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Supramolecular effects involving the incorporation of guest substrates in imidazolium ionic liquid networks: Recent advances and future developments

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The interest in ionic liquids (ILs) as green solvents has grown enormously in the last few years. ILs have been proved to be convenient and economical solvents due to their efficiencies, non-toxicities and recyclabilities. Logically, these new media are used in a wide range of organic reactions. Recent investigations of the physicochemical properties of imidazolium ILs suggest that they behave as polymeric supramolecules that cannot be seen as conventional solvent. Electrostatic, H-bonds and π-stacking interactions occur in imidazolium ILs. When various organic compounds are mixed with imidazolium ILs, 'inclusion complexes' are formed and complex supramolecular organisation is created. In other words, ILs can be seen as a pre-organised medium that can modify the molecular reactivity (selectivity, substrate discrimination, etc.) by the formation of 'inclusion complexes' between guests (reactive species) and the 'host networks' (ILs). This mini review is intended to describe the imidazolium IL organisation (aggregation properties, formation of 'inclusion complexes', etc.) and to underline some of the effects on the organic reactivity of the inclusion of the guest substrates in imidazolium ILs.

Keywords: ionic liquids; imidazolium salts; host networks; inclusion complexes; organic reactions

Introduction

At the beginning of the 1990s, organic chemists in academia and industry were excited about the prospect of a new green chemical revolution based on ionic liquids (ILs) that could dramatically reduce the use of hazardous and polluting organic solvents (*1–4*). ILs are defined as special 'molten salts' with melting points below 100°C. The 1,3-disubstituted imidazolium salts are the most popular and best-studied classes of ILs. The careful choice of the anion coupled with the imidazolium cation give rise to different physicochemical properties. For example, increasing anion size can reduce the viscosities, the melting points and to enhance conductivities (*5*). Regarding the anion, imidazolium ILs can be classified into four groups (*5*), i.e. (a) systems based on relatively hygroscopic anions like [Cl^-] and [$AlCl_4^-$], (b) stable systems based on anions such as [$CF_3SO_3^-$] (≡[OTf]) and [$(CF_3SO_2)N^-$] (≡[NTf_2]), (c) systems based on water reactive anions that can generate HF by hydrolysis, e.g. [PF_6^-] and [BF_4^-] and (d) systems based on alkylsulphates (*6*) and alkylsulphonates (*7, 8*). The combination of different cations and anions can allow for designing salts for specific applications, for example, as solvents for organic, organometallic and enzymatic catalyses (*9–12*), separation processes and nano- and electrochemistry (Figure 1) (*13–22*).

Structural aspects

The origins of the low melting behaviour of ILs, including extensive thermochemical studies and characterisation of phase behaviour, have been the subject of many recent reports (*23, 24*). The formation of the liquid phase in ILs may be guided by the same principle governing the melting point of classical ionic compounds such as NaCl. The larger the ions and the smaller the charge, the lesser the energy is necessary to break the bond, which causes a depression of the melting point. Relatively large quaternary ammonium salts such as 1,3-dialkylimidazoliums are more difficult to fit into a lattice than classical alkaline halides and, as a result of a lower lattice energy, such ionic compounds may exist as liquids at room temperature. It is worth emphasising again that one of the main differences between room temperature ILs and simple molten salts is the molecular asymmetry built into at least one of the ions. This asymmetry opposes the strong charge ordering due to the ionic interactions that normally would cause the system to crystallise, and thus a wide liquid range is obtained. Computational methods are available to predict the melting points of imidazolium salts or other ILs with reasonable accuracy (*25, 26*). There are mainly two approaches for describing and rationalising the properties of ILs when used in chemical reactions: they behave as a solvent or as a liquid support. Although

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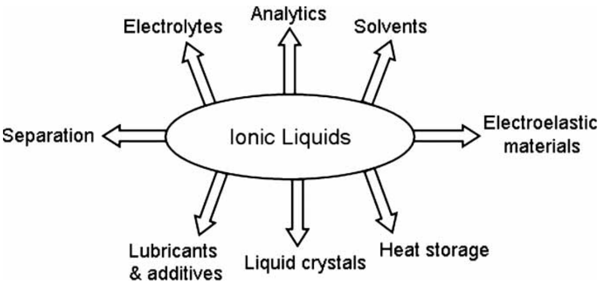

Figure 1. Uses and applications of ILs.

different and sometimes contradictory solvent properties have been derived from several studies, such as polarity (mainly using solvatochromic dyes), linear-free relationships and partitioning investigations (*27–37*), it is almost a consensus that ILs, in particular those based on the 1,3-dialkylimidazolium cation, have polarities comparable to DMF, acetonitrile and short-chain alcohols and a coordination ability similar to that of dichloromethane (*19, 38–43*).

This approach is usually helpful for the rationalisation of the physical and chemical processes occurring in ILs, but in various cases this approach is insufficient. However, ILs may also be regarded as supramolecular networks in which the introduction of other molecules occurs with the formation of inclusion-type compounds (*44, 45*). This model is based on the fact that imidazolium-based ILs display a pronounced self-organisation in the solid, liquid and even in the gas phase (*46*). Indeed, simple analysis of the physicochemical properties of solid salts can yield important information about the structural features of the same material in the liquid phase. For example, various X-ray and neutron scattering studies of solid and liquid NaCl suggest that the structural organisation observed in the crystal exists in the liquid phase (*47, 48*). Furthermore, while long-range order is lost on going from the crystal to the liquid, similarities remain as a consequence of the Coulomb forces between cations and anions of the ILs. Long-range Coulomb interactions in organic ILs can lead to longer spatial correlations than those in comparable classical van der Waals organic liquids (*49*). This approach has also been used in the case of contemporary ILs, in particular for imidazolium salts. In this respect, several physical studies such as IR (*50–52*), Raman (*53*), neutron diffraction analysis (*54*), XRD (*55, 56*), NMR (*57–61*) and electrospray ionisation mass spectrometry (ESI-MS) (*62*) indicate that indeed 1,3-dialkylimidazoliums possess analogous structural patterns in the solid, liquid and gas phases.

Imidazolium IL host networks are a platform decorated with a number of binding sites (H-bonds, electrostatic interactions, π-stacking and combinations of these forces; Figure 2) that present obvious advantages for the production of molecular receptors, but a disadvantage in that precise organisation of an invited organic reaction in the IL network is not known. Therefore, the introduction of other molecules and macromolecules occurs with a disruption of the H-bond network and this generates nanostructures with polar and non-polar regions where inclusion-type compounds can be formed, i.e. chemical and physical processes in ILs are akin to processes occurring in a pure universal ligand template. These inclusion compounds can involve small molecules, macromolecules and/or nanoparticles and the stabilisation of this process is mainly due to the electronic and steric effects provided by the nanostructures of the type $\{[(I)_x(X)_{x-n}]^{n+}, [(I)_{x-n}(X)_x]^{n-}\}$ (I: imidazolium cation and X: anion) (*63*).

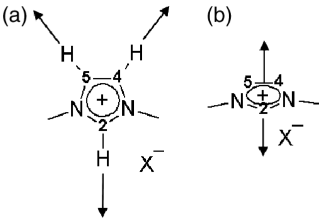

Figure 2. (a) The three T-stacking and H-bond donors of an imidazolium ring and their directionality and (b) π-stacking.

Self-assembly of pure imidazolium ‘host network’

The self-assembly of pure imidazolium ILs have already been extensively described and we invite the reader of this mini review to consult these more specific reviews (*24, 45*). Here, we are not intending to present a comprehensive compilation of self-organisation of imidazolium ILs, but only to illustrate some of the organisations observed in pure imidazolium ILs in order to understand the inclusion phenomenon of guest compounds in the imidazolium IL network.

Solid phase

The most interesting and used ILs are those that are liquids under 100°C and their crystal structures have already been determined by X-ray diffraction. It is the case of 1,3-disubstituted imidazolium ILs, as they are one of the most popular ILs. Almost all 1,3-disubstituted imidazolium salts present a typical organisation in the solid state by forming supramolecular networks of cations and anions connected by H-bonds (Figure 3).

This simplest organisation is generally obtained for small and spherical anions with symmetrical cations (*45*). For example, in the case of the octahedral $[PF_6]^-$ anion, all the equatorial fluoride atoms participate in the H-bonding network, but in the case of the tetrahedral $[BF_4]^-$ anion only three of the fluoride atoms are involved in H-bond interactions. Different H-bonds are developed in these systems, the strongest H-bond

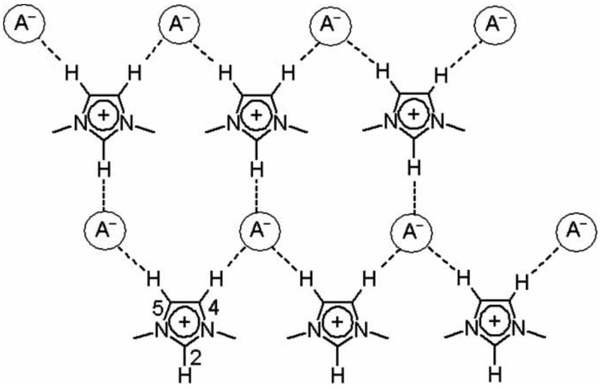

Figure 3. Simplified two-dimensional structural organisation of the imidazolium ILs.

involving the most acidic H(2) of the imidazolium cation, followed by the two H(4) and H(5) and sometimes by the protons of the α-carbon on nitrogen. These H-bond interactions are weak to moderate and are mostly electrostatic in nature (H···X bond lengths >2.2 Å, C—H···X bond angles between 100° and 180°). The supramolecular framework can also involve other interactions between the cations and the anions. For anions with phenyl residues, such as $[B(Ar)_4]$ anions, a network can be formed through relatively strong C—H···π stacking.

Generally, with spherical anions, the two-dimensional organisation, described above, is completed in the three-dimensional by the arrangement of the imidazolium channels and anion chains (Figure 4). Sometimes, π-stacking interactions occur between the imidazolium rings, or in the case of 1-alkyl-3-methylimidazolium salts a relatively weak C—H···π interaction via the methyl group and the π-system of the imidazolium ring.

However, the structural arrangement described above depends on the anion geometry, and the internal arrangements along the imidazolium columns vary with the type of the *N*-substituents (e.g. the presence of heteroatoms). Moreover, it is important to note that π–π stacking, entropy effects and electrostatic interactions may not always favour the formation of structures of the type shown in Figure 3. The three-dimensional arrangement of the imidazolium ILs is generally formed through chains of the imidazolium rings. This molecular arrangement generates channels in which the anions are generally arranged as chains. This structural pattern depends on the anion geometry and the internal arrangements along the imidazolium columns, and varies with the type of *N*-alkyl substituents. These IL structures can adapt to the inclusion of many species, as they provide hydrophobic or hydrophilic regions and a high directional polarisability that can be oriented parallel or perpendicular to the included species.

Liquid phase

The concept of Coulomb interactions between cations and anions in ILs maintained in the liquid phase of imidazolium salts has been demonstrated by several modern physical studies such as IR (*50–52*), Raman (*53*), neutron diffraction analysis (*54*), XRD (*55, 56*) and NMR (*57–61*) indicating that 1,3-dialkylimidazoliums possess analogous structural patterns in the solid and liquid phases. The intrinsic strength of the H-bonds between imidazolium cation and anions follows the order $[CF_3CO_2] > [BF_4] > [PF_6] > [BPh_4]$, as shown by the IR and NMR spectrometry studies.

Gas phase

The mass spectrometry experiments on various 1,3-disubstituted imidazolium ILs demonstrated that structural organisation is similar in solid, liquid and gas phases (Figure 5). ESI-MS was found to gently and efficiently transfer small to large as well as singly to multiply charged $(I^+)_n(X^-)_m$ supramolecules of imidazolium ion (I^+) ILs

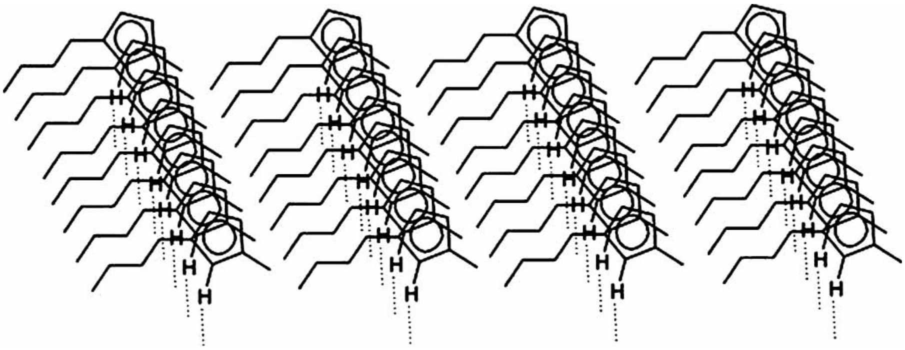

Figure 4. Simplified three-dimensional structural organisation of the imidazolium ILs.

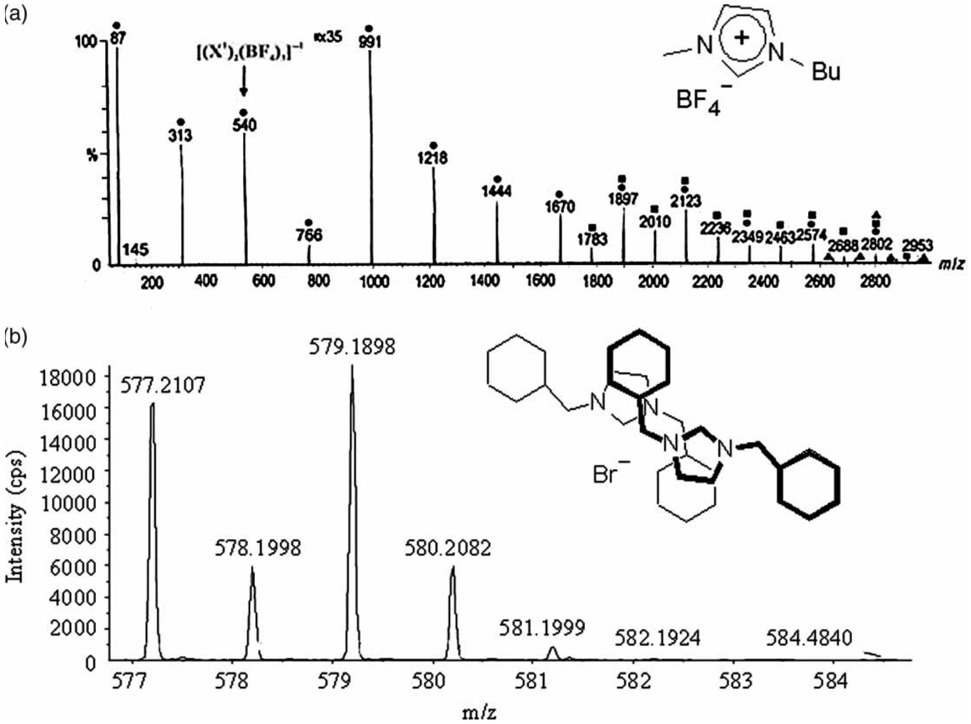

Figure 5. (a) ESI-MS mass spectrum in the negative ion mode of an acetonitrile solution of 1-butyl-3-methylimidazolium[BF_4] ([BMIM][BF_4]). Note the series of singly negatively charged gaseous $[(BMIM)_n(BF_4)_{n+1}]^-$ supramolecules of *m/z* 313, 540, 766, 991, etc. ($\Delta m/z$ 226 for ^{11}B). The intensity scale has been increased from *m/z* 900 to show more clearly the series of doubly charged supramolecules $[(BMIM)_n(BF_4)_{n+2}]^{-2}$ ($n = 13–25$) of *m/z* 1783, 1897, 2010, etc. ($\Delta m/z$ 113 for ^{11}B), and the triply charged ones $[(BMIM)_n(BF_4)_{n+3}]^{-3}$ ($n = 34–39$) of *m/z* 2648, 2723, 2799, 2802, etc. ($\Delta m/z$ 75.3 for ^{11}B). The 'magic' number supramolecule $[(BMIM)_2(BF_4)_3]^{-1}$ is indicated. ●, singly; ■, doubly; ▲, triply charged (Reproduced with permission from Ref. (*46*). Copyright Wiley-VCH Verlag GmbH & Co.). (b) Partial HR-MS spectra of the ([1,3-dibenzylimidazolium])$_2$[Br] dimer observed in water solution at 30 mM. The double bonds are voluntary omitted on the dimer structure (Reproduced with permission from Ref. (*64*). Copyright American Chemical Society).

to the gas phase, and to reveal the 'magic numbers' for their most favoured assemblies (*46, 64*).

Liquid crystal

The merging of imidazolium ILs and liquid crystal chemistry has indeed begun to lead to a new range of materials (Figure 6). The origin for this supramolecular organisation can be found in the formation of 'Coulombic layers' where the ionic head groups interact with the counterions, and 'van der Waals' layers built from (anti)parallel stacking of the alkyl chains. Hexafluorophosphate salts combined with imidazolium ILs bearing eicosyl and methyl alkyl chains have been investigated by differential thermal analysis and show one or more LC transitions. Melting to isotropic liquids occur at rather high temperatures (>100°C) (*65*).

It is evident that 'pure' 1,3-dialkylimidazolium ILs in the solid, liquid and gas phases are well-organised H-bonded polymeric supramolecules. Moreover, there is now much evidence indicating that the supramolecular organisation can be maintained when they are mixed with other substances.

Molecular inclusion of guests in the imidazolium 'host network'

Examples of inclusion of small molecules

One of the most widely used and studied IL families is the one based on imidazolium cations, in particular [1-alkyl-3-methylimidazolium][PF_6]. The cations are composed of a polar head group, where most of the electrostatic charge is concentrated and of a non-polar alkyl side chain, whereas the [PF_6] anion is octahedral, hence almost spherical. The main difference between room temperature ILs and simple molten salts (*66, 67*) is the molecular asymmetry built into (at least one of) the ions, usually the cation, as in the example given. This asymmetry opposes the strong charge ordering due to the ionic interactions that normally would cause the system to crystallise, and, thus, a wide liquid range is obtained. Due to the molecular structure of the cations in [1-alkyl-3-methylimidazolium][PF_6] ILs, liquid crystalline phases are observed for alkyl side chains longer than dodecyl, but up to C_{12}, the liquid phase is isotropic (*68*).

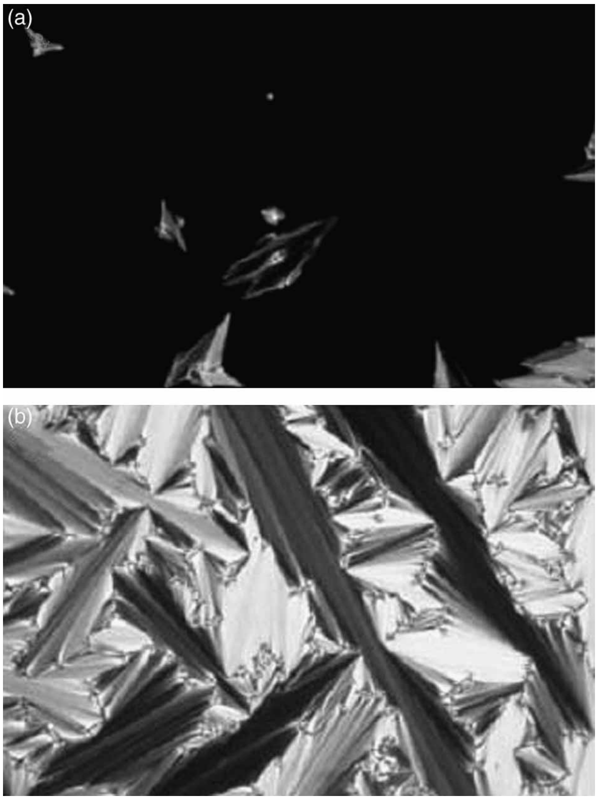

Figure 6. (a) Polarising optical microscope image observed upon slow cooling of the isotropic melt clearly show the emergence of batonnets with positive units. (b) Typical smectic-A phase obtained from **1c** between 117 and 175°C (Reproduced with permission from Ref. (*65*) Copyright Wiley-VCH Verlag GmbH & Co.).

To our knowledge, Compton was the first to postulate that ILs containing dissolved water 'may not be regarded as homogeneous solvents, but have to be considered as nanostructured with polar and non-polar regions' (*69*), to explain the large differences in the diffusion of neutral and charged solutes that are observed when comparing dry and wet ILs. These authors did not extend such a hypothesis to pure ILs, but one of them considered the existence of H-bond networks (*70*). Such H-bond networks observed in solution are also found in the solid phase.

Insertion of water molecules into the crystal structure has recently been reported for [1,3-dibenzylimidazolium][Br], where an atypical supramolecular network organisation of cations and anions, compared with the other reported imidazolium salt crystals has been observed. No direct H-bonds between cations and anions were observed in this case, but water molecules connect anions and cations in the supramolecular network (Figure 7). Organisation of water molecules in the lattice supports the hypothesis of polar and non-polar regions of the supramolecular network (*64*).

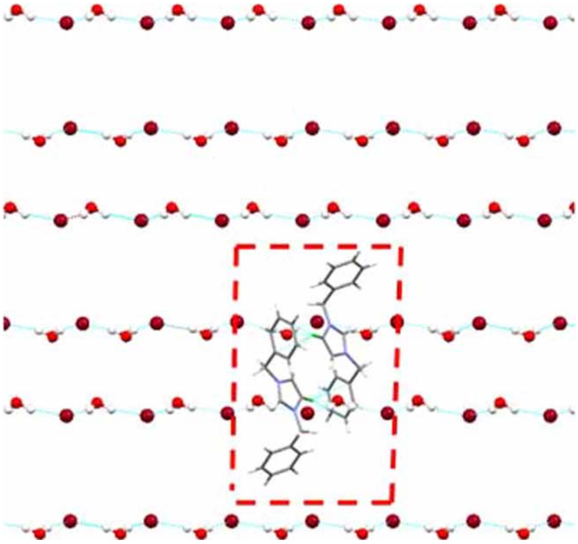

Figure 7. Network and dimer formed by 1,3-dibenzylimidazolium[Br] (see CCDC reference number 665763).

Benzene in ionic liquids

The stabilisation of the pre-organisation process of ILs is mainly due to the stereoelectronic effects provided by the nanostructures of the type $\{[(\mathrm{I})_x(\mathrm{X})_{x-n}]^{n+}, [(\mathrm{I})_{x-n}(\mathrm{X})_x]^{n}\}$ described above. Therefore, the proper combination of imidazolium cations and anions can lead to highly selective materials for the extraction of aromatic compounds. Moreover, different types of H-bonds may be operative depending on the structural and electronic properties of both the IL and aromatic compounds. 1,3-Dialkylimidazolium IL aromatic mixtures form liquid clathrates, and in the case of a [1,3-dimethylimidazolium][PF_6]–benzene mixture the inclusion compound $[([1,3\text{-dimethylimidazolium}][PF_6])_2(\text{benzene})]_n$ have been trapped and its X-ray structure determined (Figure 8) (*71*). Three-dimensional arrays of H-bonded anions and cations result in the formation of channels in which the benzene molecules are included. The benzene molecules are isolated within the channels and they are staggered through $\pi-\pi$ sandwiches between two imidazolium cations. It is worthwhile to note that again one cation is surrounded by three anions and in its turn, each anion is surrounded by three cations. The formation of clathrate phases is an example of the organisation of an aromatic guest molecule in the pre-organised host network.

In another study, the addition of benzene to [1,3-dimethylimidazolium][PF_6] leads to an expansion of the cation–cation contacts (*72*). Around the benzene molecule, alternating cation–anion layers are observed. The incorporation of benzene is found to displace the anions with approximately three benzenes replacing each anion, suggesting benzene intercalation into the structure as found in the solid. Benzene is also found

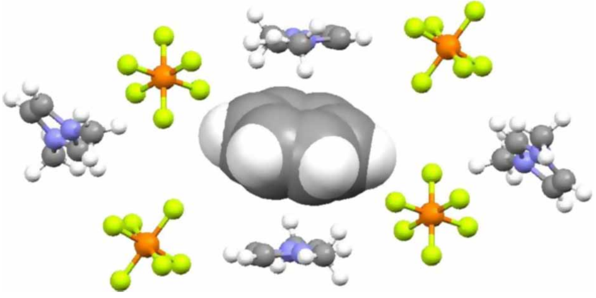

Figure 8. View of the local assembly around a benzene in crystalline clathrate of 1,3-dimethylimidazolium[PF_6], $\frac{1}{2}$ benzene (see CCDC reference numbers 200588–200590).

to be homogeneously distributed throughout the IL with no evidence of micellar formation. Similar homogeneous mixtures have been proposed for water in ILs where the H-bonding interaction with the ions breaks up the water–water interactions (*73*). This may be compared with the mixtures of water in alcohols, for example, where the mixtures phase separate on a microscopic scale to form hydrophobic and hydrophilic regions (*74*). Moreover, it has been shown that the interaction of alkylbenzenes and sulphur heterocycles with the 1,3-dialkylimidazolium IL is preferentially through CH···π stacking and the quantity of these aromatics in the IL phase decreases with the increase in the steric hindrance imposed by the substituents on the aromatic nucleus. Competitive extraction experiments suggested that benzene, pyridine and dibenzothiophene do not compete for the same H-bond sites of the IL (*75*).

Inclusion of ions in the host network

Insertion of charged molecules in the IL network has also been observed in the case of [1-alkyl-3-methylimidazolium][TfO] when mixed with tetrabutylammonium trifluoromethanesulphonate salts (*76*). In each case, the crystal is composed of one imidazolium cation, one tetrabutylammonium cation and two trifluoromethanesulphonate anions. It is worth mentioning that for all cases no water or residual solvent molecules were present in the lattice, implying that the cohesion of the crystal is ensured only by the ionic components. Moderate H-interactions, principally between imidazolium rings and triflate ions, form a cage around the tetrabutylammonium cation (Figure 9).

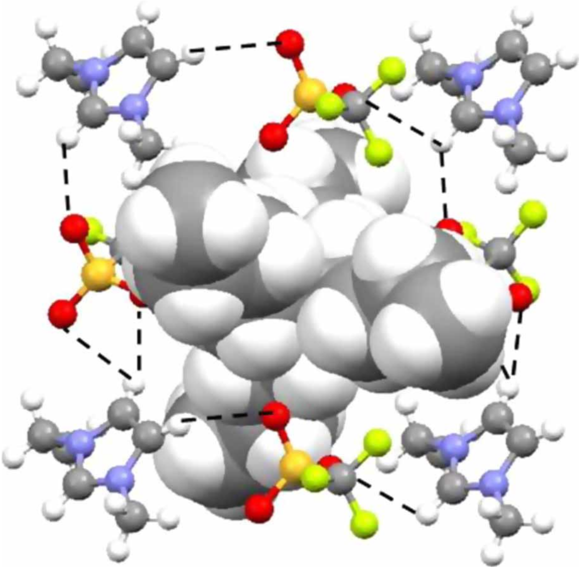

Figure 9. View of the local assembly around a tetrabutylammonium cation in co-crystal of 1-ethyl-3-methylimidazolium[TfO] (see CCDC reference numbers 621900, 685809–685811).

Examples of inclusion of macromolecules

Many research groups have reported that ILs are able to stabilise enzymes and increase their activity and selectivity (*77–79*). Park and Kazlauskas (*17*) correlated the behaviour with the polarity of ILs characterised by Reichardt's polarity scale and H-bond basicity. Solvents with higher polarity increase the solubility of polar substrates, leading to faster reactions and changes in selectivity. But the relationship between ILs and enzymes seems to be more complicated. Several other factors of ILs such as anion nucleophilicity, H-bond basicity, excipients, impurities, pH and the overall enzyme–substrate–medium relationship strongly influence the stability and activity. The presence of these H-bonded nanostructured networks with polar and non-polar regions may be responsible for the stabilisation of enzymes supported in ILs that can maintain their functionality under very extreme denaturative conditions. It is well known that the thermal stability of enzymes is enhanced in both aqueous and anhydrous media containing polyols as a consequence of the increase in H-bond interactions. Thus, both the solvophobic interactions essential to maintain the native structure and the water shell around the protein molecule are preserved by the 'inclusion' of the aqueous solution of free enzyme into the IL network, resulting in a clear enhancement of the enzyme stability (Figure 10) (*80*).

Examples of inclusion of nanoparticles in the ILs networks

The structural organisation of ILs can be used as 'entropic drivers' for spontaneous, well-defined and extended ordering of nanoscale structures (*21*). Furthermore, these IL structures can adapt to many included species, as it provides hydrophobic or hydrophilic regions and a high directional polarisability that can be oriented parallel or perpendicular to the included species. The formation and stabilisation of transition-metal nanoparticles in

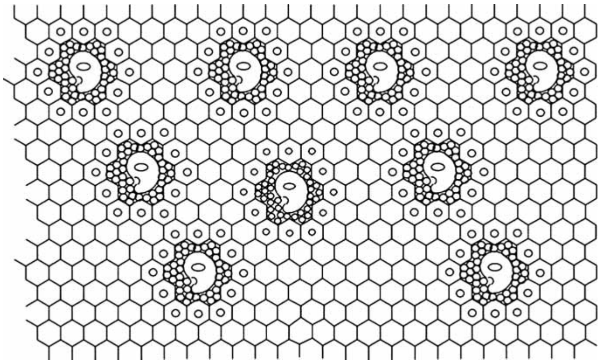

Figure 10. Enzymes in ILs (Reproduced with permission from Ref. (*80*). Copyright Biochemical Society).

1-butyl-3-methyl imidazolium ILs occurs with the reorganisation of the H-bond network and generates nanostructures with polar and non-polar regions where the nanoparticles are included. The IL forms a protective layer surrounding the transition-metal nanoparticles surface with an extended molecular length of around 2.8–4.0 nm depending on the type of anion, suggesting the presence of semi-organised anionic species composed of supramolecular aggregates. This structural organisation is similar to that already observed in the solid, liquid, gas phases and in the solutions of imidazolium ILs. This protective layer is probably composed of imidazolium aggregate anions located immediately adjacent to the nanoparticle surface – providing the Coulombic repulsion – and counter-cations that provide the charge balance (*81*).

Nickel nanoparticles (82)

The unique combination of adaptability towards other molecules and the strong H-bond-driven structure makes ILs potent tools in the preparation of chemical nanostructures. By increasing the range of the organisation of these salts, it is possible to improve the control of diameter, size distribution and shape of the nanomaterials prepared in these fluids. It has recently been reported that the size of stable colloid solutions containing nanoparticles of cyano-bridged molecule-based magnets prepared in [1-alkyl-3-methylimidazolium][BF_4] ILs can be controlled by varying the length of the *N*-alkyl chain on the imidazolium cation (*83*). Moreover, the type of the IL cation has a dramatic effect on the grain size of electrochemically made nanoparticles (*84–86*). The increase in the supramolecular organisation (which increases with the length of the alkyl side chain) induces the formation of nanoparticles with a smaller diameter and size distribution. Moreover, the organised Ni nanoparticles dispersed in the ILs are active catalysts for the hydrogenation of olefins under relatively mild reaction conditions.

Ruthenium and palladium nanoparticles

Due to their high degree of self-organisation, ILs present two interesting effects for the synthesis of transition-metal nanoparticles. On the one hand, they can act as stabilisers (an ionic ligand or a neutral ligand of metal nanoparticles), and on the other hand, they are able to isolate metal nanoparticles, due to their organisation in microdomains and prevent aggregation. The direct correlation between the self-organisation of ILs and the resulting size of the metal nanoparticles generated *in situ* has been recently reported (*87*). The strategy was to establish whether the IL's three-dimensional organisation could affect the size of the ruthenium (*88–90*) or palladium (*90, 91*) nanoparticles generated *in situ*. They demonstrated that ILs can act as supramolecular matrices and allow the formation of very well-defined nanoparticles of very small size, a size generally difficult to control in other media.

Laser excitation can constitute a complementary method for the generation of stable metal colloids in ILs and also for the regeneration of small-sized nanoparticles that may result from their agglomeration after different applications such as catalysis (*92*).

Organic reactions performed in the imidazolium 'host network'

Despite a great interest in the recent years in the self-assembly of imidazolium ILs in pure (solid, liquid and gas phases) or diluted phase (solvent and other organic molecules inclusion), most of the chemical reactions performed in ILs are not rationalised in terms of supramolecular interactions. The following discussion is intended to describe the imidazolium IL's effect on the chemical reactivity, in terms of H-bonds, ion pairs and π-stacking effects. However, the classification of reactions by the nature of interactions involved in each case is very difficult. In fact, the combination of many supramolecular interactions exists in the imidazolium IL network and these interactions can act on the guest reaction. Herein, a review of the principal reactions performed in imidazolium ILs is given and a careful detail of the supramolecular interactions is given for each.

Diels–Alder Cycloadditions

Recently, several key experimental and computational findings proved that metal-free organocatalysed Diels–Alder (DA) reactions are possible via H-bonds. In the DA reaction of a diene with an electron-deficient α,β-unsaturated carbonyl compound, even water can have a significant effect. In this reaction, there are several debated reasons for this acceleration (solvent polarity, hydrophobicity, internal pressure, etc.) (*93, 94*), but the H-bond effect can be highlighted. Jorgensen et al. showed for the DA reaction (*95, 96*) that two water molecules coordinate

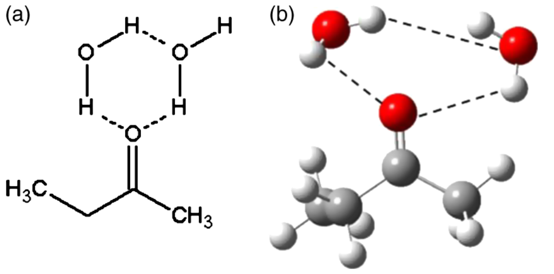

Figure 11. Jorgensen's models of explicit water H-bonding interactions in the Diels–Alder reaction of butanone: two waters flank the carbonyl group.

to the carbonyl function, leading to a preferential stabilisation of the transition states and to rate enhancements (Figure 11). Such coordination is confirmed by X-ray structural studies (*97*).

Imidazolium ILs have been studied as a substitute of water in the DA reaction. In most of the cases, both rate and selectivity improvements were observed in ILs, compared with many molecular solvents (*98–101*). Rate enhancements were also observed for the closely related 1,3-dipolar cycloaddition reactions in ILs (*102*). In a careful investigation of the effects of changing both the cations and anions of the ILs on the reaction of methyl acrylate and cyclopentadiene (Figure 12(a)), it was demonstrated that the rate and selectivity enhancements observed were due to an explicit H-bond between the most acidic proton H(2) of the imidazolium ring and the carbonyl group of the methyl acrylate (Figure 12(b)) (*103*).

Moreover, the DA reactions lead to a mixture of *exo* and *endo* products and the imidazolium ILs also influence the selectivity of the reaction. Generally, acceleration of the DA reaction was obtained, compared with non-polar organic solvents and the reactions showed a high preference for the *endo* product. This effect is also attributed to the H-bonds, but solvophobic interactions, that generate an 'internal pressure' and promote the association of the reagents in a 'solvent cavity' during the activation process, can also be proposed. The H-bonds suggested by the existence of a correlation between the reaction activity and the imidazolium H(2) chemical shift. Recently, gas phase PM3 semi-empirical calculations on the DA cycloaddition of cyclopentadiene and dimethyl maleate support the predominance of H-bond effects in this guest substrate in imidazolium ILs, i.e. a transition-state stabilisation is observed when H-bonds occur between an imidazolium proton and the DA substrate (*5, 23, 104*).

We can also note that the DA cycloadditions are also possible in imidazolium ILs under ultrasound irradiation. Bravo et al. have described a series of sonochemical cycloadditions involving either cyclopentadiene or 1,3-cyclohexadiene with carbonyl dienophiles in an imidazolium IL reaction medium (*105*). In general, ultrasound irradiation does effectively improve these processes in terms of higher yields and/or shorter reaction times when compared with the corresponding silent reactions. It is important to note that the stereoselectivities remain practically unaffected by the sonication. The role of imidazolium ILs under ultrasonic activation is attributed to a cavity effect. We can also note that microwaves can be used for the DA reactions in ILs. For example, recently, the chiral imidazolium ILs with a camphor residue was used for a DA cycloaddition. The use of this salt provided small enantiomeric excess (*ee* $< 3\%$) (*106*).

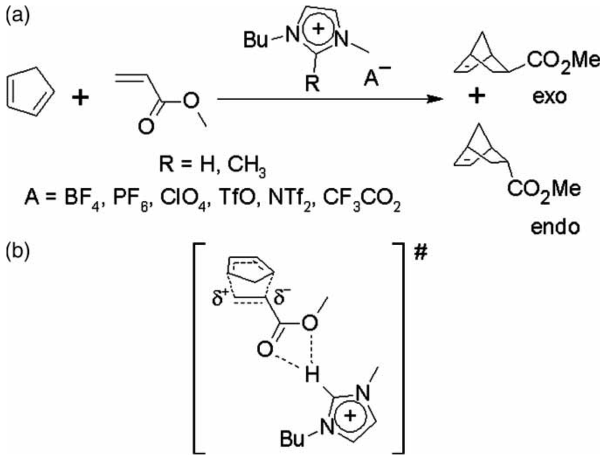

Figure 12. (a) The reaction of methyl acrylate with cyclopentadiene to give a mixture of *endo*- and *exo*-bicyclo-[2.2.1]-hept-5-ene-2-carboxylic acid methyl ester. (b) The H-bond interaction of an imidazolium cation with the carbonyl oxygen of methyl acrylate in the activated complex of the Diels–Alder reaction.

Acetylation reactions

Alcohol acetylation reactions can also be performed via ultrasonic irradiation in imidazolium ILs (Figure 13(a)) (*107*). *O*-Acetylation of alcohols was realised with acetic anhydride and different esters. In short reaction times, excellent isolated yields under ambient conditions without the need for any additional catalyst were achieved. In fact, the combination of ultrasonic irradiation and imidazolium ILs can provide both a reaction medium and a promoter. In addition, this combination is an improved practical alternative to conventional acid/base-catalysed thermal processes and environment friendly with minimal waste. The reaction shows a correlation between the chemical reactivity and the imidazolium H(2) chemical shift. The H-bond interaction of the most acidic hydrogen of the imidazolium ring with the oxygen of the acetic anhydride is proposed to facilitate the generation of the acetyl required for the reaction (Figure 13(b)).

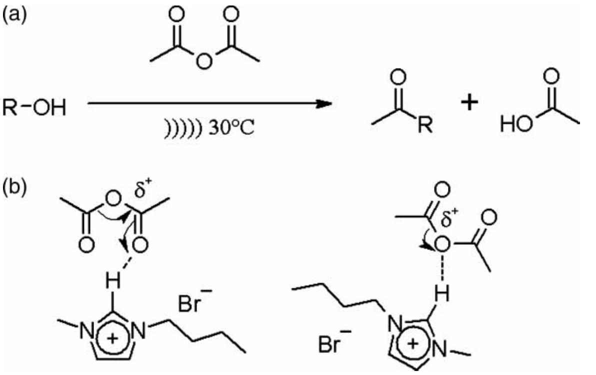

Figure 13. (a) *O*-Acetylation of alcohols in imidazolium ILs under sonication. (b) The H(2) H-bond interaction of the imidazolium cation with the carbonyl oxygen of acetic anhydride.

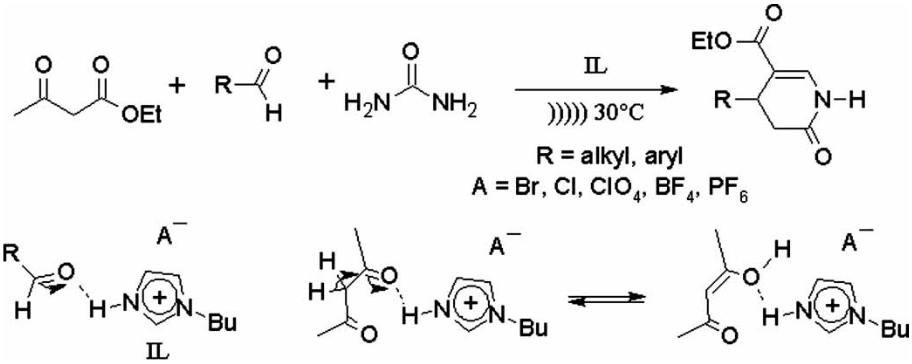

Figure 14. (a) Biginelli reaction in imidazolium at room temperature under sonication. (b) The N—H H-bond interaction of the imidazolium cation with the carbonyl of ethyl acetoacetate.

Other *O*-acetylations using ILS are described in the literature. For example, esterification reactions of acetic, methoxyacetic and methylmalonic acids with various aliphatic alcohols have been investigated in imidazolium ILs with hydrogen sulphate, dihydrogen phosphate as counter-anions and also two ILs modified with HPF_6 as a catalyst. The results show that the nature of both the counter-anion and -cation influences the behaviour of the catalyst. The reaction rate is dependent on the chosen imidazolium IL. These results suggest that the change of Brønsted acid counter-anion increases the reaction rate, and therefore the cation's change influences the polarity and the 'solvent properties' of the imidazolium IL (*108*). However, no comprehensive mechanistic investigations were reported.

The Biginelli reaction

Srinivasan et al. have recently described the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones in excellent yields in short reaction times at ambient temperature without any catalyst by the reaction of aromatic or aliphatic aldehydes with ethyl acetoacetate and urea (or thiourea) in imidazolium ILs (*109*). The reaction is activated under ultrasound irradiation. The authors described a plausible mechanistic pathway for this multi-component reaction (Figure 14) through H-bond activation of the carbonyl group to enhance the reaction rate.

Friedel–Crafts reactions

Friedel–Crafts reactions (FC), especially acylations, are of industrial importance. The use of imidazolium ILs with chloroaluminate (III) is a good alternative to classic benzene acylation (Figure 15). It has been demonstrated that acylation reactions can be carried out in acidic chloroaluminate(III) ionic liquids (*110–112*). The regioselectivities and rates observed in these reactions are comparable to the best values known for the traditional acylations. In addition to benzene and other simple aromatic rings, a range of organic and organometallic substrates (e.g. ferrocene) have been acylated in acidic chloroaluminate(III) ionic liquids. An *in situ* IR spectroscopic study was performed on the FC acetylation of benzene in ionic liquids using $AlCl_3$ and $FeCl_3$. The results revealed that the mechanism of the FC acetylation of benzene in ionic liquids was exactly the same as that in 1,2-dichloroethane. Welton et al. have investigated, by multinuclear NMR spectroscopy and conductivity measurements the properties of 1-ethyl-3-methylimidazolium chloroaluminate (*113*), that all three of the ring

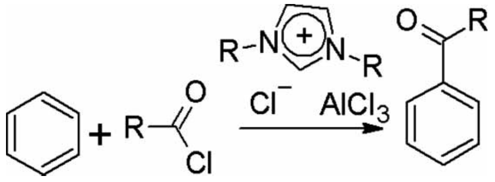

Figure 15. Friedel–Crafts acylation reaction in imidazolium ILs.

protons are involved in hydrogen bonding with halide anions. Both chemical shift and deuterium exchange data clearly demonstrate the acidity of the imidazolium ring protons, a prerequisite of hydrogen bonding. The conductivity data and multinuclear NMR chemical shift in acetonitrile data demonstrate that the chloroaluminate (III) imidazolium salt is in equilibrium between hydrogen-bonded and solvent-separated forms, while those in dichloromethane show that only the associated form is present during the FC reaction.

1-Butyl-3-methylimidazolium chloroaluminate ionic liquids have also been employed as an unconventional reaction media and as Lewis acid catalyst for FC sulphonylation reaction of benzene and substituted benzenes with 4-methyl benzenesulphonyl chloride (Figure 16) (*114*). The substrates exhibited enhanced reactivity, furnishing almost quantitative yields of diaryl sulphones, under ambient conditions.

5.5 *Other aromatic reactions*

It has been demonstrated that the reaction of toluene with nitric acid can give a nitrated product in triflate and hydrogensulphate ionic liquids that halogenation using nitric acid and a halide salt proceeds efficiently to give the monohalogenated product in excellent yield, and that nitric acid acts as an oxidising agent in methanesulphonate ionic liquids (Figure 17) (*115*). The ionic liquids in the nitration and oxidation reactions could all be reused in further reactions and were not destroyed, despite being in contact with acids under reflux. Separation of the products was achieved by vacuum distillation, solvent extraction or, most notably, steam distillation. The only by-product from these reactions was water. In all of the nitration, halogenation (with HX/O_2) and oxidation reactions, it was found that the ionic liquid plays a crucial role in the reaction. As a demonstration of the efficiency of this methodology, benzene was chlorinated with concentrated hydrochloric acid using 50 mol% [1-butyl-3-methylimidazolium][NO_3] and air as the oxidant, and the only by-product of the reaction was water. As we underlined at in the first part of this review, in the case of aromatic compounds, clathrates can be formed and π-stacking interaction can occur in imidazolium ILs (*71*). Even, if the mechanism of the reaction does not change, the stabilisation of ionic intermediates is probably responsible for the selective nitration, oxidation and halogenation of toluene in imidazolium ILs. In these cases, the outcome of the reaction is controlled by the nature of the anion (*115*).

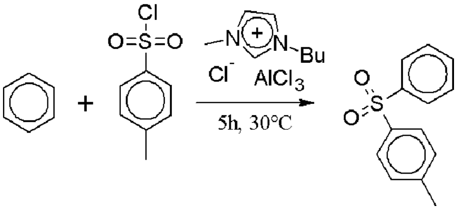

Figure 16. Benzene sulphonylation with tosyl chloride in imidazolium ILs.

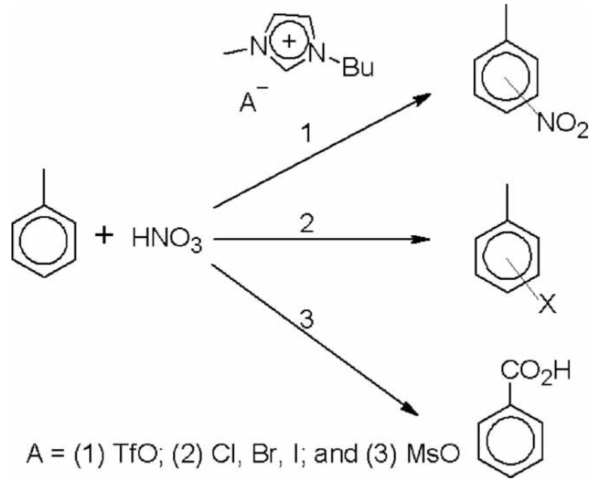

Figure 17. Oxidation of toluene by HNO_3 in three different imidazolium ILs.

Baylis–Hillman reaction

The Baylis–Hillman (BH) reaction is an emerging carbon–carbon bond-forming reaction. It involves the coupling of activated alkenes with carbon electrophiles under the influence of a tertiary amine (Figure 18) (*116*). Mechanistic studies show that the BH reaction most likely proceeds via an addition–elimination mechanism that is initiated by a Michael-type nucleophilic attack on the alkene by the tertiary amine to produce a zwitterionic species, which then attacks the aldehyde to give the product (Figure 19).

Generally, the rate of the BH reaction is enhanced in protic solvents (methanol), which can be attributed to the involvement of H-bonds (*117*). As the imidazolium acidic proton H(2) is known to act as a donor to H-bond acceptors (*118*), the BH reaction is accelerated in the presence of imidazolium ILs, a fact that can be seen as the stabilisation of ionic intermediates/transition states. This hypothesis has been demonstrated by ESI-MS experiments on the BH reaction. Loosely bonded supramolecular species, formed

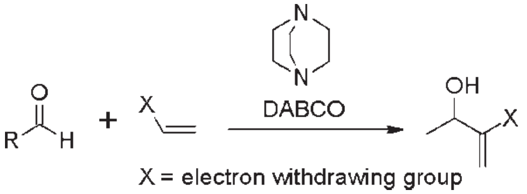

Figure 18. Typical Baylis–Hillman reaction with diazabicyclo [2.2.2]octane (DABCO).

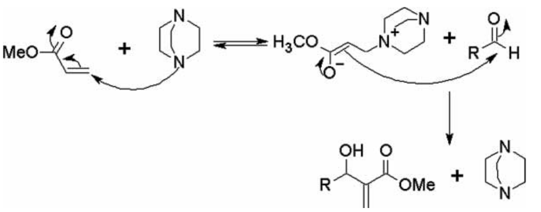

Figure 19. Mechanism of the Baylis–Hillman reaction via zwitterionic species.

by the coordination of neutral reagents, products and the protonated forms of zwitterionic BH intermediates with cations and anions of ILs have been smoothly transferred directly from the solution to the gas phase. Mass spectrometry measurements and structural characterisation of these H-bonded species have been performed via collision-induced dissociation in tandem mass spectrometric experiments. The interception of these species with inherent catalytic activity indicates that ILs co-catalyse BH reactions by activating the aldehyde towards nucleophilic enolate attack and by stabilising the zwitterionic species that acts as the main BH intermediates (*119*).

Halogenation and related reactions

Recently, investigations of the nucleophilicity of halides in imidazolium ILs as counter-cations have been performed by Welton et al. (Figure 20(a)) (*120*).

The study of halide nucleophilicity in imidazolium ILs has been performed and the effect of anions has been investigated ([BF_4], [PF_6], [SbF_6], [TfO] and [$N(Tf)_2$]). The results show clearly that the nucleophilicity of all the halides were lower in all of the imidazolium ILs than that in dichloromethane. However, the order of nucleophilicity is affected by the anion linked to the imidazolium cation (i.e. the nucleophilicity of each halide was different in each IL). The authors suggest that increasing the cation H-bonding donor effect decreases the nucleophilicity of the halides through a direct interaction with the nucleophile. The activation parameters $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ have been measured for the reaction of chloride in each of the imidazolium ILs. A careful comparison of these data with a similar reaction in dichloromethane shows that the reaction in the imidazolium ILs has a high activation-free energy barrier, due to the solvent–solute interactions (which combine electrostatic interactions and H-bonds) within the imidazolium ILs. In other words, the halides' encapsulation limit the nucleophilicity, i.e. the nucleophilicities of Cl^-, Br^- and I^- ions are lower in imidazolium ILs than in non-H-bond donor molecular solvents (*120*) and that changing orders of nucleophilicity in different ILs (*121*), reflected in reaction rates, are readily predicted by a classical Hughes–Ingold approach to solvent effects (Figure 20(b)) (*122*).

Another very interesting study has been performed by Chiappe et al. on the effect of imidazolium ILs in the reaction of ICl_2^- with alkenes and alkynes (Figure 21) (*123*). In this work, the kinetic constants and the activation parameters for the reactions of Br^{3-} and ICl^{2-} with different alkenes and alkynes have been determined in the ILs. A careful investigation of the imidazolium cation's and anion's structures was performed and the obtained data can be compared with those of a reaction performed in 1,2-dichloroethane. Important information on the imidazolium ILs' features and the correlation with the ILs' solvent properties have been obtained from the kinetic study of this reaction. The results showed that the rates of reactions increase on going from 1,2-dichloroethane to ILs. This fact suggests that while the H-bonding ability of the imidazolium cation is probably the main factor able to increase the rate of the addition of ICl_2^- to double and triple bonds, this property has no effect on the electrophilic addition of Br_3^- to alkenes and alkynes. In the case of the ICl_2^- reaction, the H-bonding ability of imidazolium ILs has been exploited by authors to suppress the unwanted nucleophilic substitution reaction on the products by the Cl^- anion. These results clearly show the potential effects of the IL's cations as H-bond donors in electrophilic

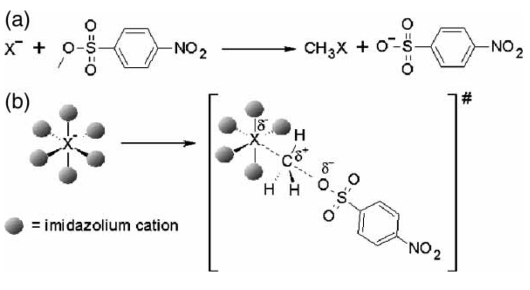

Figure 20. (a) Reaction of methyl *p*-nitrobenzenesulphonate with halide to give methyl halide and *p*-nitrobenzenesulphonate anion. (b) Schematic of the activated complex with the imidazoliums that complex the halide anion.

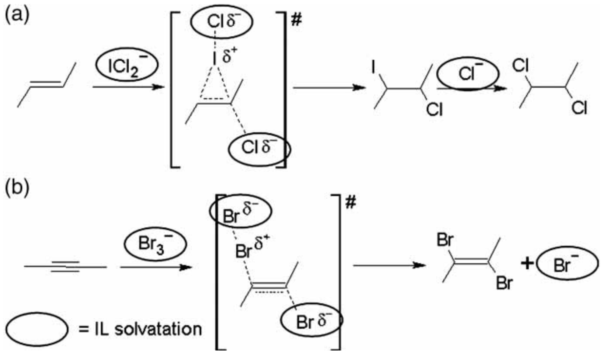

Figure 21. Addition of trihalides to unsaturated compounds in imidazolium ILs: (a) mechanism in which the ability of the imidazolium IL to form H-bonding with the leaving Cl^- plays a major role. (b) Concerted mechanism for Br_3^- addition to alkynes.

addition reactions in imidazolium ILs and corroborate with the work of Xiao et al. (*124*) (see below). Note that ILs, such as [1-butyl-3-methylimidazolium] and [1-hexyl-3-methylimidazolium][Br_3] salts, have been effectively used as aromatic brominating agents (*125*). Conversion was found to be higher when the protic IL, crystalline hexyl residue, was employed (compared with butyl residue), but product distributions in both imidazolium ILs were similar (*126*).

Conversion of epoxides to halohydrins

The generation of halohydrins from epoxides can be achieved in the presence of imidazolium ILs (Figure 22) (*127*). This method using HX or hypohalite-water is quite versatile and a wide variety of epoxides can be converted to the corresponding halohydrin in good yields in ILs' media. However, *trans*-stilbene oxide did not yield the corresponding halohydrin. Instead, the epoxide underwent a rearrangement to give the deoxybenzoin. This is also an interesting observation because the rearrangement of *trans*-stilbene oxide typically proceeds via a phenyl group migration to give diphenylacetaldehyde as the major product (*128*). In this case, the chloride attacking the oxirane ring is H-bonded to the imidazolium cation (see mechanism in Figure 24).

Synthesis of cyclic carbonates

Varma et al. have reported the synthesis of a series of tetrahaloindate(III)-based imidazolium ILs for use in the coupling reaction of carbon dioxide and epoxides to generate cyclic carbonates (*129*). These thermally stable imidazolium ILs were synthesised by the microwave promoted reaction of indium chloride ($InCl_3$) with a variety of imidazolium ILs. Using FT-IR and ^{13}C-labelling NMR studies, the authors demonstrate the importance of H-bonds between the halide ion and the ring protons of the imidazolium cation on the catalytic activity of the IL (Figure 23).

Other systems with ZnX_2, ZnX_2Y_2, FeX_3, FeX_2, MgX_2, LiX, NaX or ZnO (X = Cl, Br, I and Y = Cl, Br) incorporated in imidazolium ILs were also described in the literature (*130, 131*). Arai et al. reported on mechanistic details studied during the use of imidazolium ILs and various metal halides. The mechanism proposed involves the following steps. (i) First, the epoxide is coordinated to the Lewis acid to form the metal–epoxide complex and then the Cl^- anion of the imidazolium ILs makes a nucleophilic attack on the less hindered carbon atom of the coordinated epoxide causing a ring opening and an oxyanion species (see the synthesis of halohydrins above). (ii) Second, carbon dioxide is coordinated to the complex through interactions with Br^- and O^-, resulting in the formation of IV. (iii) Finally, styrene carbonate is produced by SN2 displacement, regenerating the catalytic components (Figure 24).

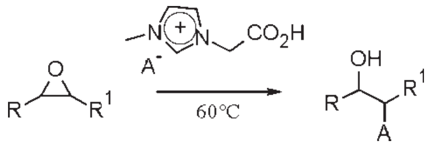

Figure 22. Synthesis of β-halohydrins from 1,2-epoxides with acidic imidazolium IL.

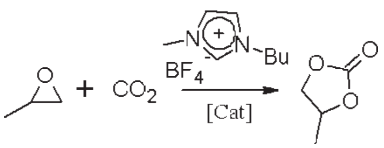

Figure 23. Synthesis of cyclic carbonates using imidazolium ILs with catalyst.

In this mechanism, the different transition states are stabilised by the H-bond interactions. In other words, the transition states are accelerated by lowering the activation barrier ($\Delta G^{\#}$).

The Tsuji–Trost reaction

The Tsuji–Trost (TT) reaction has been studied in both biphasic conditions (methylcyclohexane/[1-butyl-3-methylimidazolium][Cl]) (*132*) and in homogeneous solvents (*133*). Under monophasic conditions, the effects of imidazolium cation on the TT reaction have been studied in terms of possible H-bonding interactions. Xiao and Ross have demonstrated that the base or base precursor enters into hydrogen bonding with the imidazolium cation and is thus made less readily available for deprotonation of pre-nucleophiles (Figure 25) (*124*).

In fact, the analogous TT Pd(0)-catalysed allylic alkylation reaction is also inhibited by H-bonds caused by

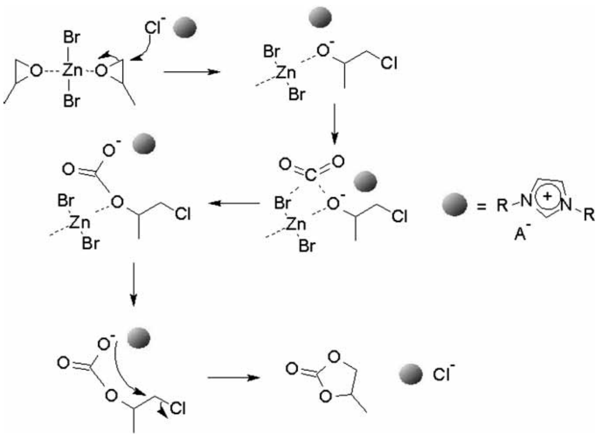

Figure 24. Proposed mechanism for the synthesis of styrene carbonate from styrene oxide and CO_2 with $ZnBr_2$/1-butyl-3-methylimidazolium[Cl] catalyst.

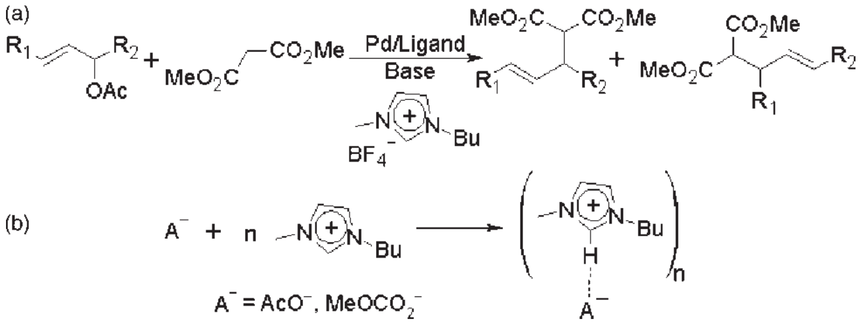

Figure 25. (a) Allylic alkylation in 1-butyl-3-methylimidazolium[BF_4]. (b) Proposed role of 1-butyl-3-methylimidazolium[BF_4] as H-bond donor that inhibits nucleophilic attack by basic agents (AcO^- and $MeOCO_2^-$).

the presence of [1-butyl-3-methylimidazolium][BF_4], such that the addition of even a small amount of imidazolium IL to the reaction mixture in THF resulted in a reduction of the rate of reaction. NMR titration studies reveal the existence of a 2:1 complex between two imidazolium cations and one acetate anion (Figure 26). Thus, the base is no longer available to deprotonate the incipient nucleophile HNu, dramatically decreasing the reaction rates.

Moreover, Xiao et al. have also reported the effect of imidazolium ILs on the catalytic species of TT reactions when compared with typical organic solvents (Figure 27) (*134*).

The authors proposed that in [1-butyl-3-methylimidazolium][BF_4], the allylpalladium intermediate exists as a free cation, but in THF, it forms ion pairs with the acetate anions. The effect of this dissociation can dramatically affect the reaction by the modification of the micro-environment of the catalytic species. As an example, in THF the ion-pair-induced steric hindrance can inhibit the coordination of sterically bulky ligands to palladium or the attack by nucleophiles at the allylpalladium species containing such ligands, thus further reducing the reaction rates when these ligands are employed. In the polar ionic environment provided by imidazolium ILs, ion pairing between the allylpalladium cation and acetate anion may not occur, since the solvent anions could easily exchange places with the acetate ions (*135*).

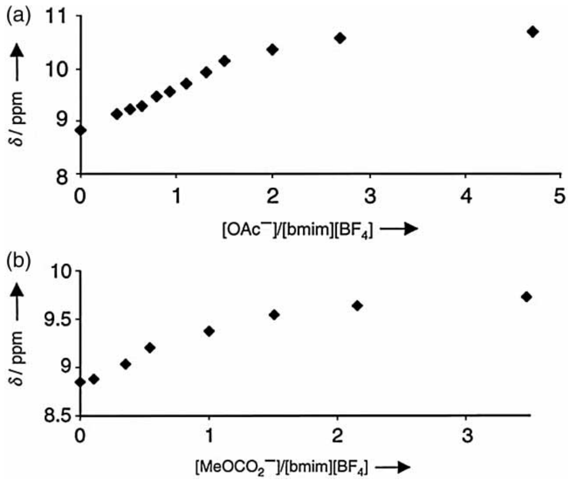

Figure 26. (a) ^{1}H NMR titration profile for the addition of 1-butyl-3-methylimidazolium[BF_4] (26–323 mM) to [n-Bu_4N][OAc] (123 mM) in $CDCl_3$ at 21°C, the first point on the chemical shift axis corresponding to 680 mM in 1-butyl-3-methylimidazolium [BF_4]. (b) ^{1}H NMR titration profile for the addition of [$MeOCO_2$][HDBU] (0–112 mM) to [BMIM][BF_4] (32.2 mM) in $CDCl_3$ at 21°C (Reproduced with permission from Ref. (*124*). Copyright Wiley-VCH Verlag GmbH & Co.).

Moreover, the importance of H-bonds was recently highlighted by the discovery of co-crystals of imidazolium and tetrabutylammonium cations. In fact, when tetrabutylammonium acetate is used in the TT reaction, the tetrabutylammonium cation can promote the organisation of the imidazolium ILs (*76, 136*).

Hydrogenation

Schulz et al. have reported the asymmetric hydrogenation of a ketone in an imidazolium IL with a chiral anion (*137*). The chiral imidazolium IL has been prepared by the protonation of methylimidazole with (R)-camphorsulphonic acid followed by a Michael-type addition of methyl vinyl ketone (Figure 28) (*138*). The imidazolium IL consists of a prochiral cation and chiral anion and the hydrogenation of the ketone can take place using a heterogeneous, achiral Ru/C catalyst in ethanolic solution. The authors showed that the *ee* is dependent on the concentration of the

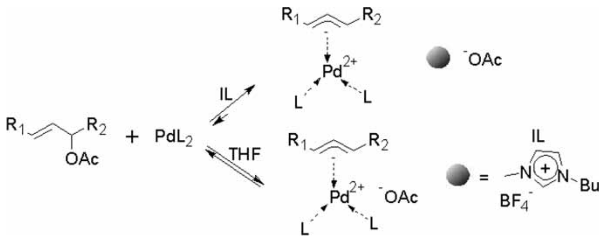

Figure 27. Effects of THF and imidazolium ILs on the intermediate allylpalladium complex arising from the oxidative addition of acetate to the active catalyst, Pd(0)L_2 (L = phosphine).

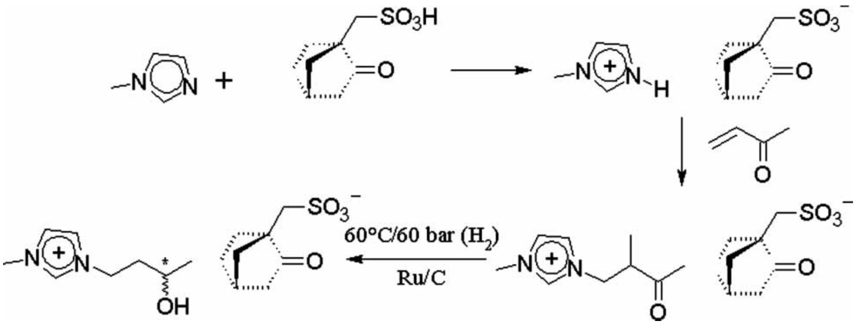

Figure 28. Synthesis of the prochiral imidazolium IL and hydrogenation of the keto-functionalised imidazolium IL.

imidazolium ILs. In fact, the *ee* increases from 32 to 80% when the imidazolium ILs concentration increases from 0.2 to 0.5 M. This observation demonstrates the potential of ion pairing effects to transfer chiral information from an ion to the transition state of a reaction at its prochiral counterion. The authors state that: 'Apart from aspects of chiral synthesis, our study also reveals some fundamental aspects of ion pairing effects in ILs. A better understanding of the nature of cation–anion interactions is the key to the rational design of ILs as these interactions determine physicochemical properties as well as interactions with dissolved substances and thus reactivity' (*137*).

Hydroformylation

Recently, the influence of imidazolium ILs on the biphasic hydroformylation of dec-1-ene and styrene has been studied by Leclercq et al. (Figure 29) (*139*).

The authors have obtained competitive rates with the use of imidazolium triflate ILs. A careful investigation of the reaction mixture proved the formation of 'inclusion complexes' with the phosphine ligands used in conjunction with the rhodium catalyst. A part of the study is based on ^{31}P NMR titrations (Figure 30) and 2D NMR T-ROESY experiments (Figure 31). The results of ^{31}P NMR titration proved association between the phosphine ligands (triphenylphosphine (TPP), monosulphonated TPP (TPPMS) and trisulphonated TPP) and the imidazolium ILs.

Each ^{31}P NMR spectra contained identical concentrations of TPP or TPPMS, while the concentration of the IL [(*S*)-(2-methylbutyl)-3-methylimidazolium][TfO] ([MBMIM][TfO]) was changed. The results point to a 1:1 complex between the imidazolium IL and the two phosphines, and have proposed that for the sulphonated phosphine the imidazolium ILs are principally anion receptors through C—H···X$^-$ H-bonding. For the neutral TPP, other supramolecular links such as π-stacking interactions take place. To substantiate these assumptions, 2D NMR experiments have been performed with the aim of detecting spatial interactions between the sulphonated ligand TPPMS and the pure IL. The T-ROESY experiments identified cross-peaks between the sulphonated and unsulphonated aromatic groups of the ligand and the protons located on the imidazolium ring, suggesting interactions and arrangement of the phosphine into the ILs (Figure 31).

The weak cross-peaks observed between the imidazolium IL protons H(2), H(4), H(5), N—CH3, H(9) and H(10) of the imidazolium cation and those of the sulphonated phenyl residue of the TPPMS suggest that the TPPMS exchanges the sodium for an imidazolium cation in the mixture. On the other side, the non-sulphonated phenyl residue interacts strongly with H(4), H(5), N—CH3, H(6), H(9) and H(10). This NMR pattern establishes the existence of π-stacking interactions between the two aromatic rings (imidazolium and phenyl). The authors note that this stacking has been observed by Wipff et al. (*140*).

The effect of this interaction in the case of the hydroformylation reaction has also been reported. For the dec-1-ene hydroformylation, a decrease in the linear to branched aldehydes ratio for dec-1-ene has been observed and a drop in activity as a function of sulphonation of the ligand. This effect was attributed to the formation of 'inclusion complexes' between the imidazolium cations and the ionic phosphine ligands. In the case of styrene hydroformylation, small *ee* (up to 12%) have been reported with the use of [(*S*)-MBMIM][TfO]. Although it has been previously reported (*141–146*), this study supports the idea that supramolecular assistance by the imidazolium salts is a phenomenon of general importance.

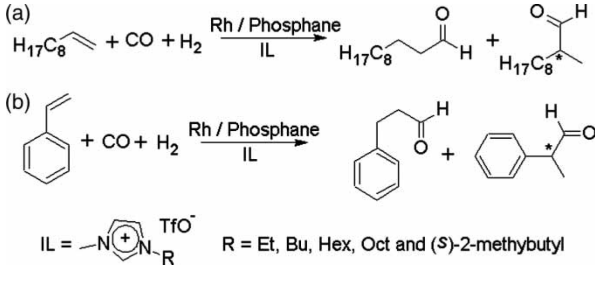

Figure 29. Hydroformylation of (a) dec-1-ene and (b) styrene in imidazolium IL biphasic systems.

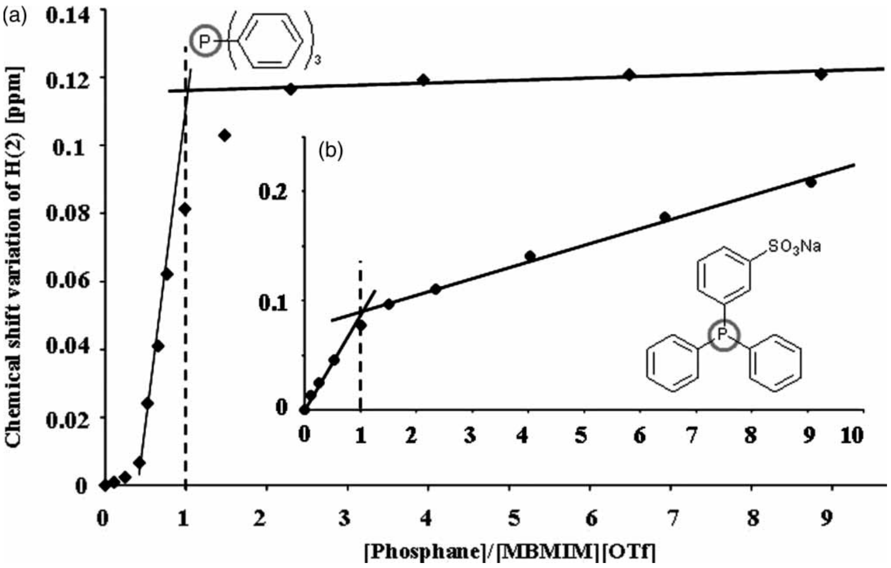

Figure 30. ^{31}P NMR titration profile for addition of 1-(2-methylbutyl)-3-methylimidazolium[TfO] to phosphines in [D8]THF at 300 K (Reproduced with permission from Ref. (*139*). Copyright The Royal Society of Chemistry).

Other reactions

In this section, we discuss some other reactions where imidazolium ILs have probably an effect on the chemical reactivity, but no investigations were performed to demonstrate this hypothesis (*147*).

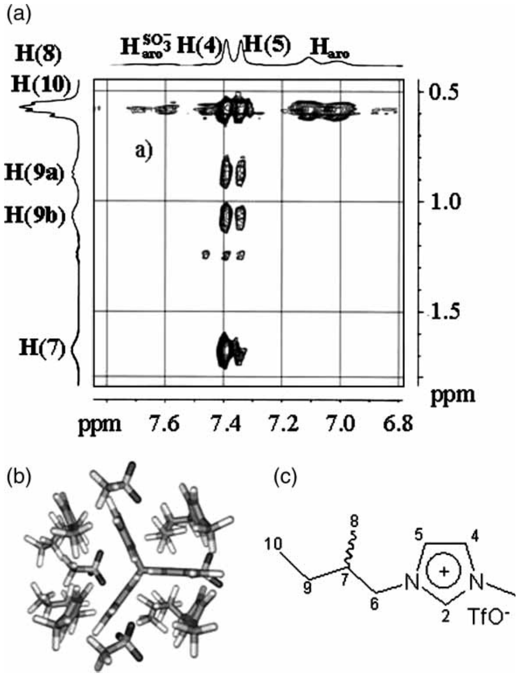

Figure 31. Partial contour plot of T-ROESY spectrum of mixture containing TPPMS and 1-(2-methylbutyl)-3-methylimidazolium[TfO] 16% (m/m), 300 K, external lock: D_2O. The structure deduced for the 1-(2-methylbutyl)-3-methylimidazolium[TfO]–TPPMS complex is also presented (Reproduced with permission from Ref. (*139*). Copyright The Royal Society of Chemistry).

This synthesis of imidazoles by Srinivasan et al. is a one-pot and rapid synthesis without the use of any catalyst (Figure 32). Different imidazolium-based ILs, 1-butyl-1*H*- and 1,3-dibutylimidazolium cations were screened and their efficacy in terms of acidity and polarity have been correlated with the yields and the reaction activity. This one-pot methodology resulted in excellent isolated yields in short reaction times and is characterised by simple work-up procedures and efficient recovery and recycling of the IL, which acts as a promoter. In fact, the author's corroborate the chemical shift of the most acidic imidazolium proton to the reaction efficiency. Two cases were observed: (i) in the case of 1-butyl-1*H*-imidazolium cations (the most efficient), the activity can be assigned to the labile most acidic —N—H hydrogen (i.e. Brønsted acidity) and (ii) in the case of 1,3-dibutylimidazolium cations, no explications are given by the authors, but the activity may be assigned to the labile most acidic H(2) hydrogen activating the aldehydes. However, further experimental investigations must be conducted to confirm this hypothesis.

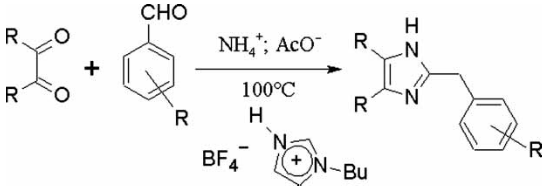

Figure 32. Room temperature imidazolium IL promoted synthesis of 2,4,5-trisubstituted imidazoles from aryl aldehydes and 1,2-diketones or α-hydroxyketones.

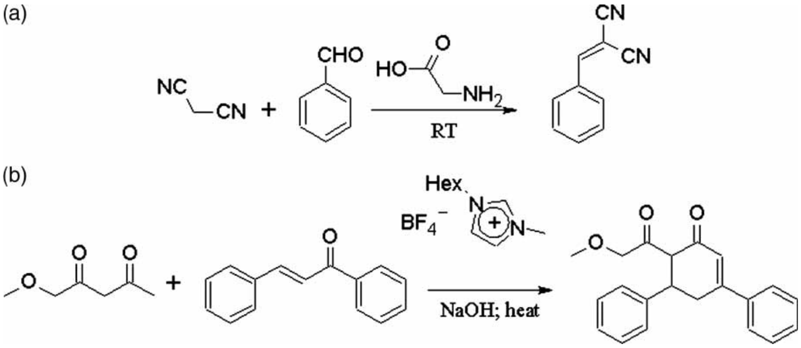

Figure 33. Knoevenagel condensation and Robinson annulation reactions in IL.

The Knoevenagel condensation and Robinson annulation were also studied in imidazolium ILs ([1-hexyl-3-methylimidazolium][PF_6]) by Morrison et al. (Figure 33) (*148*). The enhancement of the reaction rate is attributed to the reaction of the imidazolium cations with the added base to give imidazolidene carbenes. These imidazolidene carbenes are supposed to be the active catalysts in the Knoevenagel condensation and Robinson annulation reactions. However, a simple acceleration of transition states may also be possible.

Conclusion and outlook

Despite a great numbers of reports on the supramolecular organisation in imidazolium ILs, their effect in chemical reactions remains poorly understood in terms of supramolecular interactions. However, the imidazolium ILs seem to have a considerable influence on the reaction mechanism. A majority of the examples cited in this review prove that the reactions involve charge-separated intermediates or transition states, and are accelerated in the presence of imidazolium ILs. The publication of Welton et al. and Chiappe et al. on the halogenation reactions are good examples of H-bond effects on the nucleophilic substitution (*120, 123*). The publications of Xiao et al. have proved that ILs can alter the intrinsic properties of the organometallic catalyst and dramatically modify the reaction rate (*124, 134*). The ion pairing of imidazolium ILs was enhanced by Schulz et al. in the hydrogenation of a ketone (*137*). Finally, the supramolecular interactions observed in this media (H-bonds, π-stacking and electrostatic interactions) can be used to perform asymmetric reactions (*139*). The control of the IL interaction with various species provides valuable elements for further developments in organometallic catalysis, as well as for various organic reactions. The pre-organisation of imidazolium ILs presents an extension of the host–guest concept, i.e. the host is the reaction medium in which a guest reaction can occurs. This new concept is now clearly demonstrated and can explain the special kinetic effect observed for reactions in ILs (5), the influence of dilution or impurities in such medium (*40, 60, 149–152*). However, further developments will undoubtedly be linked to a better understanding of the supramolecular interactions between organic guest and the imidazolium host network. A big challenge that remains in the use of IL as organic reaction media is the possibility to predict the interactions involved in each system. Understanding in details the interactions involved in each system may allow a rational design of the IL components for precise applications.

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