

# Organic reactions enter a new phase

*Ionic liquids could help the chemical industry clean up its act by doing away with volatile organic solvents. David Bradley reports.*

In the late 1940s, Frank Hurlay and Tom Weir of the Rice Institute in Texas made a ground-breaking discovery. Searching for a method of electroplating aluminium under mild conditions, they added an *N*-alkylpyridinium salt to aluminium chloride. When they warmed the test tube, something strange happened: the solid mixture spontaneously formed a clear, colourless liquid.

This fluid was the first reported example of an ionic liquid — an odd group of substances made up of free ions moving around in the liquid phase.

The discovery, however, went largely unnoticed. Hardy and Weir published their results in 1951 but there was little follow-up research. What limited interest there was came from a small band of chemists looking for molten salts to use in batteries.

One of these researchers was Robert Osteryoung, now at North Carolina State University but then at Colorado State University in Fort Collins. 'It was desirable to find lower temperature molten salt systems,' he says. One of Osteryoung's students, Bernard Gilbert, mixed 1-butylpyridinium chloride and aluminium chloride. Although not too stable, the resulting compound was the world's first genuine room temperature ionic liquid (RTIL).

By the 1970s Osteryoung and others, including nearby US Air Force Academy chemists John Wilkes and Charles Hussey, were searching for more stable ionic liquids. Wilkes and Hussey eventually came up with stable RTILs based on *N,N*-dialkylimidazolium ions.

The key to their success was the ion's size and shape. Ionic compounds are usually crystalline solids, melting at temperatures of several hundred degrees Celsius. The melting point is determined by the energy of the interactions between the positive and negative ions, called the lattice energy. But some big ions interact weakly, producing very low lattice energies. *N,N*-dialkylimidazolium salts, for example, have such low lattice energies that they are liquid at room temperature.

## Time for a clean break?

RTILs have simmered away on the chemistry back-burner, but pressure for clean technology could soon bring them to the boil. 'We thought these would be nice electrolytes for batteries,' Wilkes told *C&I*. 'Now it's clear that they are also excellent solvents.'

Using RTILs as solvents offers clear advantages over conventional organic solvent systems, which can be difficult to handle. The ionic liquids don't evaporate easily so there are no problems with noxious fumes.

They are also non-flammable. Most importantly they often dissolve materials — especially catalysts — that are insoluble in conventional organic chemicals.

French Petroleum Institute researchers Yves Chauvin and Hélène Olivier-Bourbigou were among the first scientists to exploit the potential of RTIL solvents. Over the past ten years



Conventional solvents can be hard to handle

they and their colleagues have developed solvent systems for numerous organic reactions. For instance, they can carry out alkene dimerisations, hydrogenations, isomerisations and hydroformylation reactions without conventional solvents. The team has also developed a commercial RTIL-based process which dissolves the catalysts used in the conversion of butene to iso-octene — an important process in the production of PVC plasticisers.

## Getting the right mix

Although reaction efficiencies in RTILs are nothing special yet, Tom Welton of London's Imperial College says that these systems have one big advantage: they are effectively biphasic. The RTIL acts as a support for the catalyst but is immiscible with the reactants and products. These can be dissolved in a simple hydrocarbon such as hexane so they occupy a separate phase. Mixing the two liquids allows the reaction to take place, and the two phases can then be separated easily once the reaction is complete.

'This is the really exciting bit,' enthuses Welton, who is working on exploiting RTILs in standard industrial applications. Along with York University's Paul Dyson he has developed a method of producing clean diesel and other oil-based fuels using a cluster catalyst dissolved in an RTIL.

Welton claims that the technique combines the advantages of both homogeneous and heterogeneous catalysis. The reaction is mild, highly efficient and selective, just like a homogeneous system in which the reactants and catalyst are dissolved in the same phase. But because the catalyst is dissolved in a separate phase, separation is easy, like in a heterogeneous system.

Brazilian researchers Jairton Dupont and Roberto de Souza of the Federal University of Rio Grande do Sul believe that these advantages could now be extended to all the classical organometallic catalysts. 'This will, in principle, enable direct transposition of the plethora of known homogeneous catalytic reactions to two-phase systems without having to design and synthesise new ligands or complexes,' Dupont explains.

Meanwhile, Kenneth Seddon of Queen's University Belfast believes the new media offer the possibility of carrying out novel reactions. Ionic solvents could promote reaction mechanisms not possible in organic liquids, he says.

Seddon's focus is industrial Friedel-Crafts reactions, which allow acyl and alkyl groups to be added to aromatic compounds. By using an ionic liquid solvent, his team has managed to react a number of aromatic compounds at high efficiency. For example, they produced a fragrance molecule, traseolide, with a 99% yield. The approach can work just as well with agrochemicals and pharmaceuticals.

## Solutions for separation

Ionic liquids are not only finding use in syntheses, Robin Rogers and colleagues at the University of Alabama realised the new solvents could replace volatile organic compounds (VOCs) in standard separation processes.

Using the RTIL butylmethylimidazolium hexafluorophosphate, Rogers' team has extracted benzene derivatives from water at an efficiency comparable to the conventional method using octan-1-ol. The major advantage is avoiding the use of VOCs, with their toxicity, flammability and disposal problems.

Liquid-liquid extractions have always been a favourite of process engineers, Rogers says, but the use of RTILs might now provide a more benign and clean separation method. RTIL separations could have all sorts of uses. 'For example, removing environmental pollutants from industrial waste streams, or in the remediation of polluted areas,' he says. 'They may also find application in recycling of valuable solutes during a manufacturing process.'

With increasing pressure to cut back on the use of noxious solvents, RTILs could be the solution industry has been looking for.