NONAQUEOUS ROOM-TEMPERATURE IONIC LIQUIDS: A NEW CLASS OF SOLVENTS FOR CATALYTIC ORGANIC REACTIONS.

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Room-temperature organic-inorganic ionic liquids of the BMI⁺A⁻ type (BMI⁺=l-butyl-3-methylimidazolium, A⁻=Al₂Cl₇⁻, AlCl₄⁻, BF₄⁻, PF₆⁻ and SbF₆⁻) have been used as a new class of solvents for two-phase catalytic reactions. The chemical and physical properties of these media can be varied with the nature of the A⁻ anions and can be adjusted to the catalyst precursors and reactions involved. They are good solvents of various transition-metal catalysts and are poorly soluble with aliphatic hydrocarbons and aldehydes. Thus, the separation of the reaction products from the catalyst, one of the main drawbacks of homogeneous catalysis, can be easily achieved by simple decantation. Ionic liquids offer the opportunity to extend the field of two-phase catalysis to substrates, complexes and ligands which are poorly soluble or unstable in water.

The solvent in organic catalytic reactions can influence the course of a reaction by increasing reaction rates and allowing better reaction control of chemo-, regio-, stereo- and enantioselectivities. Despite the advantage of using a solvent, the major disadvantage is its separation from the catalyst and the products. An alternative approach is to use a solvent for the active species, which is a poor solvent for the reactant(s) and reaction product(s). All industrial applications of this two-phase catalysis technology have been restricted to aqueous-organic systems (1). However, water is a highly coordinating protic solvent and it is reactive toward many organometallic catalysts. For this reason, we have been investigating the use of room-temperature 1-butyl-3-methylimidazolium (BMI⁺) ionic liquids as a new class of nonaqueous solvents for two-phase catalytic hydrocarbon transformations (2).

The organochloroaluminate ionic liquids, based on the mixture of aluminium trichloride and 1-butyl-3-methylimidazoliumchloride (BMICl), have the attractive property that their Lewis acidity can be controlled with the composition of the liquid. They favor the dissociation of ionic transition-metal complexes and may be regarded as Lewis acidic noncoordinating media. We have extended this class of liquids to aluminium compounds bearing an aluminium-carbon bond, such as EtAlCl₂ and its mixture with aluminium trichloride (3, 4). Nevertheless, acidic organochloroaluminate liquids are highly sensitive to moisture and may react with functionalized organic products and/or reactants. For this reason, we have extended the use of molten salts to the systems which make use of anions such as [BF₄]⁻, [PF₆]⁻, [SbF₆]⁻, [CF₃SO₃]⁻ (5), etc. Contrary to the [AlCl₄]⁻ anion, such anions do not combine with their corresponding Lewis acids and thus do not form polynuclear anions. Hence these salts are neutral stoichiometric compounds and cannot have a potential acidity.

We have initiated a series of studies using these salts as solvents for catalytic reactions involving charged species (carbeniums and carbanions) or transition-metal
complexes. To this end, the solvation and coordination ability of ionic liquids is of the utmost importance. In this way ionic liquids can be classified according to the complexing ability of their anions (Table 1).

**Olefin dimerization.**

We first applied the two-phase catalysis concept to the dimerization of olefins catalyzed by nickel complexes. The active species involved in this reaction is a cationic nickel complex of the type [LNi-CH₂R']⁺ [AlCl₄]⁻ (L=PR₃) (6). Non coordinating acidic organochloroaluminate liquids proved to be superb solvents for stabilizing the active nickel catalyst. At 5°C and under atmospheric pressure, the propene dimerization reaction productivity was more than 250 kg of dimers per g of nickel, which is much greater than that obtained with organic solvents. The reaction products form a second upper phase which can easily be separated by simple decantation. The pale yellow-orange catalyst remains in the ionic phase and can be reused several times (7, 8).

The main advantage of performing the dimerization reaction in ionic liquids is a better use of nickel complexes, aluminium compounds and costly phosphine ligands which make possible the production of interesting propene dimerization isomers.

**Olefin metathesis (9).**

The reaction is usually described by the following equilibrated disproportionation of olefins and can be applied to most olefins:

\[
2\text{CH}_3\text{CH}═\text{CHCH}_2\text{CH}_3 ⇋ \text{CH}_3\text{CH}═\text{CHCH}_3 + \text{CH}_3\text{CH}_2\text{CH}═\text{CHCH}_2\text{CH}_3
\]

We have obtained very good results in pen-2-ene metathesis by using W(OAr)₂Cl₄ complexes (ArOH = 2,6-diphenylphenol or 2,4,6-triphenylphenol) dissolved in BMIC:AlCl₃:EtAlCl₂ (1:0.9:0.2) ionic liquids. The reaction equilibrium was reached in 4 hours. Active species are quite soluble, remain in the polar phase and can be reused several times after decantation of the hydrocarbon layer. Pent-1-ene is converted into ethylene and oct-4-ene, and the mixture of cyclopentene and pent-2-ene affords the expected telomers.

**Hydrogenation of C=C bond.**

As ionic liquids are known to dissolve charged species, we first applied them to the hydrogenation of pent-1-ene using the Osborn [Rh(NBD)(PPh₃)₂]⁺PF₆⁻ complex (NBD=norbornadiene) as the cationic catalyst precursor (10). Remarkable solvent effects are observed. When BMI+SbF₆⁻ salt is used, hydrogenation rates are nearly five times higher compared to the homogeneous reaction in acetone, in spite of the expected limited solubilities of reactants in the polar phase. When using ionic liquids prepared from BMI⁺Cl⁻ and CuCl (1:1.5), only isomerization to pent-2-ene with 100% selectivity (98% of cis-pent-2-ene) is observed, in sharp contrast to the previous results. This demonstrates that the selectivity can be strongly influenced by the nature of the anion.

Conjugated diolefins such as cyclohexa-1,3-diene and 2-methylbuta-1,3-diene have also been hydrogenated. This is all the more interesting since diolefins are more soluble in ionic liquids than the corresponding monoalkenes (e.g. cyclohexa-1,3-diene is five times more soluble than cyclohexene in the MBI⁺SbF₆⁻ salt). This can potentially improve the selectivity of the hydrogenation.
In all these experiments, the ionic solutions containing the catalyst can be reused. Only a negligible loss of rhodium was observed (less than 0.02%; under the detection limit). Thus, as ionic liquids are known to stabilize preferably cationic species and do not solvate the Rh-complex, we assume that the prevailing active catalyst is a cationic not solvated Rh-dihydrido complex which has two free coordination sites. To our knowledge, this is the first example of two-phase hydrogenation reactions in which an active rhodium catalyst is "immobilized" in a polar phase without special ligand design.

Olefin hydroformylation.

Two-phase pent-1-ene hydroformylation can also be achieved, as hexanal is poorly soluble in ionic liquids. Experiments using the Rh(CO)$_2$(acac)/PPh$_3$ uncharged molecular system as catalyst precursor, show high catalytic activity in the BMI$^+$PF$_6^-$ salt (TOF = 333 h$^{-1}$). After removal of the organic products, the ionic phase can also be reused and gives quite similar activity. However, a small part of the active Rh-catalyst is extracted into the organic phase. Thus, in contrast to the hydrogenation reactions, the uncharged Rh(CO)$_2$(acac) catalyst precursor has to be immobilized in the salt by a polar ligand. For this purpose, the sodium salts of monosulfonated (TPPMS) and trisulfonated (TPPTS) triphenylphosphine ligands have been used. In this way, extraction of the Rh-catalyst could be completely avoided.

Butadiene dimerization.

"Fe(NO)$_2$" is a well known catalyst for the Diels-Alder dimerization of conjugate diolefins, such as butadiene, into 4-vinylcyclohexenes (11). This species is usually obtained by reduction of Fe$_2$(NO)$_4$Cl$_2$. The slightly coordinating [MBI]$^+$[AF$_6^-$] (A=P or Sb) ionic liquids proved to be adequate solvents for stabilizing the active intermediate. The "ionic liquid solvent effect" is quite remarkable. Electrochemical reduction of the Fe$_2$(NO)$_4$Cl$_2$ complex could be used with confidence in high-conductivity ionic liquids.

Organochloroaluminates as acidic catalysts (12).

The alkylation reactions of olefins with isobutane may proceed, in acidic chloroaluminates, in a way similar to that previously described with conventional liquid catalysts. However, one of the advantages of using organochloroaluminates is that their catalytic activity may be readily controlled through the [Al$_2$Cl$_7^-$] anion concentration. Very acidic BMICl$_3$/AlCl$_3$ (1:2) mixtures promote the alkylation of ethene with isobutane (neither HF nor H$_2$SO$_4$ acids are effective for this reaction). The reaction provides 2,3-dimethylbutane as the main reaction product. The alkylation of but-2-ene with isobutane can be performed with the same acidic ionic liquids. However, due to the higher reactivity of butene, the acidity of the salt has to be carefully controlled to prevent side reactions. Some additives can improve the reaction. The catalyst productivity is eight time greater than that obtained with sulfuric acid catalyst, while the alkylate composition is maintained as described below. The imidazolium salt can be recovered by hydrolysis.

CONCLUSION

Ionic liquids show great promise as solvents for two-phase catalysis. It may be assumed that most of the known transition-metal catalyzed reactions could be carried out in organic-inorganic ionic liquids by fitting the liquid composition with the selected

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catalyst precursors. This technique appears to be particularly valid in many cases: when transition metals and ligands are costly (e.g. in asymmetric catalysis); when the disposability of the catalyst systems raise difficulties. On other hand, advantage can be taken of the solubility of reactants and the poor solubility of products.

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Table 1: Non aqueous room-temperature ionic liquids.

| Cations | Anions | Coordination ability |
|---------|--------|---------------------|
| [NR₄⁺][a] | BF₄⁻ | strong (basic) |
| PR₄⁺ | PF₆⁻ | weak (neutral) |
| SR₃⁺ | SbF₆⁻ | |
| CF₃SO₃⁻ | CuCl₂⁺ | |
| AlCl₄⁻ | Cu₂Cl₃⁺, Cu₃Cl₄⁺ | no (acidic) |
| Al₂Cl₇⁺, Al₃Cl₁₀⁻ | |

[a] N-alkylpyridinium, 1,3-dialkylimidazolium