

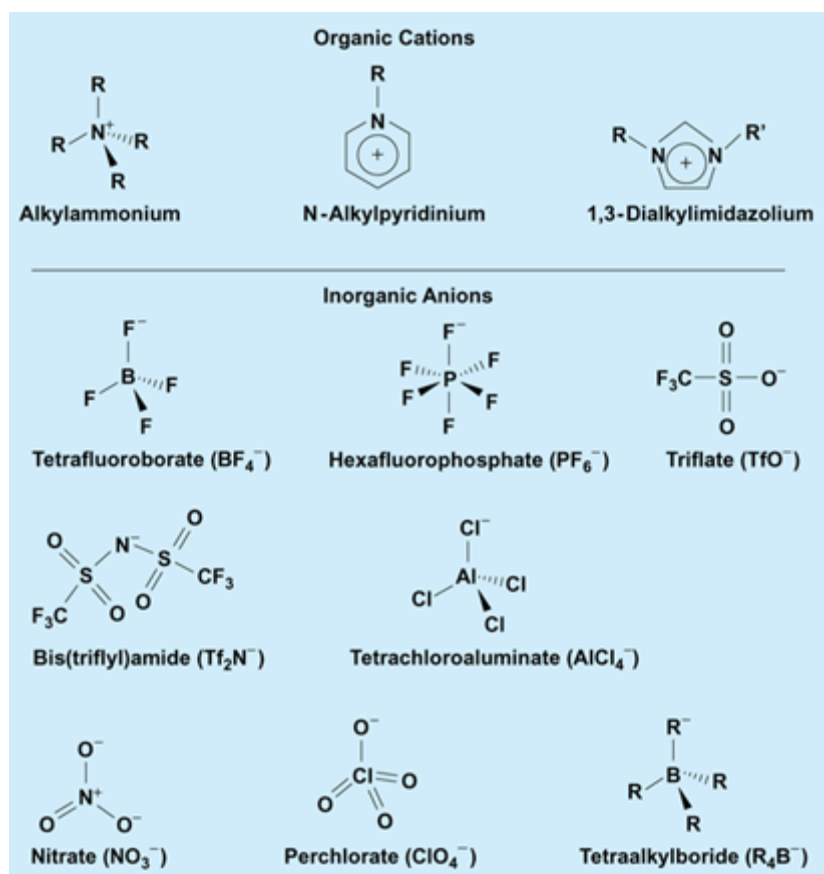
RESEARCH UPDATE

Green chemistry

The pursuit and development of green (environmentally benign) technologies is one of the highest priorities for today's chemists. The United States chemical industry generates approximately 350 million tons of toxic waste per year, corresponding to more than 10 pounds per person per day. The safe disposal of this hazardous waste comes at the high price of \$20 billion per year. A significant source of chemical waste that is often overlooked is the use of organic (or molecular) solvents. These solvents are deleterious to the atmosphere because they are volatile liquids and thus difficult to contain. Nonvolatile ionic liquids (or molten salts), composed exclusively of ions, are attractive substitutes for traditional molecular solvents. Sodium chloride (NaCl) melts above 800°C and could serve as a solvent for reactions proceeding at temperatures greater than 800°C. However, the number of feasible chemical reactions at such a high temperature is limited. Room-temperature ionic liquids (RTILs), however, are salts that melt at or below ambient temperature ($\sim 20^\circ\text{C}$ or 70°F), a quality that renders them useful as reaction media.

Numerous low-melting ionic liquids are known. The majority consist of nitrogen-containing organic cations and inorganic anions (see **illus.**). Recently, imidazolium salts of carboranes (negatively charged cages composed of carbon and boron), which are among the weakest nucleophiles known, have been prepared. Even though research on the use of RTILs as solvents has prospered only in the past few years, ionic liquids are by no means new. The first RTIL, ethylammonium nitrate ($[\text{CH}_3\text{CH}_2\text{NH}_3][\text{NO}_3]$), was reported in 1914. Among the many attractive features that make ionic liquids interesting as solvents are that they (1) have no detectable vapor pressure; (2) display excellent thermal stability; (3) exhibit a large electrochemical window ($>4\text{ V}$); (4) are liquids over a wide temperature range, which allows for exceptional kinetic control; (5) are polar solvents, yet poorly coordinating; (6) in some cases, are hydrophobic; (7) are immiscible with a number of organic solvents such as diethyl ether and alkanes; (8) are highly conductive; and (9) dissolve a wide variety of organic and inorganic compounds.

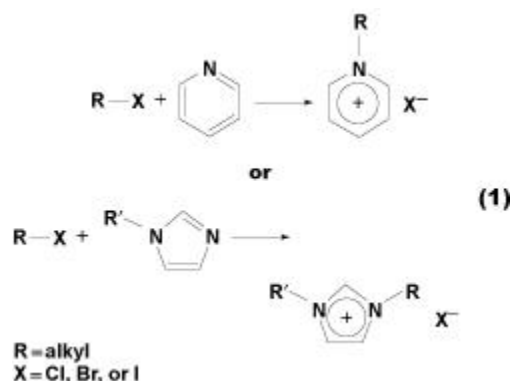
Organic cations combine with inorganic anions to produce room-temperature ionic liquids. R, R' = alkyl group, usually methyl (CH_3), ethyl ($\text{—CH}_2\text{CH}_3$), or *n*-butyl ($\text{—CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).



Ionic liquids containing chlorocuprates, chloroaurate, and halogenoaluminates as anions are of limited usefulness because they are extremely sensitive to moisture and air. Hence, these ionic liquids must be handled under vacuum or in an inert atmosphere. Alkylammonium and imidazolium salts of tetraalkylborides, perchlorates, or nitrates are either difficult to prepare or weakly conducting. Furthermore, organic nitrates and perchlorates are potentially explosive, especially when dry. For these reasons, tetrafluoroborate, hexafluorophosphate, triflate, and to a lesser extent bis(triflyl)amide salts of *N, N'*-dialkylimidazolium cations are most commonly used, and hold the highest promise for application (see illus.).

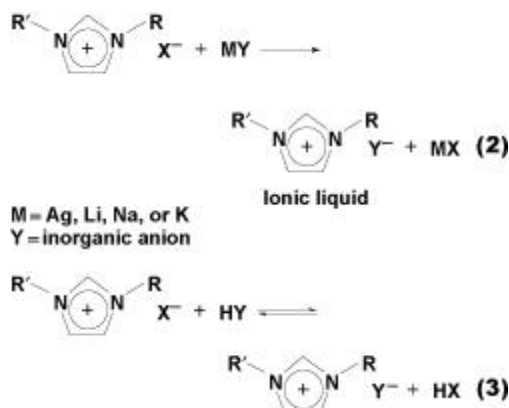
Preparation

Many alkylammonium halides are available commercially at low cost. Alkylpyridinium and dialkylimidazolium halides can be prepared easily by the reaction of an appropriate halogenoalkane with pyridine or alkylimidazole [reaction (1)].

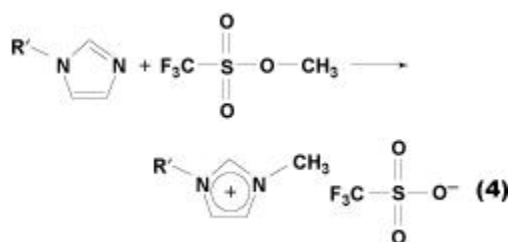


Preparation of alkylammonium halides that are not commercially available can be achieved similarly. The

desired ionic liquid is synthesized from the halide salt via metathesis with a silver, an alkali metal (group 1), or ammonium salt of the inorganic anion [reaction (2)]. An alternative method is acid-base neutralization [reaction (3)]. Ionic



liquids of triflate salts are made in a single-step reaction in which the 1-alkylimidazole is reacted with a stoichiometric amount of methyl triflate [reaction (4)].



The halogenoaluminate ionic liquids are made simply by mixing the appropriate pyridinium or imidazolium halide salt directly with the aluminum(III) halide in the necessary ratios to give the desired composition.

The influences of alkyl substituents and anion size on the physical properties of imidazolium ionic liquids have been studied systematically. The results show that the desirable properties of an ionic liquid, including low melting point, low viscosity, and high conductivity, are favored by (1) small cation and anion sizes, (2) delocalization of charge, (3) low symmetry of the imidazolium cation, and (4) no alkylation of the C-2 on the imidazolium ring. The physical properties for a few ionic liquids are shown in the [table](#).

Physical properties of some room-temperature ionic liquids*				
Ionic liquid	mp, °C	d, g mL ⁻¹	Viscosity, cP	Conductivity, mS cm ⁻¹
[MeBuIm][AlCl ₄]	65	1.10	—	—
[BuBuIm][AlCl ₄]	55	1.01	—	—
[EtMeIm][BF ₄]	15	1.18	38	14
[EtMeIm][TfO]	-9	1.39	45	8.6
[EtMeIm][Tf ₂ N]	-3	1.52	34	8.8
[BuMeIm][TfO]	16	1.29	90	3.7
[BuMeIm][Tf ₂ N]	-4	1.43	52	3.9

Despite their extreme moisture sensitivity, corrosiveness, and toxicity, halogenoaluminates are the most studied family of ionic liquids to date, probably because they were among the first RTILs prepared. Halogenoaluminates react with water to generate hydrochloric acid (HCl), which is itself a toxic gas. Nevertheless, dialkylimidazolium salts of tetrachloroaluminate ($[\text{RR}'\text{Im}][\text{AlCl}_4]$) have been successfully used in spectroscopic and electrochemical investigations of transition-metal halides. Several metal halides, such as hexachloromolybdenum(IV) (MoCl_6^{2-}), that are only transients in molecular solvents were found to be stable in ionic media. The halogenoaluminates have also been used to deposit several aluminum-transition-metal alloys. In addition, the first catalytic reaction to be investigated in ionic liquids involved the use of the aluminates both as solvent and catalyst for electrophilic aromatic substitutions. Acidic compositions of chloroaluminates can give rise to superacidic protons, which stimulated much of the research in this area. Several patents have been issued for the use of chloroaluminate ionic liquids in oligomerization and polymerization of alkenes as well as in the preparation of branched oligomeric fatty acids from linear fatty acids.

Uses

Ionic liquids have found uses in four distinct areas: chemical synthesis, catalysis, separation science, and electrochemistry. Among the noncatalytic reactions that have been investigated in ionic liquids are cycloaddition of cyclopentadiene and methyl acrylate (Diels-Alder reaction), and alkylation of sodium β -naphthoxide. Catalytic science and technology will undoubtedly play a central role in providing a path to environmentally sustainable development. Thus, in the context of green chemistry, the most promising application for RTILs is in catalysis. While homogeneous catalysts offer high reactivity and selectivity, they suffer a major drawback, which is the difficulty of separating the catalyst from the products. When ionic liquids are employed as solvents, catalysts are easily recovered and recycled. The net result is a combination of the efficiency, "atom economy," and selectivity of homogeneous catalysis with the ease of separation inherent in heterogeneous catalysis.

RTILs have been used successfully in the following catalytic transformations: (1) hydrogenation of carbon-carbon double bonds ($\text{C}=\text{C}$) and carbon monoxide (CO) with a variety of rhodium and ruthenium catalysts (the hydrogenation of carbon monoxide yields mixtures of ethylene glycol, methanol, and ethanol); (2) dimerization of butadiene catalyzed by palladium complexes; (3) hydroformylation of olefins catalyzed by a rhodium acetylacetonate complex; (4) coupling of an organoboron reagent with arylhalides (the Suzuki reaction) catalyzed by palladium phosphine complexes; (5) coupling of aryl halides or benzoic anhydride with alkenes (the Heck reaction) brought about by palladium catalysts; (6) epoxidation of alkenes and allylic alcohols with hydrogen peroxide (itself a green reagent) as oxidant and methyltrioxorhenium as catalyst; (7) asymmetric oxygen transfer to alkenes in methylene chloride/ionic liquid mixtures with a manganese catalyst; (8) copper-mediated polymerization of methyl acrylate to give narrow-dispersity polymers. All of the reported catalytic reactions that employ RTILs as solvents either exhibit selectivity and reaction rates comparable to those observed in molecular solvents or show pronounced enhancement in rates due to stabilization of the reactive form of the catalyst. For example, the Suzuki coupling reaction between bromobenzene and phenylboronic acid in organic solvents affords the biphenyl product with 88% yield in 6 hours, but in the ionic liquid dialkylimidazolium tetrafluoroborate the yield is 93%; more importantly, in the ionic liquid the reaction is completed in 10 minutes (36 times faster). All catalytic transformations in ionic liquids greatly improve product separation and catalyst recovery.

In separation technology, ionic liquids have been used to improve nuclear fuel processing, extract organic matter known as kerogen from oil shale, remove hydrogen sulfide (H_2S) and carbon dioxide (CO_2) from contaminated natural gas, process biomass-derived renewable feedstock, and extract metal ions from

aqueous media. In the field of electrochemistry, ionic liquids are promising electrolytes for batteries and solar cells.

Prospects

Although ionic liquids have the potential to be a major contributor in the development of green technologies, it is highly unlikely that they will provide all the answers. Alternative green reaction media include water, supercritical fluids such as supercritical carbon dioxide (CO₂), and fluoruous phases. Some transformations might not require a solvent at all. In order to be successful in conquering the highly competitive world of existing chemical technologies, RTILs have to be less expensive, cleaner, and easier to purify. Purification could be of major concern if small amounts of halide contamination are detrimental to the application or process at hand. Most conventional preparation methods produce ionic liquids that contain a small amount of halide reactants. Nevertheless, ionic liquids will most likely soon be put to use in the fine-chemical sector.

Despite all the recent research attention given to RTILs, there is still a serious lack of physical scientific data. Comprehensive studies dealing with the toxicity, biodegradation, safety, and environmental risk and impact of ionic liquids are needed. In addition, analytical tools for assessing the purity of ionic liquids await development. However, the exploration of chemical reactions (catalytic and noncatalytic) in ionic liquids remains an exciting endeavor, since any reaction could produce an unexpected result. Pronounced differences in the behavior of many chemical reactions have already been observed between ionic liquids and molecular solvents, and many more are awaiting discovery.

See also: Catalysis; Chemical separation techniques; Electrochemistry; Fused-salt solution; Heterogeneous catalysis; Organic synthesis; Salt (chemistry); Solvent

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How to cite this article

Mahdi M. Abu-Omar, "Green chemistry", in AccessScience@McGraw-Hill, <http://www.accessscience.com>, DOI 10.1036/1097-8542.YB020405

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