularly interesting to note that, in order to form the stable form of the solution, halide ions needed to be added to the melange. Subsequent investigation of the reaction conditions and analysis of the catalytically active solutions revealed the presence of a mixed phosphine–imidazolylidene palladium complex (Fig. 5) [95]. This work has now moved on to identify the 1-butyl-2-phenyl-3-methylimidazolium cation in the product mixture of the reaction [96]. This is likely to have been formed by reductive elimination from a palladium species containing both a phenyl ring and a C$_4$C$_1$imy ligand, so confirming the involvement of NHC's in the process.

The Suzuki reaction has also been reported in [C$_4$C$_4$im][BF$_4$] using ultrasound as the energy source [97]. Significant homo-coupling of the phenylboronic acid was reported when the reactions were performed under air, but this could

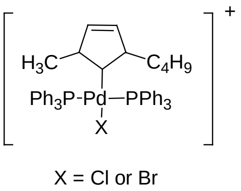


Fig. 5. The phosphine–imidazolylidene palladium complex $[(C_4C_1im)(PPh_3)_2PdX]^+$.

be reduced by using an inert argon atmosphere. Palladium decomposition prevented repetitive catalytic runs. However, when $[PdX_2(C_4C_4imy)_2]$ was independently prepared and used as the source of palladium for the reaction it gave comparable conversions to $Pd(OAc)_2$ but with no decomposition to metal or homo-coupling reported, even when the reaction was conducted under air. The $[PdX_2(C_4C_4imy)_2]$ complex was quantitatively recovered and used in three repetitive catalytic runs for the reaction of 4-bromoanisole with phenylboronic acid, with only a slight decrease in activity. In contrast to when this complex was used for ultrasound irradiated Heck reactions under similar conditions (see below) [98], TEM revealed no evidence of nanoparticle formation.

Clearly, it is possible for NHC metal complexes to form in situ in imidazolium based ionic liquids, and this should always be a consideration when unexpected reactivities or catalyst stabilities are observed in this sub-group of ionic liquids. It is also clear that they can take part in catalytic chemistry, even to the point of creating by-products. It is not at all clear that these complexes are the primary catalyst species in any of the reactions described above. However, it is notable that the preparation of the catalyst solution described in Xiao and co-worker's allylations [91] is very similar to that required for a successful Suzuki reaction and for the synthesis of the $[(C_4C_1imy)(PPh_3)_2PdX]^+$ (X: Cl or Br) complex in the $[C_4C_1im][BF_4]$. The need for the presence of halide ions would seem to be a major contributor to whether an NHC complex can be formed. It may also explain why NHC complex formation is sometimes seen, but not at others, when the reactions being investigated are largely similar. As the evidence looks at the moment, it would appear that such complexes are forming in the Suzuki reactions and are providing long term stability for the palladium in solution, but perhaps not in the Heck reactions as currently described.

An interesting observation has been made during the hydrodimerization of butadiene in $[C_4C_1im][BF_4]$ when $[C_4C_1im]_2[PdCl_4]$ is used as the catalyst precursor [18]. It was found that the imidazole complex $[PdCl_2(C_1im)]$ (Fig. 6, where C_1im: 1 methyl imidazole) was formed in the presence of water. The authors proposed that this was the consequence of two successive oxidative additions of $[C_4C_1im]^+$, each followed by a β-elimination of butane and then the reductive elimination of HCl. However, it is also possible that the complex arises from a Hofmann type elimination of 1-methylimidazole from the $[C_4C_1im]^+$ cation, which then displaces a Cl^- ligand from the $[PdCl_4]^{2-}$ complex.

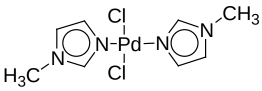


Fig. 6. bis(1-Methylimidazole)palladium dichloride.

4.3. The formation of nanoparticles in ionic liquids

Notwithstanding the discussion above, there have been a number of direct observations of the formation of nanoparticles in ionic liquids and their use in catalysis. The use of nanoparticles as catalysts has become an area of increasing interest in recent years [99].

The first palladium catalyzed reaction reported in an ionic liquid, by Kaufmann et al. in 1996, was a Heck reaction [100]. A series of aryl bromides were efficiently coupled with *n*-butyl acrylate in tributylhexadecylphosphonium bromide ($[C_{16}PBu_3]Br$) or tetrabutylammonium bromide ($[Bu_4N]Br$) to afford the *trans*-cinnamates in yields of over 90% in some cases. Product isolation was achieved by distillation from the ionic liquid or by solvent extraction.

$[PdCl_2(PPh_3)_2]$ was used as a palladium source to provide stable yellow homogeneous solutions in both ionic liquids at 70–80 °C without any need to add another ligand. For the reaction of bromobenzene with butyl acrylate it was possible to achieve a >99% yield in $[C_{16}PBu_3]Br$. No catalyst decomposition was reported, even after complete consumption of the aryl halide. In addition, comparable catalytic activities were achieved for two successive runs following product isolations. Perhaps more surprisingly, $Pd(OAc)_2$ and $PdCl_2$ could be used in just the same way, although catalyst decomposition was evident during the reaction with $PdCl_2$. There was no discussion of why the ionic liquids provided a stable catalytic system.

Tetraalkylammonium salt additives have previously been reported by Jeffery [101,102], for biphasic (organic solvent–water) Heck reactions where it was believed that the salts were acting as phase-transfer catalysts. While one of the positive effects of using the ionic liquid may have been to increase the solubility of the organic starting materials in the catalyst solution, the ability to generate a stable form of the catalyst without the addition of stabilizing ligands suggests that more complex factors are operating. Tetraalkylammonium salts have also been used to stabilize nanoparticles/colloids when used as a solute in molecular solvents [103]. It was suggested by Herrmann and Böhm that this may be occurring when $[Bu_4N]Br$ was being used as the ionic liquid [104,105].

Calò et al. have used the NHC complex ($[PdI_2(C_1bth)_2]$ (C_1bth: methylbenzthiazolylidene, Fig. 7) as a source of palladium in $[Bu_4N]Br$, with no added ligands [106]. They have identified the formation of nanoparticles of 2–6 nm diameter as responsible for the reactivity of the system. They speculate that reaction of the metallic palladium with the aryl

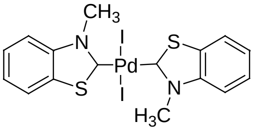


Fig. 7. bis(Methylbenzthiazolylidene)palladium diiodide.

halide of the Heck reaction and a halide anion of the ionic liquid, which both they and the Herrmann group have shown to be necessary, leads to the formation of $[ArPdX_3]^{2-}$, which then goes on to react with the olefin.

Palladium nanoparticles (2–5 nm) have been formed by reducing a solution of palladium acetate in $[C_4C_1im][PF_6]$ with H_2 [107]. Phenanthroline was added to the reaction mixture to stabilize the nanoparticles. The suspension of the particles was then used to catalyze the hydrogenation of alkenes, and could be recycled several times without loss of activity. When the phenanthroline was omitted, the system severely lost its reactivity on the first recycle. This was, presumably, due to aggregation of the particles into larger lumps that separated from the ionic liquid.

Platinum nanoparticles (2–2.5 nm) have also been precipitated from $[C_4C_1im][PF_6]$ [108]. $Pt_2(dba)_3$ was dispersed in the ionic liquid and reduced by applying H_2 (4 atm) at 75 °C. Under these conditions the nanoparticles catalyzed the hydrogenation of both alkenes and arenes. The ionic liquid suspension gave a less reactive system (lower TOF) than the same particles under solventless conditions or in acetone. There was no discussion of whether the system could be reused.

Iridium and rhodium nanoparticles have also been used as hydrogenation catalysts, suspended in $[C_4C_1im][PF_6]$ [109]. The nanoparticles were precipitated from solutions of $RhCl_3{\cdot}3H_2O$ or $[Ir(COD)Cl]_2$ by applying H_2 (4 atm) at 75 °C, giving particles of mean diameter 2.3 and 2.1 nm, respectively. The nanoparticles were used to hydrogenate benzene, but in both cases were less reactive than the same nanoparticles under either solventless conditions or in acetone. The iridium particles remained unchanged by reaction, whereas the rhodium particles clearly agglomerated. Neither system could be recycled effectively.

5. Ionic liquids as the solvent for the reaction

The final role that can be played by an ionic liquid in a catalytic process is simply as the solvent for the reaction. It is in this role that ionic liquids have been most widely used. Most studies in this area have, so far, been of the screening of reactions type, with a single ionic liquid being used as the solvent for some catalytic process without optimization or systematic investigation. In this section, I will try to focus on investigations that have provided some kind of insight into the chemistry being observed.

5.1. Heterogenization of homogeneous catalysts

Since ionic liquids have no vapor pressure, one of the usual methods of product isolation, evaporation of the solvent, is not an option. The product isolation techniques available are distillation or sublimation of the product from the ionic liquid, precipitation of the product and extraction of the product into another solvent. With this final technique the separation of the product from the catalyst becomes an issue. In order to obtain a pure product from a catalytic process by solvent extraction it is preferable to have the product soluble in the extracting solvent and the catalyst not, so that it remains in the ionic liquid phase. This prevents the need for subsequent purification steps to remove the catalyst from the product. In many situations, such as when solid starting materials only have limited solubility in the ionic liquid, it is preferable to have the extracting solvent present during the reaction itself. Hence, ionic liquids are often used in liquid–liquid biphasic systems.

This is not the place to review the whole of biphasic catalysis, which has received a great deal of attention recently [110], and previous reviews of ionic liquids have covered this aspect very well [4]. However, it does lead to one of the areas in which there is a great deal of activity being the development of catalysts that are not easily extracted from ionic liquids. On the whole, ionic liquids are excellent solvents for other ionic species. Therefore, one way in which to have a highly ‘ionophilic’ catalyst is for it to be charged. This was recognized in one of the earliest uses of ionic liquids in catalysis [111], where the cationic Osborne’s catalyst was found to remain in the ionic liquid phase upon product separation whereas the neutral Wilkinson’s catalyst was extracted with the products. However, there are concerns arising from work with simple organic substitution reactions that show that charged species react more slowly in ionic liquids than equivalent neutral species [112]. Another way of viewing this is to question more closely the idea of the ionic liquids being composed of ‘non-coordinating’ ions. When there is a positive charge on the transition metal centre itself the anions of the ionic liquid will bind to the metal more strongly than when the metal centre is uncharged. This, in turn, leads to the anion competing more effectively for the metal site and reducing the ability of the substrate(s) to bind to the metal centre and, therefore, slowing the catalytic reaction. To avoid this problem while still making the catalyst more ionophilic it is possible to achieve this by using an ionic ligand.

Fortunately, ionic ligands have been prepared to make catalysts that are soluble in water for some time [2,113]. Some of these ligands are even commercially available. Again, the seminal Chauvin paper was the first to use this technique by preparing a hydroformylation catalyst from $[Rh(CO)_2(acac)]$ and either monosulfonated- (TPPMS) or trisulfonated- (TPPTS) triphenylphosphine ligands [111]. Although catalyst retention was greatly increased, the reactivity of the catalyst decreased in comparison to the neutral PPh_3 complex. Other ligands that have been used in this way include: guanidinium [114], imidazolium [115], and pyridinium substituted aryl phosphines [116] and 1,1′-bis-(diphenylphosphino)cobaltocenium hexafluorophosphate [117]. These investigations are still in their infancy and much remains to be done. For instance, it would be interesting to know whether the sign of the charge on the ligand has any kinetically significant effect on the way in which the ionic liquid interacts with the catalyst.

There are many different catalyst separation and recovery techniques under investigation at this time. It is rare for more than one technique to be investigated in a single set of experiments with control over the many different variables that can affect the reactivities and selectivities (where relevant) of catalysts. This makes direct comparison of the different methods very difficult. However, recently Cole-Hamilton has published an excellent review of the use of several different techniques in rhodium catalyzed hydroformylations [118]. He points out that it really is too early to pick favorites in this area.

5.2. Alkene hydrogenation reactions

Although there had been earlier examples of the use of ionic liquids in transition metal catalysis; Parshall in 1972 [81], Knifton in 1987 [119], and Carlin and Wilkes in 1990 [120], it is the publication by Chauvin et al. [111] in 1995 of their paper on rhodium catalyzed hydrogenation and hydroformylation reactions that seems to have kick-started this field. This is probably because the new ‘air-stable’ ambient temperature ionic liquids were used for the first time, liberating the worker from the constraints of working with solvents that were difficult to handle. These initial experiments used Osborne’s catalyst, $[Rh(nbd)PPh_3][PF_6]$ (where nbd: norbornadiene) for the hydrogenation of pent-1-ene. In both $[SbF_6]^-$ and $[PF_6]^-$ ionic liquids, the hydrogenation rates were significantly greater than in acetone. There has been no study published to date that reveals why the ionic liquids give this improvement and even the identity of the actual catalyst is in question (see below). The results using $[C_4C_1im][BF_4]$ were disappointing, which is now accepted to be due to dissolved chloride ions remaining from the synthesis of the ionic liquid. The separation of the product alkenes from the reaction mixture was simple and the catalyst containing ionic liquid solution could be recycled.

At almost the same time a paper that is often overlooked came from DuPont and co-workers [121], using $RhCl(PPh_3)_3$ and $[Rh(cod)_2][BF_4]$ (where cod: cyclooctadiene) for the hydrogenation of cyclohexene in $[C_4C_1im][BF_4]$. Here, the advantage claimed was effective recycling of the catalyst solution. Although $RhCl(PPh_3)_3$ gave higher turnover rates, the use of $[Rh(cod)_2][BF_4]$ lead to higher final overall conversion of the cyclohexene to cyclohexane. The ionic $[Rh(cod)_2][BF_4]$ showed greater solubility in the ionic liquid than $RhCl(PPh_3)_3$. The ionophilic form of Wilkinson’s catalyst, with TPPTS as a ligand, has also been used to hydrogenate a number of low molecular weight polymers in $[C_4C_1im][BF_4]$ [122].

It should be noted that there has been some speculation that hydrogenation in ionic liquids is by colloidal, or nanoparticulate, rhodium [123]. However, although the formation of rhodium nanoparticles in $[C_4C_1im][PF_6]$ has been observed [109], and their activity as arene hydrogenation catalysts described, there have been no studies published to date to confirm that they are responsible for the hydrogenation of alkenes, which occurs under milder conditions.

One area in which the ionic liquids are attracting a great deal of interest is in chiral induction and chiral catalysis in particular [124]. The promise that ionic liquids hold for providing systems for the reuse of expensive catalyst solutions and ligands is particularly appealing in this area and a number of reactions have been investigated. This is a particularly pressing concern because of the lack of success that heterogeneous catalysis has had in this area. There has been no suggestion to date that anything other than genuine solution processes are occurring in these reactions. This may well simply be the result of the chelate effect. Since all of these catalysts contain a C_2 symmetric bidentate ligand, they can be expected to form more stable complexes and reduce the tendency towards reduction to the metal.

Chauvin first reported the hydrogenation of α-acetamido cinnamic acid to (*S*)-*N*-acetylphenylalanine [111], using $[Rh(COD)\{(-)\text{-DIOP}\}][PF_6]$ in a biphasic $[C_4C_1im][SbF_6]/^{i}PrOH$ (3/8) system. This, presumably unoptimized, reaction gave a relatively poor selextivity (ee = 64%) and no attempts were made to recyle the catalyst solution.

The non-volatile nature and low solubility of O_2 [125] in ionic liquids makes them particularly easy to prepare oxygen free. This has been used to stabilize the air sensitive catalyst $[Rh(COD)(MeDUPHOS)][CF_3SO_3]$ in a $[C_4C_1im][PF_6]/^{i}PrOH$ biphasic system [126]. This offered a significant handling advantage over using $^{i}PrOH$ alone for the hydrogenation of enamides.

An investigation of the asymmetric hydrogenation of 2-phenylacrylic acid and 2-(6-methoxy-2-naphthyl)acrylic acid in $[C_4C_1im][BF_4]$ using the chiral catalyst $[RuCl_2\text{-}(S)\text{-}BINAP]_2.NEt_3$ revealed similar conversions and selectivities as seen in, the usually preferred, alcohol solvents under the same conditions [127]. Further to this, it was demonstrated that the catalyst solution could be recovered and used again. The enantioselectivity was found to be independent of the hydrogen pressure. The enentioselectivities of these hydrogenations are known to be positively dependent on the availability H_2 to the catalyst and hence the hydrogen concentration in the solution. This suggests that at the hydrogen pressures used (35–100 bar) the hydrogen concentration in the solution was maintained at the saturation concentration in the ionic liquid and that H_2 transfer into the ionic liquid was fast in comparison hydrogen uptake by the substrate [128]. More recent results using both $[C_4C_1im][BF_4]$ and $[C_4C_1im][PF_6]$ as solvents for the hydrogenation of α-acetamido cinnamic acid with $[Rh(COD)(EtDUPHOS)][CF_3SO_3]$ showed that it was indeed the saturation concentration of H_2 in the different ionic liquids at a given pressure that controlled both the activity and the selectivity of the catalyst rather than the H_2 pressure (5–100 bar) in the reaction vessel itself [129]. The authors saw similar results for the kinetic resolution of methyl-3-hydroxy-2-methylenebutanoate by $[RuCl_2\text{-}(S)\text{-tol-BINAP}]_2\cdot NEt_3$. The ability to recycle the catalyst solution was demonstrated once more, although the conversion dropped on successive runs, suggesting that some catalyst leaching into the product layer was occurring. This problem is being addressed by derivitizing the ligand with posphonic acid [130] or imidazolium [131], or using a complex with other ionic ligands, such as the carborane $[C_2B_9H_{11}]^{2-}$ [132], to increase the solubility of the catalyst in the ionic liquid. In this latter example, it is believed that the carborane ligand plays an active role in the catalysis.

Jessop et al. [133] have studied the selectivities of the $[Ru\{(R)\text{-tol-BINAP}\}(CH_3CO_2)_2]$ catalyzed hydrogenations of *trans*-2,3-dimethylacrylic acid (tiglic acid) and 2-phenylacrylic acid (atropic acid) in a variety of ionic liquids. The interesting feature of these substrates is that the enantioselectivity of the hydrogenation of tiglic acid is negatively dependent on the hydrogen concentration (higher selectivity at low concentration), whereas that of atropic acid is positively dependent (higher selectivity at high concentration).

For tiglic acid it was found that the selectivities were excellent and increased in the order $\{[C_4C_1im][PF_6]/^iPrOH\} < [C_2C_1im][OTf] < [C_4C_1im][BF_4] = [C_1C_4py][BF_4] = \{[C_4C_1im][PF_6]/\text{toluene}\} < [C_4C_1im][PF_6] = [C_3C_1C_1im][Tf_2N] < [C_2C_1im][Tf_2N]$ at low (5 bar) pressure. For atropic acid the selectivities were poor for the pure ionic liquids and increased in the order $\{[C_4C_1im][PF_6]/\text{toluene}\} < [C_4C_1im][BF_4] < [C_2C_1im][OTf] < [C_4C_1im][PF_6] = [C_2C_1im][Tf_2N] < \{[C_4C_1im][PF_6]/^iPrOH\} < [C_3C_1C_1im][Tf_2N]$ at moderately high (50 bar) pressure.

The trend for tiglic acid is very much an anion effect for the pure ionic liquids as has been seen for H_2 solubility [134]. However, although the anion seems to be important in determining the selectivity of the hydrogenation of atropic acid in the pure ionic liquids, it is not quite so dominant and there is not the simple reversal of the behaviors that one might expect if a single parameter were the only cause of the observed selectivities. It is possible that for atropic acid, for which maintenance of the highest possible H_2 concentration is essential to maintain the selectivity, the rate of hydrogen transfer to the ionic liquid becomes important and other properties, such as viscosity, begin to play a role. This notwithstanding, hydrogen solubility is clearly one of the principal variables in the selection of the most appropriate ionic liquid for enantioselective hydrogenations and, indeed, which substrates are going to give good selectivities in ionic liquids.

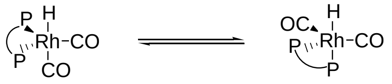
The hydrogenation of but-2-yne-1,4-diol has been used demonstrate the possibility of using a thermally controlled ionic liquid–water biphasic or homogeneous system for catalysis [135]. $[C_8C_1im][BF_4]$ is immiscible with water at room temperature, but fully miscible at the reaction temperature of 80 °C. This removes many of the concerns associated with mass transfer when the reaction is occurring. Firstly, there is no interface for the reagent to cross and secondly the water reduces the viscosity of the ionic liquids considerably. Then, when the system is cooled to room temperature, it separates into two phases and the product is removed with the water phase and the catalyst remains in the ionic liquid.

5.3. Hydroformylation

Hydroformylation has also been extensively studied in ionic liquids. This is in spite of the fact that there is already a highly efficient aqueous or organic biphasic industrial process for thee hydroformylation of olefins. However, the current process can only be used with short-chain ($\leq$5 C) olefins, because heavier olefins are insufficiently soluble in water for an effective reaction to occur. Ionic liquids, with higher solubilities for these higher olefins, offer the possibility of replacing the water layer and extending the usefulness of the biphasic technique [115–117].

Olivier-Bourbigou and co-workers [116] investigated the hydroformylation of 1-hexene in a variety of ionic liquids with imidazolium and pyrrrolidinium cations and a range of different anions. Initially they introduced the rhodium as $[Rh(CO)_2(acac)]$ with four equivalents of the charged phosphine TPPMS and measured the turnover frequency of the catalyst in the different ionic liquids. For the $[BF_4]^-$, $[PF_6]^-$, $[CF_3SO_3]^-$, and $[CF_3CO_2]^-$ ionic liquids they found that the TOF of the reaction was dependent upon the solubility of the 1-hexene in the ionic liquid, possibly suggesting a mass transfer limited process. However, when they used three different $[(CF_3SO_2)_2N]^-$ based ionic liquids the TOF did follow the solubility of the 1-hexene in these ionic liquids, but the TOF's of the whole set were lower than expected when compared to the other ionic liquids. It is not at all clear why this discrepancy exists. Given that the $[(CF_3SO_2)_2N]^-$ ion is one of the least basic of the anions used [21], and that $[(CF_3SO_2)_2N]^-$ ionic liquids are generally at the low end of ionic liquid viscosities [1], one might have expected any deviation to be in the other direction. When this puzzle is solved it may be possible to design ionic liquids that will give greater reactivities.

The paper also investigated the effect of different ionophilic ligands, some positively and others negatively charged [116]. Phosphites are widely used as ligands for hydroformylation, but their hydrolytic instability precludes their use in aqueous systems. Therefore, the ionic liquids allow a rare opportunity to use them in a biphasic system. This gave improved catalytic activity and selectivity for the linear aldehyde than was achieved with the phosphine ligands used, offering another potential route to an effective method for the hydroformylation of longer chain olefins.



Scheme 8. The equilibrium between two forms of a hydroformylation catalyst in $[C_4C_1im][PF_6]$.

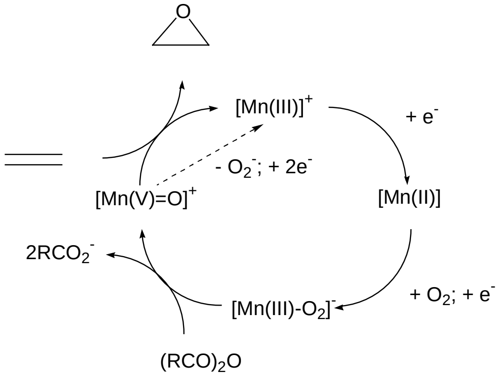
The effect of co-solvents on the hydroformylation of 1-octene has also been investigated [136]. The rhodium was introduced as $[Rh(CO)_2(acac)]$ with four equivalents of 2,7-bissulfonate-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (sulfoxanthos). Selectivity to linear aldehyde was best in pure $[C_4C_1im][PF_6]$ than in the same ionic liquid with added water or toluene. The TOF in the pure ionic liquid and in the ionic liquid–toluene system were the same, but lower than that in the ionic liquid–water system. Subsequently in [137], it was shown that the rhodium is present in solution in equilibrium between two trigaonal bipyramidal forms (Scheme 8). The position of the equilibrium is dependent upon both the temperature and the pressure of syngas applied, but is not disturbed by the presence of the substrate.

Hydroformylation has excellent potential as a reaction for use with ionic liquid–$scCO_2$ systems. The reagents and products have good solubilities in the $scCO_2$ while using a charged ligand for the catalyst ensures that it remains in the ionic liquid throughout the process, allowing continuous flow reactors to be used [13d]. This system also offers the possibility of reducing mass transfer constraints, by the $scCO_2$ increasing reagent solubility in the ionic liquid phase and reducing its viscosity. Initial results have been extremely promising, with the hydroformylation of hex-1-ene in a $[C_4C_1im][PF_6]$–supercritical CO_2 biphasic mixture giving much higher selectivity to the desired aldehyde product than the pure ionic liquid, although at some cost in conversion. Degradation of the $[PF_6]^-$ anion was noted as the reason for a drop off in both reactivity and selectivity after several repeated runs.

5.4. Oxidation

Although most ionic liquids currently in use are stable to oxidation, and so they provide ideal solvents for oxidation processes, this chemistry has only developed in ionic liquids in the last few years.

$Ni(acac)_2$ has been used as the catalyst for a number of aerial oxidations of para-substituted benzaldehydes with moderate yields of the corresponding acids in $[C_4C_1im][PF_6]$ [138]. In the absence of the catalyst very little oxidation was observed. The same combination of catalyst, ionic liquid and oxidant has also been used in the synthesis of ethylbenzene hydroperoxide from ethylbenzene [139]. However, in this case it is more accurate to describe the reaction system as a solution of the catalyst and ionic liquid in ethyl benzene. The two principle advantages of the ionic liquid are that it has a greater solubility in the ethylbenzene and the poorly coordinating anion competes less well for the metal centre than the previously used tetraalkylammonium halide salts.

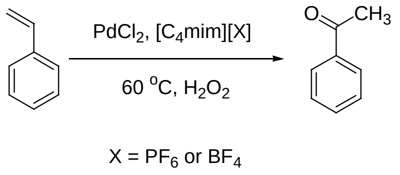


Scheme 9. Proposed mechanism for the electro-assisted activation of oxygen by Jacobson's catalyst.

Jacobsen's catalyst has been used for asymmetric epoxidations with aqueous NaOCl in $[C_4C_1im][PF_6]/CH_2Cl_2$ (1:4) mixtures [140]. The mixed solvent system was used because the ionic liquid itself was solid at the reaction temperature. Yields and selectivities were similar to those in the absence of the ionic liquid, but the use of the ionic liquid gave faster reactions. The ionic liquid and the reaction products were found in the organic phase, which was separated from the aqueous phase. The CH_2Cl_2 was removed from the ionic liquid–catalyst–product mixture in vacuo, before the product was washed from the ionic liquid with hexane. The resultant solution of the catalyst in the ionic liquid could then be reused with a small drop in enantioselectivity. Subsequent electrochemical investigations revealed some of the details of the mechanism for the reaction (Scheme 9) [141].

$[C_4C_1im][PF_6]/CH_2Cl_2$ mixtures have also been used for the epoxidation of styrene by $PhI(OAc)_2$ with a manganese porphyrin catalyst [142]. It was shown that the volume fraction of $[C_4C_1im][PF_6]$ in the mixture greatly affected the yield of the epoxide, with maximum results being achieved between 40 and 60 volume percent ionic liquid. Unfortunately, it is not possible at this stage to be sure if it is the $[C_4C_1im][PF_6]:CH_2Cl_2$ ratio, the $[C_4C_1im][PF_6]$:catalyst ratio or a combination of both that is giving the effect.

The rich redox chemistry of ruthenium makes its compounds useful oxidation catalysts. As a salt itself, tetrapropylammonium perruthenate is an ideal candidate for an ionic liquid integrated catalyst, with the hope of providing a recycle route and that the ionic liquid might stabilize this usually unstable compound [143,144]. The initial report [143] used solutions of $[C_2C_1im][PF_6]$ or $[Et_4N]Br$ in dichloromethane (1:10 (w/v)) as the medium for the oxidation of alcohols to aldehydes and ketones by *N*-methylmorpholine *N*-oxide. By moving to ionic liquids that are free-flowing liquids at room temperature, it was possible to remove the dichloromethane from the system entirely [144]. In this study, it was found that the results of the catalyses were dependent not only on the ionic liquid used, but also its method of preparation and



Scheme 10. The reaction of styrene with H_2O_2 in the presence of ionic liquids.

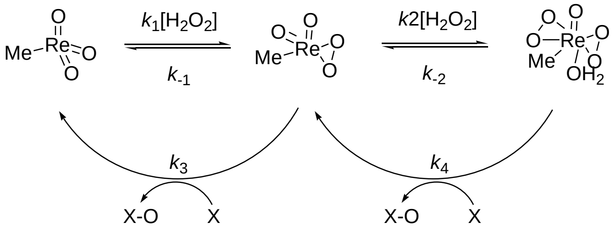
purification. This indicated that even minor impurities that were present in the ionic liquids were important in determining the outcome of the reactions. Given that catalysts are often used in very low concentration, this is likely to be true of many catalytic processes. These systems have also been used for aerobic oxidations [143,144], as have other ruthenium catalysts in ionic liquids [145].

It is well known that the presence of water often leads to significant over oxidation of aldehydes to acids in this reaction. This is usually dealt with by the addition of molecular sieves to the reaction mixture. Hence, it is particularly interesting that, even in the hydrophilic ionic liquid $[C_4C_1im][BF_4]$, this was not necessary and, even upon the addition of water, no over oxidation was seen. The same lack of over oxidation has also been seen in the TEMPO–CuCl catalyzed oxidation of alcohols to aldehydes [146]. It is known that the anions of the ionic liquids interact strongly with water [15], and it is possible that this interaction makes the water unavailable for reaction with the aldehyde. This could prove to be useful in other water-sensitive processes.

The oxidation of styrene to acetophenone (Scheme 10), the Wacker oxidation, has been reported to be catalyzed by $PdCl_2$ in the presence of $[C_4C_1im][BF_4]$ and $[C_4C_1im][PF_6]$ [147]. The need for only a small excess (1.15 equivalent) of aqueous H_2O_2 was demonstrated, which is a significant increase in H_2O_2 utilization over previously reported methods. As with several of the oxidations described above, it was shown that even a very small amount of ionic liquid could improve the reaction rate significantly.

The Wacker oxidation of hex-1-ene has also been investigated in ionic liquid–$scCO_2$ biphasic mixtures and the results compared to those in ionic liquid or $scCO_2$ alone [148]. Selectivity for hexan-2-one was found to be appreciably greater (>90%) in the biphasic system than in either pure $scCO_2$ or $[C_4C_1im][PF_6]$, without any loss in conversion, and also with greater stability of the catalyst.

Benzyl alcohol has been dehydrogenated with oxygen and a palladium acetate catalyst source in a variety of substituted imidazolium based ionic liquids to benzaldehyde with higher rates than in DMSO [149]. In $[C_6C_1im]Cl$ a homogeneous solution of $[PdCl_4]^{2-}$ was formed, conversion rates were low and dibenzyl ether was produced in addition to benzaldehyde. When $[BF_4]^-$ ionic liquids were used, the palladium acetate precipitated palladium metal under the same reaction conditions and high rates were achieved without the formation of any by-products. Again the over-oxidation of the benzaldehyde to benzoic acid was not observed without the deliberate addition of water.



Scheme 11. Rhenium oxo- and peroxo- species present in the MTO-UHP epoxidation system in ionic liquids.

The epoxidation of alkenes with urea hydrogen peroxide (UHP) with methylrhenium trioxide (MTO) as the catalyst has received some attention [150]. This reaction is usually heterogeneous in organic solvents, because of the poor solubility of the UHP. However, in $[C_2C_1im][BF_4]$ a homogeneous solution is formed. Yields of the epoxides vary from fair to excellent and are comparable to those reported in other systems. In addition, the catalyst solution can be recycled after extraction of the products with ether. Spectroscopic evidence showed that both monoperoxo- and diperoxorhenium species were present in the solution and active in the oxidation chemistry (Scheme 11). The use of this system, with $[C_4C_1im][BF_4]$ as the ionic liquid, has been extended to the epoxidation of glycols [151]. Here, no attempt was made to isolate the somewhat unstable epoxide and the reaction was conducted in the presence of dibutylphosphate, which gave the glycosyl phosphate product.

Detailed kinetic investigations have shed some light onto the operation of this system in ionic liquids [152]. First, it was determined that the rate of the oxidation by the diperoxorhenium species (k_4) is greater than that by the monoperoxorhenium species (k_3) for all substrates investigated in all of the ionic liquids used, whereas in acetonitrile they are approximately the same. For most of the substrates used the k_4 values in $[C_2C_1im][BF_4]$ were similar to those in a 1:1 CH_3CN/H_2O mixture. In the study of the effect of different ionic liquids, it was shown that there was no real effect of changing the cation of the ionic liquid, but there was a distinct effect on changing anion, on both k_3 and k_4. This was attributed to the greater coordinating ability of the $[NO_3]^-$ ion leading to it interfering with the oxidation reactions more than the less coordinating $[BF_4]^-$.

The kinetics of the formation of the two peroxo species in ionic liquids (k_1 and k_2) have also been investigated [153]. The formation of the monoperoxorhenium species was found to be very fast and measurement of k_1 was outside the range of the study. However, k_2 could be deduced using either UHP or aqueous H_2O_2 (30%) as the peroxide source. In pure $[C_4C_1im][NO_3]$ k_2 was approximately the same as in Acetonitrile, but as water was added the rate constant increased. Several water miscible ionic liquids were compared as 9:1 (v/v) ionic liquid–water solutions and k_2

$$2\mathrm{ArX} + 2e^- \longrightarrow \mathrm{Ar{-}Ar} + 2\mathrm{X}^-$$

$$\mathrm{X} = \mathrm{Cl\ or\ Br}$$

Scheme 12. The electroreductive homo-coupling of an aryl halide.

was found to be the same for both peroxide sources in all of them.

5.5. *Nickel catalyzed oligomerisation of ethene*

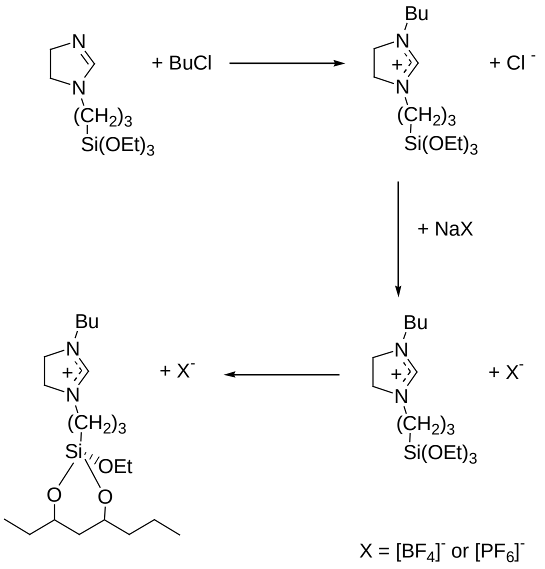
Finally, in this section, I would like to mention this reaction because of the attempt to correlate the TOF of the catalysis with the results of solvatochromic probe measurements [154]. A cationic nickel catalyst was used in four [$C_nC_1$im][PF_6] ($n = 4$, 6, 8 or 10) ionic liquids, dichloromethane and butane-1,4-diol. It was found that the TOF of the oligomerisation was in great part determined by the coordinating ability of the solvent as reported by the UV–vis spectrum of [Cu(acac)(tmen)][BPh_4]. This was the first time that this type of analysis was applied, but will probably not be the last.

6. Ionic liquids as solvents for electrocatalysis

As conducting media, often with large electrochemical windows, ionic liquids clearly have potential as solvents for electrosynthesis. In fact, I find it surprising that there has not been more activity in this area. Recently, the nickel catalyzed electroreductive homo-coupling of alkyl, benzyl and aryl halides has been reported (Scheme 12) [155,156]. In both of these studies (bipy)NiX_2 (X: Cl or Br) was used as the homogeneous catalyst. It was proposed that the Ni(II) complex is reduced to a Ni(0) species, which then reacts by oxidative addition to the aromatic halide. In [C_8C_1im][BF_4]/DMF (9:1 (v/v)) bromobenzene gave 80% yields of biphenyl [155], whereas only a 35% yield was achieved in neat [C_4C_1im][Tf_2N] [156]. This methodology is in its infancy in ionic liquids, but has great potential for the future.

7. Supported ionic liquids

Whilst there are many advantages to a reaction system being a liquid, sometimes there is a need to immobilize it. Hence, there has been some interest in immobilizing ionic liquid solutions. The first of these used a poly(vinylidene fluoride)–hexafluoropropylene copolymer to prepare an ionic liquid–polymer gel [157]. The gels produced from a series of 1-butyl-3-methylimidazolium based ionic liquids with suspensions of Pd on activated carbon gave flexible films (ca. 0.06 cm thick) that held their shape well. These were then successfully used for the hydrogenation of propene. This was then followed up by using solutions of Wilkinson's catalyst to prepare the gels [158]. Hydrogenation of the olefin took place as the olefin diffused through the gel mounted on an in-line filter.



Scheme 13. The preparation of surface anchored ionic liquid phase.

There have been a number of reports of the immobilization of chloroaluminate(III) and chloroferrate(III) ionic liquids [159]. However, these are really a way of preparing solid catalysts from ionic liquids. A different approach has been taken by Mehner et al. [160] and Fehrmann and co-workers [161] who have both coated support materials with a layer of a [C_4C_1im][PF_6] solution of catalyst, so combining the advantages of the solid support and the solution chemistry. Both groups noted that the catalysts showed both high reactivities and good long-term stabilities. In a further development, Mehner et al. [162] went on to anchor the cation of the ionic liquid to the support by preparing 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydoimidazolium chloride and reacting it with the basic surface of silica gel (Scheme 13).

8. Conclusions

The study of ionic liquids has spread throughout the chemical community at a staggering pace. Only time will tell whether this will be sustained into the future. I hope that I have been able to demonstrate here that, in catalysis at least, there is enough of interest to support a great deal of further research. The available literature in the field clearly 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. However, the promise is there that one day it will become possible to use that understanding to manipulate reactions and to develop applications for ionic liquids in a sophisticated manner. It is, therefore, encouraging that detailed studies are beginning to appear in the literature, such as kinetic investigations and systematic comparisons of different ionic liquids. It will only be by gaining a thorough understanding of these fascinating liquids that their true potential will be realized. Good luck in your research.

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