Catalytic reactions using superacids in new types of ionic liquids†

Mark A. Harmer,*[a] Christopher P. Junk,[a] Vsevolod V. Rostovtsev,[a] William J. Marshall,[a] Liane M. Grieco,[a] Jemma Vickery,[b] Robert Miller[a] and Stella Work[b]

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We will describe the use of superacids, in particular 1,1,2,2-tetrafluoroethanesulfonic acid (TFESA) and 1,1,2,3,3,3-hexafluoropropanesulfonic acid (HFPSA) in the presence of ionic liquids for improved chemical processing for a range of industrially important chemical reactions. In a number of cases the reaction mixture starts as a single phase, allowing for high reactivity, then separates into two phases upon completion of the reaction. This allows for ease of product separation P. T. Anastas and T. C. Williamson, *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes*, Oxford University Press, 1998.[1]

Introduction

In this paper, we will expand upon our earlier work, namely the use of new Brønsted superacidic catalysts for a number of acid catalyzed reactions of industrial importance.[2,3] Traditional homogeneous acids, such as hydrofluoric (exceptionally hazardous) and sulfuric acids have a number of drawbacks in industrial processes including the generation of large amounts of waste associated with product separation. Replacement of these acids with highly active catalysts (such as superacids) that can be recycled and easily separated has the potential to reduce waste, reduce energy needs, cut down the process time, and make the overall process safer and more economical. For example, triflic acid is already employed in fine chemical synthesis, and ionic liquids (anions). Interest in these materials is growing.[4–7]

We have recently described the use of superacids of the form $RCHFCF_2SO_3H$ (R = F, Cl, CF_3, or fluoroalkoxy).[2] Compared to triflic acid, these acids are safer to handle due to their higher boiling point/lower volatility. They also incorporate an easily identifiable proton that can be monitored by NMR.

Acid catalysts are employed in an extensive range of commercial reactions.[8] Alkylations are common in the commercial production of ethyl benzene, trimethylpentane for high octane fuels, and cumene and linear alkyl benzenes for the surfactants industry. Traditionally, homogeneous acid catalyst such as $AlCl_3$, $FeCl_3$, H_2SO_4, HF and BF_3, are employed.[9,10] Isomerization products are used in refining and preparation of lubricants[11] and acylation is important in a wide range of areas.[12,13] The use of ethers and polyethers also have a wide range of applications.[14,15]

Here, we describe the use of fluoroalkylsulfonic acids such as 1,1,2,2-tetrafluorethanesulfonic acid (TFESA) and 1,1,2,3,3,3-hexafluoropropanesulfonic acid (HFPSA). As we have discussed before, these have acidities similar to triflic acid, a well known superacid.[7] The present work utilizes the conjugate base of these acids to make a range of ionic liquids, and then uses the ionic liquid in combination with the conjugate acid as a catalyst system for a range of reactions.

The main aim of this work is to develop simplified chemical reactions where the catalyst can easily be removed and separated from the products. Effective catalyst separation, leading to minimum waste, is one of the underlying goals of green chemistry.[1] While catalysts are available for many kinds of reactions, it is often quite difficult to remove the catalyst from the products.[16] Techniques such as distillation, liquid–liquid extraction, and absorption onto some kind of sacrificial absorbent are often employed. All of these approaches are energy intensive. In our studies we have developed a catalyst-ionic liquid system for two different reaction types. These are single phase at the beginning of the reaction, but become two phase at the end. This leads to easy separation of the catalyst from the products *via* simple decantation. In this paper we describe our preliminary findings.

Results and discussion

In this paper we describe a series of new ionic liquids where the anion is derived from the superacids 1,1,2,2-tetrafluorethanesulfonic acid and 1,1,2,3,3,3-hexafluoropropanesulfonic acid. These ionic liquids are similar to the well known ionic liquids which have triflate as the anion. We also show how to use the ionic liquids in conjunction with the superacid to catalyze a variety of reactions, namely, alkylation, isomerization of olefins and etherifications. The ionic liquids can be conveniently prepared from the potassium salt of the anion and the corresponding imidazolium salt *via* a simple metathesis reaction (see Scheme 1 and Experimental Section).

For example, 1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate [EMIM-TFES] can be synthesized from EMIM-Cl and TFESK in acetone. Potassium chloride

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[a] *DuPont Central Research and Development, Experimental Station, Wilmington, Delaware, 19880, USA. E-mail: Mark.A.Harmer@USA.DuPont.Com*
[b] *School of Chemistry, University of Bristol, UK*

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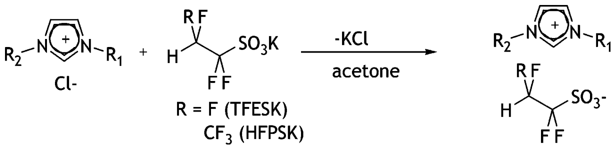


Scheme 1

precipitates out of the acetone solution and the ionic liquid is isolated as a pale yellow liquid, which crystallized upon standing. Compared to triflate-based ionic liquids, and indeed the vast majority of ionic liquids reported in the literature, one important feature of these ionic liquids is the ability to track both the cation and the anion *via* ^{1}H NMR. As we have discussed previously,[2] both 1,1,2,2-tetrafluoroethane- and 1,1,2,3,3,3-hexafluoropropanesulfonates have characteristic ^{1}H NMR signals around 5.6 and 6.1 ppm, respectively. Therefore, EMIM-TFES has well-defined ^{1}H signals from both the anion and cation allowing for a simple check on cation/anion ratio as well as any variations that may result as an effect of ion exchange due to impurities, Fig. 1. This allows for ease of monitoring of the ionic liquids during their use in chemical reactions.

Several ionic liquids have been synthesized based upon the above two superacids. These include BMIM-TFES, EMIM-TFES, BMIM-HFPS, B2MIM-HPFS and a phosphonium based ionic liquid TBP-TFES (TBP = tetrabutylphosphonium), and their physical properties are summarized in Table 1. All of the ionic liquids show high thermal stability (see a representative TGA on Fig. 2), allowing for a wide range of operating temperatures. Most of the ionic liquids were miscible with water and polar organic solvents such as acetone, ethanol, ether, tetrahydrofuran and acetonitrile, and only slightly soluble in toluene and hexane. TBP-HFPS is less polar, as evidenced by its low solubility in water, but high solubility in toluene. In addition to the above ionic liquids, we also synthesized 1-dodecyl-3-methylimidazolium-TFES which is more hydrophobic. A number of these ionic liquids have been used with superacids as reaction medium for a range of transformations.[17,18]

It is interesting to note that EMIM-TFES was liquid for several weeks at room temperature before undergoing a sudden exothermic crystallization. Suitable crystals for X-ray diffraction were grown for EMIM-TFES[19] and EMIM-nonaflate[20,21] and the single crystal structures were completed in order to compare the effects of the CHF_2 group *versus* the purely fluoroalkyl CF_3 on the crystal packing and close contacts. The packings are shown in Fig. 3 (see ESI for the packing of EMIM-nonaflate†). The overall packing of EMIM-nonaflate is layered along the crystallographic b-axis with the negative SO_3 and positive EMIM regions alternating with fluoroalkyl chain regions. The EMIM-TFES structure forms a much different non-layered packing motif. The TFES anions form in a head-to-tail arrangement with each other driven by the strong CH···O interaction of the CHF_2 group with a short CH···O distance of 2.27 Å. Not surprisingly, an examination of the environment around the SO_3 groups show close O···H contacts to neighboring sp^2 hydrogen on the cationic EMIM for both structures. It is the additional strong CH···O contacts from the CHF_2 group that differentiates the EMIM-TFES structure. The structure of EMIM-triflate[22] found in the literature compares well with the layered EMIM-nonaflate structure in terms of overall packing and close contacts.

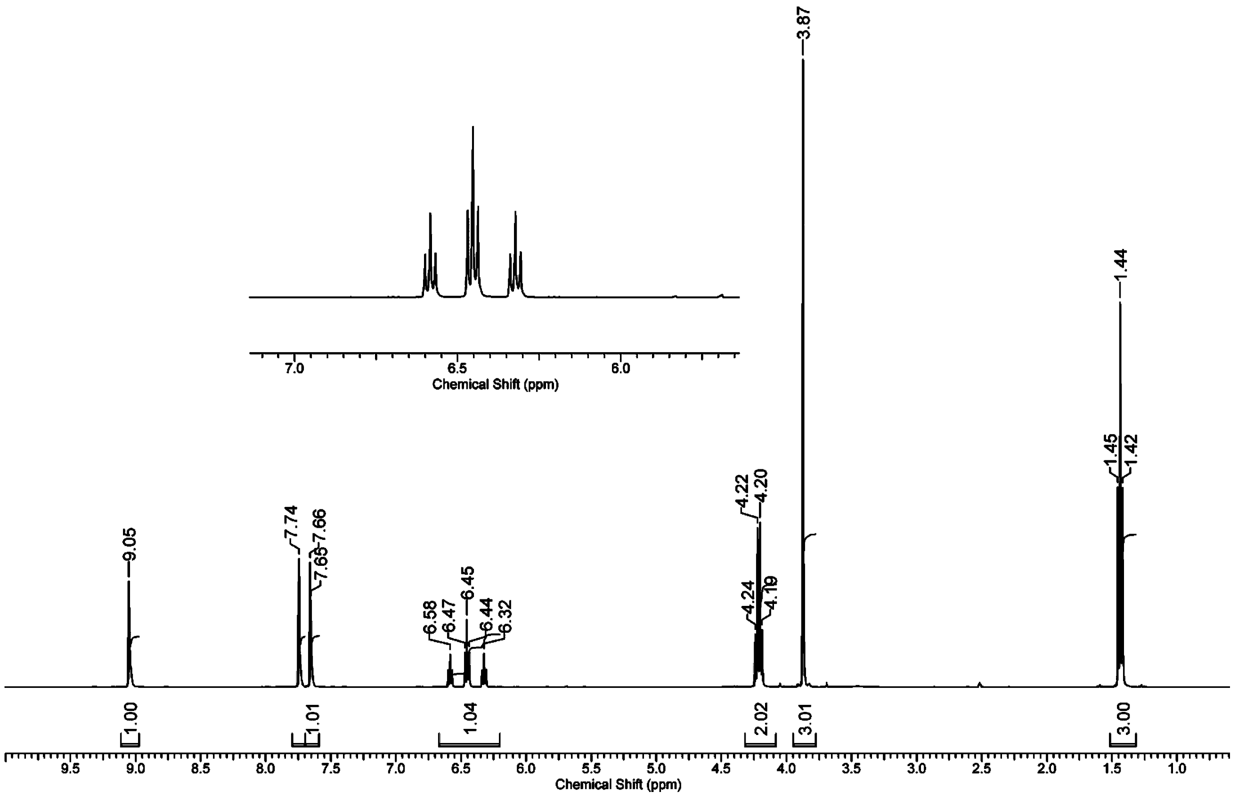
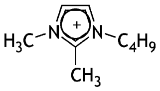


Fig. 1 ^{1}H NMR of EMIM-TFES, showing both the anion and cation peaks.

Table 1 Physical properties of ionic liquids

Name	Structure	mp, °C	T_{10}, 10% decomposition temperature, °C	Viscosity at 25 °C, cp
BMIM-TFES	 $HCF_2CF_2SO_3^-$	<25	375	167
EMIM-TFES	 $HCF_2CF_2SO_3^-$	45	397	84
BMIM-HFPS	 $CF_3CHFCF_2SO_3^-$	<25	360	293
TBP-HFPS	$(C_4H_9)P^+$ $CF_3CHFCF_2SO_3^-$	73	360	—
B2MIM-HFPS	 $CF_3CHFCF_2SO_3^-$	<25	375	690

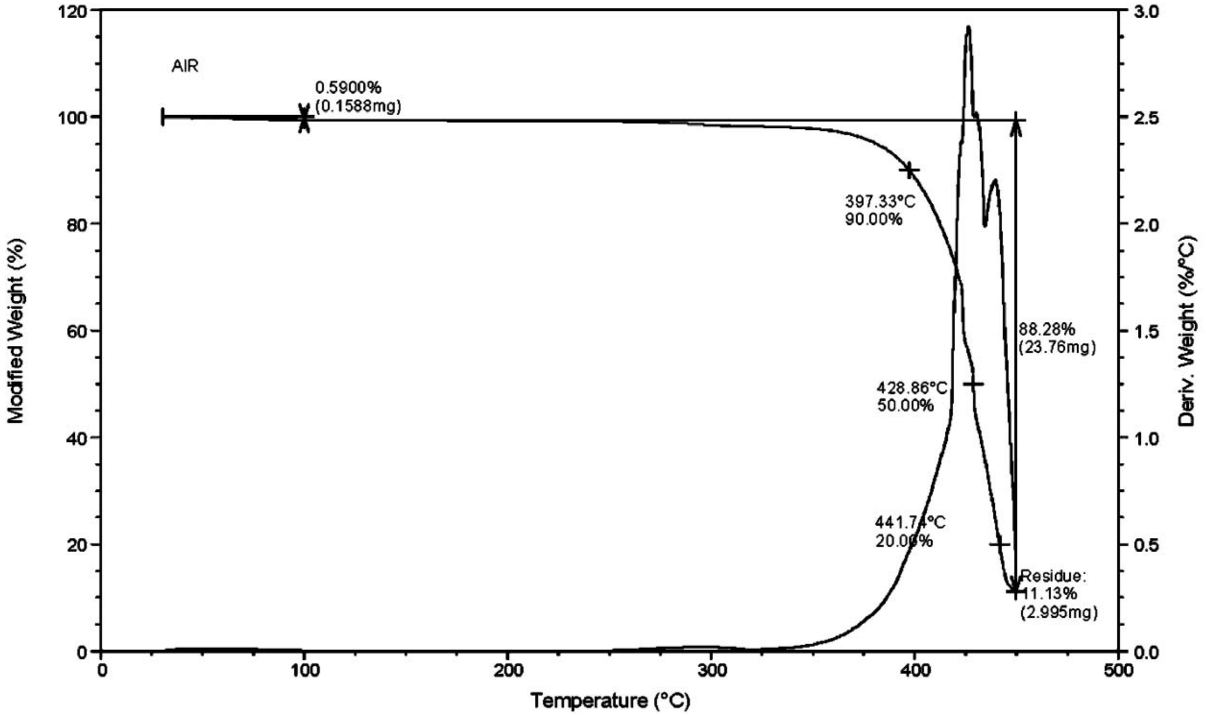


Fig. 2 TGA of the ionic liquid EMIM-TFES.

The alkylation of aromatic compounds such as benzene and benzene derivatives with olefins is carried out on a large scale in the chemical industry.[23] Alkylbenzenes have many industrial uses. For example, ethyl benzene, formed by the reaction of ethylene with benzene, is an intermediate in styrene production. Alkylation of benzene with propylene yields cumene, an intermediate in phenol and acetone production. Linear alkyl benzenes are synthesized from the reaction of longer-chain olefins (*ca.* 10–18 carbon atoms) with benzene or benzene derivatives; the linear alkyl benzenes are then sulfonated to produce surfactants. One disadvantage to these reactions is the cost associated with separating the catalyst from the reaction product(s). The main catalyst used is HF.[24] It is clearly advantageous to carry out the alkylation reaction in such a way that the catalyst could be easily separated from the reaction product(s).

Ionic liquids are liquids composed of only ions that are fluid around or below 100 °C.[25] Ionic liquids exhibit negligible vapor pressure.[26] Much research has been devoted to design and

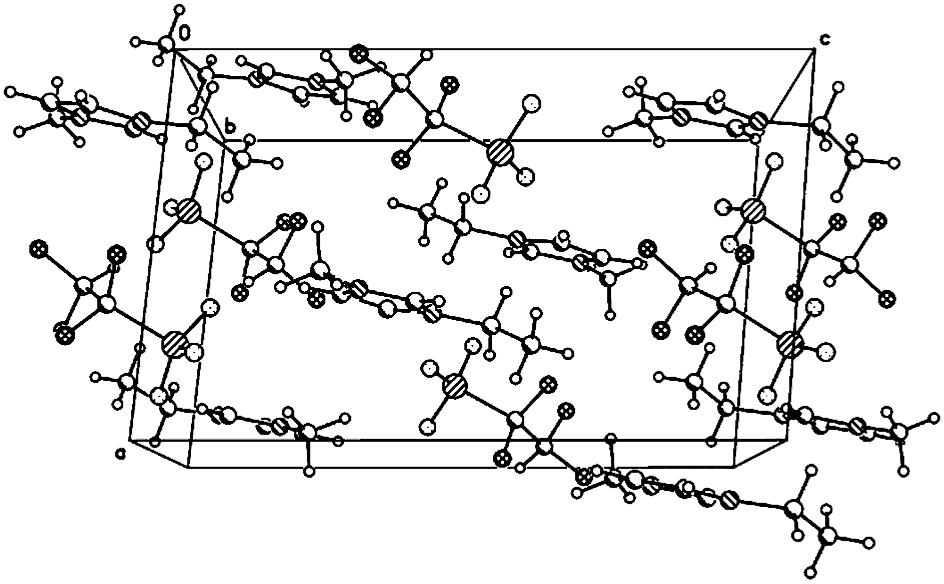
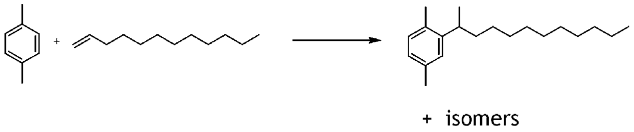


Fig. 3 Crystal packing of EMIM-TFES.

development of ionic liquids as replacements for conventional solvents in an effort to reduce the amount of volatile emissions and decrease the level of aquifer and drinking water contamination. We have found that aromatic alkylation reactions can be carried out in ionic liquids, and that the homogeneous acid catalyst can be easily removed as the reaction mixture separates into two phases after the product is formed.

The combination of ionic liquids and superacid catalysts including TFESA and HFPSA was investigated using the Friedel–Crafts alkylation reaction. This process currently uses homogenous acids (hydrofluoric and sulfuric) as catalysts of choice.[24] There is a drive in industry to replace these acids with more benign alternatives and the use of ionic liquids as reaction medium provides one potential solution to this problem.



(1)

The alkylation of *p*-xylene with 1-dodecene was studied for the majority of this work, however similar results were also obtained using benzene. Our preference for initially using xylene is simply the fact that it is less toxic and safer to use than benzene. Initial experiments investigated the activity of the acids in the absence of any ionic liquid. Complete conversion to alkylated products (>99%) was observed after 15 minutes, however the reaction product was deep red and the acid appeared to be dissolved in the alkylate product, making separation difficult (see Experimental Section). The product distribution has been previously described[2] in terms of the olefin isomers, with the 2-aryl-isomer being most preferred. There was no observed skeletal isomerization of the olefin prior to alkylation, which can lead to unwanted non-linear alkyl aromatics. With a single-phase solution formed at the end of the reaction, a purification step is required to separate the acid catalyst from the alkylated products using either distillation or absorption of the catalyst on a basic support. Our initial idea was to use an ionic liquid that might yield a biphasic system, with the acid catalyst-IL system in one phase and the reactants in the second phase.

Two ionic liquids were investigated: 1-butyl-3-methylimidazolium 1,1,2,2-tetrafluorethanesulfonate (BMIM-TFES) and 1-dodecyl-3-methylimidazolium 1,1,2,2-tetrafluorosulfonate (C_{12}MIM-TFES) with HFPSA as the catalyst (although similar results were found using TFESA). These ionic liquids were chosen to compare the effect of the the imidazolium cation structure on the outcome of the reaction. We found that initially the system formed a single phase, but as the amount of product increased, the reaction mixture phase-separated into products in one phase and the acid and ionic liquid in the other phase (shown in Fig. 4). This phase separation enabled easy isolation of the products from the catalysts. Following alkylation, phase separation occurs with between 95–99% conversion of the 1-dodecene with excess xylene (see Experimental Section). The ionic liquid also serves as a ‘solvent’ that sequesters the acid at the end of the reaction. The separation time is between 30 and 60 min.

With excess xylene, the conversion to alkylated product (95–99%) is obtained after 1 hour reaction time (followed by GC), which is longer than when the acid is used by itself. There was no significant difference in activity between the two ionic liquids, BMIM-TFES and C_{12}MIM-TFES, with HFPSA. Note that the amount of ionic liquid is quite low (less than 10 vol%) which is preferable economically.

Interestingly, the ratio of the acid to ionic liquid had a very strong effect upon both the activity and conversion. The ratio was varied, allowing determination of the optimum acid to ionic liquid ratio. The results are shown in Table 1, which gives % conversion values for the formation of alkylated products from the starting reagents varying the ratio of acid-IL. The results show that the highest conversion rates are seen when there is an excess of acid (Table 2).

Table 2 Alkylation of xylene with 1-dodecene in the presence of the superacid HFPSA and C_{12}MIM-TFES, with different ratios of the superacid to the ionic liquid at 100 °C (see Experimental section for details)

Molar Ratio of Superacid to IL	% conversion after 15 mins	% conversion after 60 mins	% conversion after 120 mins
3:1	70.4	95	96
1:1	5.7	50	85.7
1:3	0	0	<1

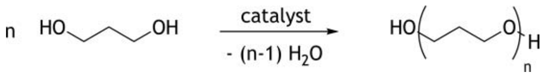
Fig. 4 HFPSA-catalyzed alkylation of xylene in the absence (left) and presence (right) of an ionic liquid.

The data show that there is an optimum acid/ionic liquid ratio. High activity and conversion were obtained at the high superacid/IL ratio. Careful analysis of the alkylate phase, after exhaustive water extractions following separation from the ionic liquid/acid phase, reveals that less than about 1% of the acid is present in the product phase (with greater than 99% in the ionic liquid phase). We also estimate that there is less than 1% of the ionic liquid in the product phase. The ionic liquid/acid phase has also been recycled to yield 99% conversion upon one re-cycle, but with a lower conversion on the second recycle (60–70%).

Post-reaction phase separation is a simple and effective way to separate the products. We also note that a similar reaction using an ionic liquid with a Lewis acid, $Sc(OTf)_3$, has been reported.[27] Interestingly, alkylation is not observed when EMIM-triflate is used as the ionic liquid. The authors used an excess of EMIM-triflate and it is possible that reaction was prevented by the deactivation of catalyst by ionic liquid (acidity of superacids is lowered in ionic liquids[17,28]). It is also possible that ionic liquid may improve the phase compatibility of the catalyst with the hydrophobic organic reactants, acting as a pseudo phase transfer catalyst. It would be interesting to see if lowering the amount of IL (a high catalyst/IL ratio) gives rise to alkylation. From a practical point of view, it would be ideal to have both minimum acid and minimum IL, yielding a phase-separated system after reaction.

We also investigated the acid catalyzed polymerization of 1,3-propanediol in the presence of an ionic liquid and acid catalyst. 1,3-Propanediol can be prepared using a recently commercialized fermentation process based upon corn-derived glucose. The polyether made from the acid-catalyzed condensation of 1,3-propanediol, PO3G, is 100% renewably resourced and is now available under the trade name Cerenol®.[29] The desired polymer molecular weight M_n can be varied from 250 to 3000 depending upon the reaction conditions, giving a range of low viscosity liquids to highly viscous polymers. Other renewable polymers are polylactic acid and polyglycolide.[30] These polymers are starting to find a wide range of uses as lubricants, coatings, oils, clothing, and additives in other polymer systems. The interest in renewably resourced chemicals and polymers is an active area of interest.[31–33]

Polymerization of 1,3-propanediol to polyol was performed using TFESA (bp 212 °C) and ionic liquids, such as EMIM-TFES (see Experimental section). Similar results were obtained using the ionic liquid BMIM-TFES. This reaction can also be carried out with a wide range of catalysts, including sulfuric acid, although superacids have the advantage of fewer by-products (sulfate esters are common in sulfuric acid based reactions).[34]



(2)

The homogeneous solution of 1,3-propanediol and TFESA in EMIM-TFES was heated at 160 °C under a nitrogen atmosphere. Water slowly evolved as polymerization took place and was collected in a condenser, assisted by a slow nitrogen purge. As the polymer forms, the solution goes from a single-phase to a two-phase system. Upon cooling, two phases were clearly visible. The top phase was shown *via* ^{1}H NMR spectroscopy to be polymerized 1,3-propanediol (polyol) with molecular weight (M_n) of 2907, after a reaction time of 10.5 hours. Most of the acid and ionic liquid were found to be in the lower phase. The time it took for phase separation was between one and two hours, probably due to the higher viscosity of the polymer. The lower phase can be easily separated by decantation and recycled. In this case, EMIM-TFES is readily soluble in 1,3-propanediol and as the less polar polymer is formed, both the ionic liquid and acid form a separate phase. Between 1.5 and 2 wt% of the original acid is found in the polymer layer together with less than 1 wt% of the IL. At the same time, less than 1 wt% of the product is found in the lower acid/IL phase. Traces of the acid can be removed from that layer completely by treatment with $CaCO_3$. The catalyst/IL phase was recycled and the rate of evolution of water, which is related to the conversion rate, was about the same as during the first cycle. The resulting polymer showed M_n of 3000 after reaction time of 10.5 hours (Fig. 5).

We have also investigated etherification of *n*-pentanol. Di-*n*-pentylether has a wide range of industrial uses.[15] The etherification of *n*-pentanol with a range of acid catalysts has

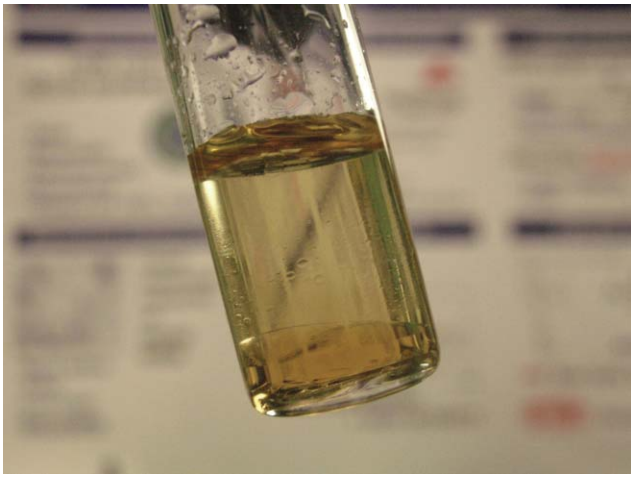
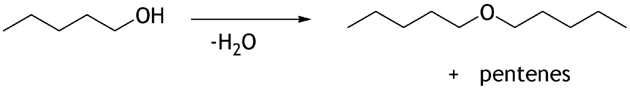


Fig. 5 Formation of the polyol product PO3G (M_n 2907, top layer), with the TFESA catalyst and ionic liquid in the lower phase.

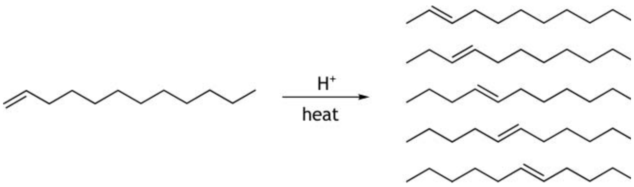
recently been described.[15] We attempted this reaction using a mixture of TFESA and EMIM-TFES at 165 °C in a sealed pressure vessel (*ca.* 25 psi, 6–8 hours). Under these conditions an equilibrium mixture is formed between di-*n*-pentylether, water, and *n*-pentanol, including about 10% dehydration to the pentenes.



(3)

Typical conversions (around 70%) were obtained after heating for 6 hours. Thus the final mixture contained about 70% di-*n*-pentylether, 15% *n*-pentanol and 15% pentenes (measured *via* GC, pentene is hard to quantify as the reaction vessel was vented at atmospheric pressure). We found that fast phase separation occurs at the end of the reaction (after shaking the two phases are reformed within 1–2 minutes). However, the product distribution in the two phases is not as distinct as in the reactions described above (as determined by careful ^{1}H NMR analysis with comparisons to the pure individual species, *n*-pentanol, di-*n*-pentylether, TFESA and EMIM-TFES). At least 10% of the *n*-pentanol and di-*n*-pentylether mixture was found in the IL phase, along with some ionic liquid being found in the main product phase (about 5 wt% of the ionic liquid). The product of this reaction is more polar than alkyl benzenes or long chain polyols, leading to a greater degree of phase miscibility with the ionic liquid phase. More work is needed to find the optimum IL-catalyst-alcohol system for this reaction.

Various methods have been described in the past for the catalytic isomerization of hydrocarbons,[35] including the use of superacids. The products, a mixture of internal olefins, are subsequently used in a range of major industrial processes in the context of petrochemical oil-refining.[36] Olefin chemistry involving *cis-trans*-isomerization, or double bond migration, is widely known.[36,37] The olefin isomer products are useful in the formulation of well fluids such as drilling mud for offshore drilling. Whereas TFESA showed virtually no catalytic activity in this reaction when used neat, when in C_{12}MIM-TFES, the same catalyst showed conversion to the thermodynamic mixture of six isomers (see below), depending upon the reaction conditions and the nature of the ionic liquid. This reaction system differs from the ones described above in that it is essentially biphasic from the very start of the reaction. Thus, the reactivity will depend on the nature of the interface and the availability of the acid to the reagents (1-dodecene in this case). As discussed below, longer chain ILs appear to be more effective.



(4)

The isomerization was investigated by mixing the ionic liquid (for example 1 g of C_{12}MIM-TFES), TFESA (0.5 g) and 1-dodecene (30 ml). The stirred mixture was heated to 100 °C for 2 hours, and the reaction progress was followed by GC as described previously.[2] GC analysis confirmed the conversion of 1-dodecene to a thermodynamic mixture of isomers, with about 15% of the 1-dodecene remaining (85% conversion). A similar result was obtained in 1-hexadecyl-3-methylimidazolium TFES ionic liquid. A series of 1-alkyl-3-methylimidazolium TFES ionic liquids was investigated. The order of activity (measured as the time to reach equilibrium distribution of isomeric olefins), based on the length of the alkyl group, was found to be hexadecyl ≥ dodecyl > hexyl >> butyl ≈ ethyl. The conversion in EMIM-TFES was less than 10% after two hours, and a similar result was obtained for BMIM-TFES. The 1-Hexyl-3-methylimidazolium TFES/TFESA system gave 50% conversion after two hours. The ratio of the ionic liquid to TFESA did not appear to have a dramatic effect on the rate of this reaction. It is likely that the longer alkyl chain on the imidazolium cation gives rise to higher activity through better dispersion of the reagent in the IL/acid phase.

Summary

We have shown that superacids such as 1,1,2,2-tetrafluoroethanesulfonic acid can be used in conjunction with ionic liquids made from the anion of the same acid in the chemical processing of a number of chemically important reactions (alkylation, etherification and isomerization). Interesting phase change behavior occurs during alkylation and etherification reactions which facilitates easy separation of the products. We applied this biphasic catalytic system to the synthesis of a new kind of polymer based upon the acid-catalyzed polycondensation of 1,3-propanediol, which can be derived from a renewable resource. Olefin isomerization can also be catalyzed using superacid-ionic liquid mixtures, although the chemical structure of the ionic liquid has a very strong effect on conversion: the longer alkyl chains on the ionic liquid gave higher conversions, presumably due to an enhanced interfacial interaction of the olefin with the catalyst. These preliminary findings point to the potential use of carefully selected ionic liquids and superacids in improved chemical processing.

Experimental section

The synthesis of TFESA and HFPSA has recently been described.[2] For TFESA: ^{19}F NMR (CD_3OD) δ –125.2 (dt, $^3J_{FH}$ = 6 Hz, $^3J_{FF}$ = 8 Hz, 2F); –137.6 (dt, $^2J_{FH}$ = 53 Hz, 2F). ^{1}H NMR (CD_3OD) δ 6.3 (tt, $^3J_{FH}$ = 6 Hz, $^2J_{FH}$ = 53 Hz, 1H). For HFPSA: ^{19}F NMR (D_2O) δ –74.5 (m, 3F); –113.1, –120.4 (AB q, J = 264 Hz, 2F); –211.6 (m, 1F). ^{1}H NMR (D_2O) δ 5.8 (m, $^2J_{FH}$ = 43 Hz, 1H).

The ionic liquids were synthesized from the respective halides of the cations and the corresponding potassium sulfonate salt of the acid. Examples of the syntheses of four ionic liquids are described below.

Synthesis of 1-butyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate (BMIM-TFES)

1-Butyl-3-methylimidazolium chloride (60.0 g) and high purity dry acetone (>99.5%, 300 ml) were combined in a one-liter flask and warmed to reflux with magnetic stirring until the solid completely dissolved. At room temperature in a separate one-liter flask, potassium-1,1,2,2-tetrafluoroethanesulfonate[2] (TFES-K, 75.6 g) was dissolved in high purity dry acetone (500 ml). These two solutions were combined at room temperature and allowed to stir magnetically for 2 hr under positive nitrogen pressure. The stirring was stopped and the KCl precipitate was allowed to settle, then removed by suction filtration through a fritted glass funnel with a celite pad. The acetone was removed *in vacuo* to give a yellow oil. The oil was further purified by diluting with high purity acetone (100 ml) and stirring with decolorizing carbon (5 g). The mixture was again suction filtered and the acetone removed *in vacuo* to give a colorless oil. This was further dried at 4 Pa and 25 °C for 6 hr to provide 83.6 g of product. ^{19}F NMR (DMSO-d_6) δ –124.7 (dt, J = 6 Hz, J = 8 Hz, 2F); –136.8 (dt, J = 53 Hz, 2F). ^{1}H NMR (DMSO-d_6) δ 0.9 (t, J = 7.4 Hz, 3H); 1.3 (m, 2H); 1.8 (m, 2H); 3.9 (s, 3H); 4.2 (t, J = 7 Hz, 2H); 6.3 (dt, J = 53 Hz, J = 6 Hz, 1H); 7.4 (s, 1H); 7.5 (s, 1H); 8.7 (s, 1H).% Water by Karl-Fisher titration: 0.14%. Analytical calculation for $C_9H_{12}F_6N_2O_3S$: C, 37.6: H, 4.7: N, 8.8. Experimental Results: C, 37.6: H, 4.6: N, 8.7. TGA (air): 10% wt. loss @ 380 °C, 50% wt. loss @ 420 °C. TGA (N_2): 10% wt. loss @ 375 °C, 50% wt. loss @ 422 °C.

Synthesis of 1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate (EMIM-TFES)

To a one-liter round-bottom flask was added 1-ethyl-3methylimidazolium chloride (EMIM-Cl, 98%, 61.0 g) and reagent grade acetone (500 ml). The mixture was gently warmed (50 degrees C) until almost all of the EMIM-Cl dissolved. To a separate 500 ml flask was added potassium 1,1,2,2-tetrafluoroethanesulfonate (TFES-K, 90.2 g) along with reagent grade acetone (350 ml). This second mixture was stirred magnetically at 24 °C until all of the TFES-K dissolved. These solutions were combined in a 1 liter flask producing a milky white suspension. The mixture was stirred at 24 °C for 24 hrs. The KCl precipitate was then allowed to settle leaving a clear green solution above it. The reaction mixture was filtered once through a celite/acetone pad and again through a fritted glass funnel to remove the KCl. The acetone was removed *in vacuo* first on a rotovap and then on a high vacuum line (4 Pa, 25 °C) for 2 hr. The product was a viscous light yellow oil, which crystallized upon standing (76.0 g, 64% yield). ^{19}F NMR (DMSO-d_6) δ –124.7 (dt, J_{FH} = 6 Hz, J_{FF} = 6 Hz, 2F); –138.4 (dt, J_{FH} = 53 Hz, 2F). ^{1}H NMR (DMSO-d_6) δ 1.3 (t, J = 7.3 Hz, 3H); 3.7 (s, 3H); 4.0 (q, J = 7.3 Hz, 2H); 6.1 (tt, J_{FH} = 53 Hz, J_{FH} = 6 Hz, 1H); 7.2 (s, 1H); 7.3 (s, 1H); 8.5 (s, 1H).% Water by Karl-Fisher titration: 0.18%. Analytical calculation for $C_8H_{12}N_2O_3F_4S$: C, 32.9: H, 4.1: N, 9.6 Found: C, 33.3: H, 3.7: N, 9.6. Mp 45–46 °C. TGA (air): 10% wt. loss @ 379 °C, 50% wt. loss @ 420 °C. TGA (N_2): 10% wt. loss @ 378 °C, 50% wt. loss @ 418 °C.

Synthesis of 1-ethyl-3-methylimidazolium 1,1,2,3,3,3-hexafluoropropanesulfonate (EMIM-HFPS)

To a one-liter round-bottom flask was added 1-ethyl-3-methylimidazolium chloride (EMIM-Cl, 98%, 50.5 g) and reagent grade acetone (400 ml). The mixture was gently warmed (50 °C) until almost all of the EMIM-Cl dissolved. To a separate 500 ml flask was added potassium 1,1,2,3,3,3-hexafluoropropanesulfonate (HFPS-K, 92.2 g) along with reagent grade acetone (300 ml). This second mixture was stirred magnetically at room temperature until all of the HFPS-K dissolved. These solutions were combined and stirred under positive N_2 pressure at 26 °C for 12 hr producing a milky white suspension. The KCl precipitate was allowed to settle overnight leaving a clear yellow solution above it. The reaction mixture was filtered once through a celite/acetone pad and again through a fritted glass funnel. The acetone was removed *in vacuo* first on a rotovap and then on a high vacuum line (4 Pa, 25 °C) for 2 hr. The product was a viscous light yellow oil (103.8 g, 89% yield). ^{19}F NMR (DMSO-d_6) δ –73.8 (s, 3F); –114.5, –121.0 (ABq, J = 258 Hz, 2F); –210.6 (m, J_{HF} = 41.5 Hz, 1F). ^{1}H NMR (DMSO-d_6) δ 1.4 (t, J = 7.3 Hz, 3H); 3.9 (s, 3H); 4.2 (q, J = 7.3 Hz, 2H); 5.8 (m, J_{HF} = 41.5 Hz, 1H,); 7.7 (s, 1H); 7.8 (s, 1H); 9.1 (s, 1H).% Water by Karl-Fisher titration: 0.12%. Analytical calculation for $C_9H_{12}N_2O_3F_6S$: C, 31.5: H, 3.5: N, 8.2. Experimental Results: C, 30.9: H, 3.3: N, 7.8. TGA (air): 10% wt. loss @ 342 °C, 50% wt. loss @ 373 °C. TGA (N_2): 10% wt. loss @ 341 °C, 50% wt. loss @ 374 °C.

Synthesis of tetradecyl(tri-n-butyl)phosphonium 1,1,2,3,3,3-hexafluoropropanesulfonate ([4.4.4.14]P-HFPS)

To a 4 l round-bottom flask was added the ionic liquid tetradecyl(tri-*n*-butyl)phosphonium chloride (Cyphos® IL 167, 345 g) and deionized water (1000 ml). The mixture was magnetically stirred until it was one phase. In a separate 2 liter flask, potassium 1,1,2,3,3,3-hexafluoropropanesulfonate (HFPS-K, 214.2 g) was dissolved in deionized water (1100 ml). These solutions were combined and stirred under positive N_2 pressure at 26 °C for 1 hr producing a milky white oil. The oil slowly solidified (439 g) and was removed by suction filtration and then dissolved in chloroform (300 ml). The remaining aqueous layer (pH = 2) was extracted once with chloroform (100 ml). The chloroform layers were combined and washed with an aqueous sodium carbonate solution (50 ml) to remove any acidic impurity. They were then dried over magnesium sulfate, suction filtered, and reduced *in vacuo* first on a rotovap and then on a high vacuum line (4 Pa, 100 °C) for 16 hr to yield the final product as a white solid (380 g, 76% yield). ^{19}F NMR (DMSO-d$_6$) δ −73.7 ((s, 3F); −114.6, −120.9 (ABq, $J = 258$ Hz, 2F); −210.5 (m, $J_{\mathrm{HF}} = 41.5$ Hz, 1F). ^{1}H NMR (DMSO-d$_6$) δ 0.8 (t, $J = 7.0$ Hz, 3H); 0.9 (t, $J = 7.0$ Hz, 9H); 1.3 (br s, 20H); 1.4 (m, 16H); 2.2 (m, 8H); 5.9 (m, $J_{\mathrm{HF}} = 42$ Hz, 1H).% Water by Karl-Fisher titration: 895 ppm. Analytical calculation for $C_{29}H_{57}F_6O_3PS$: C, 55.2: H, 9.1: N, 0.0. Experimental Results: C, 55.1: H, 8.8: N, 0.0. TGA (air): 10% wt. loss @ 373 °C, 50% wt. loss @ 421 °C. TGA (N_2): 10% wt. loss @ 383 °C, 50% wt. loss @ 436 °C.

Catalyst testing

All reagents were reagent grade.

Akylation[2]

The ionic liquid 1-dodecyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate (0.19 g) was placed in a round bottomed flask and dried at 150 °C for 48 hours. 1,1,2,3,3,3-Hexafluoropropanesulfonic acid (0.5 g) was added, followed by the addition of 5 ml of 1-dodecene and 15 ml of p-xylene. The mixture was heated to 100 °C under a nitrogen atmosphere. After 2 hours reaction time, gas chromatographic analysis showed near complete reaction (>95%) of the 1-dodecene to give the alkylated product. The ionic liquid and acid formed a distinct second phase that separated out at the bottom of the flask. GC analysis was performed as follows. Samples were diluted 1 to 20 in ether for GC analysis. All of the samples were analyzed by a Hewlett Packard 5890 Series II GC equipped with FID detectors. Product identification was carried out with a GC-MS analysis and ^{1}H NMR. The products were identified by comparison of their spectra and retention time in GC with those of authentic samples. In the case of the alkylation reactions (carried out at 100 °C with conversion close to 99%), the products contain >95% linear alkylate and the remainder (<5%) are the 4% branched alkylates from the ~ 4% branched olefins (impurity in the feed), and dimers of 1-dodecene. Full details for these reactions has been reported previously.[2]

Polyol Formation (etherification)

1,3-Propanediol (20 g) was placed in a three-neck round-bottom flask. To this was added TFESA (0.16 g, 0.8 wt% in the final solution). BMIM-TFES (4 g) was also added and the solution and contents were purged with nitrogen for two hours. The homogeneous solution was heated using an oil bath at 160 °C under a nitrogen atmosphere. Water slowly evolved and was collected in a condenser. After approximately 9–10 hours the solution went from a single phase to a two-phase system. Upon cooling to 75 °C, two phases were clearly visible. The top phase was shown *via* ^{1}H NMR spectroscopy to be essentially polymerized propanediol (polyol). The molecular weight (M_n) was 2907, after a reaction time of 10.5 hours. The acid and ionic liquid were found to be essentially in the lower phase with polyol in the upper phase. The lower phase can easily be separated and recycled.

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20 Crystal data for EMIM-nonaflate (05219): $C_{10}H_{11}F_9N_2O_3S$, FW = 410.27, monoclinic, space group P21/c, a = 9.178(4) Å, b = 34.444(13) Å, c = 10.022(4) Å, β = 91.711(7)°, U = 3167(2) Å^3, T = −100.°C, Z = 8, D_{calcd} = 1.72g/cm$^{3.}$ Data were collected using a Bruker Apex-II CCD system equipped with MoKα radiation on a non-merohedrally twinned crystal. Cell_now, Saintplus and Twinabs used to integrate data on two domains yielding 11349 total reflections. Structure solved and refined on F^2 using SHELXTL94.[38] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were idealized using a riding model. The final R values were wR$_2$ = 0.258 and R$_1$ = 0.171 using all data. The high-r factors are attributed to some un-modeled overlap twinned crystal. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with deposition number CCDC 715668.
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