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A Solventless Route to 1-Ethyl-3-methylimidazolium Fluoride Hydrofluoride, [C_2mim][F]·*x*HF

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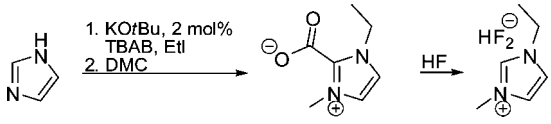
Received March 13, 2008



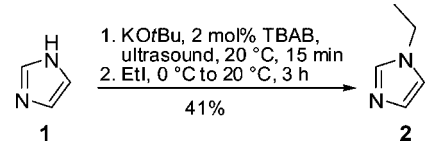
The ionic liquid 1-ethyl-3-methylimidazolium fluoride hydrofluoride, [C_2mim][F]·*x*HF, has been synthesized through a new, solventless route that excludes halogen metathesis. The byproducts are salts, alcohols, and carbon dioxide.

Dialkylimidazolium halide-based ionic liquids (ILs) have proven to exhibit the necessary basicity to dissolve cellulosic biomass[1] through the anion's ability to effectively break the hydrogen bonds that give strength to the cellulose macrostructure.[2] The original and subsequent studies[3] in this area demonstrated that the ability of these salts to directly dissolve cellulose increased with the hydrogen bond basicity of the anion in the order $Br^- \cong SCN^- < Cl^-$. However, at the time it was not possible to test F^-. The synthesis reported here was thus motivated by the wish to extend this series.

Dialkylimidazolium fluoride compounds exhibit a tendency to forming $(HF)_nF^-$ clusters, were *n* is an integer.[4] This leads to structures of the formula [C_2mim][F]·*x*HF where *x* can be a noninteger. Hagiwara et al. first reported the synthesis of [C_2mim][F]·2.3HF (C_2mim = 1-ethyl-3-methylimidazolium),[4] its unique properties,[5] and applications.[6] The compound was synthesized by halogen exchange of [C_2mim][Cl] with hydrogen fluoride. This approach, however, has a known drawback in that the Cl^- impurities are notoriously difficult to completely remove.[7]

We chose to implement a recently reported synthetic approach for formation of byproduct free imidazolium salts[8–10] to circumvent halide metathesis reactions. It involves alkylation of an alkylimidazole with dimethyl carbonate resulting in a carboxylated-dialkylimidazolium zwitterion and subsequent treatment with acid to produce the desired salt and CO_2.

SCHEME 1. Solventless Synthesis of Ethylimidazole[11]



The synthesis started with the preparation of ethylimidazole **2** (Scheme 1). Following the procedure published by Diez-Barra et al., a solventless route was used in which potassium *tert*-butoxide and imidazole were ground together with tetrabutylammonium bromide (TBAB); ultrasound was applied to this mixture of solids, and upon addition of ethyl iodide a new colorless liquid was formed.[11] Although no biphasic liquid/liquid system was involved, the addition of TBAB, a substance widely used as a phase transfer catalyst, seemed to be relevant. Under reduced pressure the newly formed ethylimidazole **2** was directly distilled from the reaction mixture in 41% yield.

The next step involved the building of the 1-ethyl-3-methylimidazolium core without introducing a halide counterion. This was performed by reaction of ethylimidazole **2** with dimethyl carbonate **3** via a $B_{Al}2$ mechanism (Scheme 2).[8–10,12] The product was a colorless, very hygroscopic crystalline substance, which was washed with dry acetone, yielding 29%.

From previous studies we assumed this compound to be 1-ethyl-3-methylimidazolium-2-carboxylate **4**, a zwitterion bearing the carboxyl group at the C2 position, rather than the anticipated 1-ethyl-3-methylimidazolium methyl carbonate.[8] The reaction is known to yield the thermodynamically favored 4-carboxylate as well, which is predominantly formed at higher temperatures (>110 °C),[9,13] but was not detected. Moreover,

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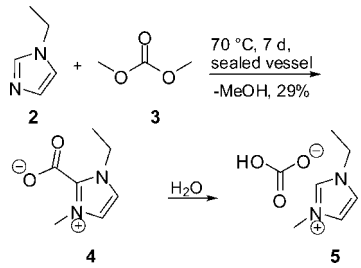
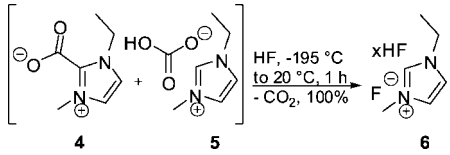
10.1021/jo800578b CCC: $40.75
Published on Web 06/13/2008

SCHEME 2. Synthesis of 1-Ethyl-3-methylimidazolium-2-carboxylate 4[a]



[a] Traces of water induce the conversion into 1-ethyl-3-methylimidazolium hydrogen carbonate **5**.

SCHEME 3. Synthesis of [C_2mim][F]·HF (6)



the kinetic product, 1-ethyl-3-methylimidazolium-2-carboxylate **4**, reacts with water to form 1-ethyl-3-methylimidazolium hydrogen carbonate **5** crystals.[9,10]

NMR studies in deuterated methanol showed a mixture of 21% 1-ethyl-3-methylimidazolium-2-carboxylate **4** and 79% 1-ethyl-3-methylimidazolium hydrogen carbonate **5** formed with water. Compound **5** showed no signal of the C-2 proton in CD_3OD due to exchange with the solvent.

The crystals of **5** were analyzed by single-crystal X-ray diffraction (see the Supporting Information). The observed structure is similar to the dimethyl analogue reported earlier.[9,10]

In the third step (Scheme 3), the crude mixture of **4** and **5** was placed in a PFA reactor and dissolved in liquid HF by condensation at −195 °C. After reaching room temperature, the excess HF was removed and the sample was dried, yielding the product quantitatively as a dark, free flowing liquid.

The reaction was complete in 100% yield in a short reaction time, despite the use of the crude mixture of 1-ethyl-3-methylimidazolium-2-carboxylate **4** and 1-ethyl-3-methylimidazolium hydrogen carbonate **5**. The final reaction was straightforward, fast, and yielded neither side products nor byproducts apart from CO_2.

A broad peak at 13.7 ppm in the ^{1}H NMR corresponds to the HF_2^- anion, which can also be seen as a doublet at −70.2 ppm in the ^{19}F NMR spectrum. The IR spectrum is similar to that reported in the literature[5] and indicates that hydrofluoride is present. Unfortunately, it proved to be difficult to completely remove the water even after overnight drying under high vacuum. Water was visible in the ^{1}H NMR spectrum and was quantified by using Karl Fischer titration, revealing an intrinsic water content between 5.9% and 6.5% (corresponding to ca. 0.5 mol of H_2O per mol of [C_2mim]$^+$). A related compound, [C_4mim][F]·H_2O, a crystalline monohydrate, has been reported to form from the hydrolysis of [C_4mim][PF_6].[14]

Thermogravimetric analysis (TGA) showed two decomposition steps and a continuous weight loss up to 200 °C. This might be due to the permanent loss of incorporated water or HF (see the Supporting Information).

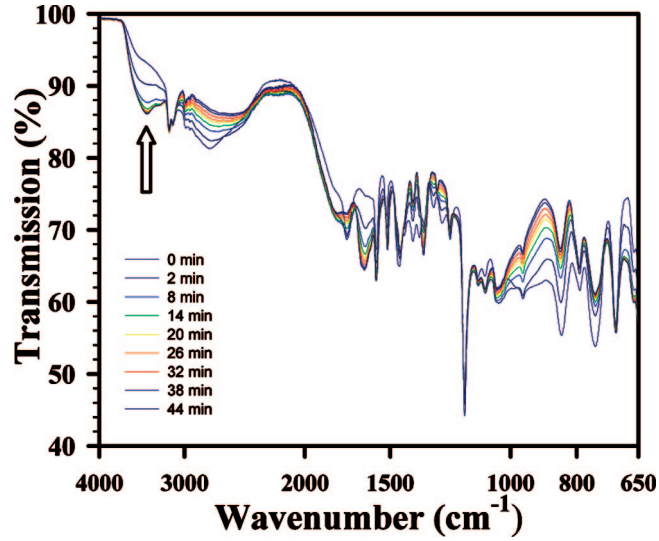


FIGURE 1. Kinetic study of water uptake by [C_2mim][F]·xHF, using ATR FT-IR. The significant peak is at 3400 cm^{-1}.

It is interesting to note that both TGA and NMR indicated that these compounds were hygroscopic, in contrast to the reports of Hagiwara et al.[15] This suggests that the hygroscopic nature of [C_2mim][F]·xHF drastically changes with x. Because of this, we measured the absorption rate of water by a combination of Karl Fischer titration and IR spectroscopy in a kinetic experiment. A single drop of the compound was placed on an attenuated total reflection Fourier transformation infrared (ATR FT-IR) spectrometer and the spectrum was recorded at different time intervals while leaving the substance under ambient atmosphere with a relative humidity of 65% (Figure 1).

The development of a signal at ca. 3400 cm^{-1}, which is specific for hydroxyl groups in hydrogen bonds, e.g. water, proved its hygroscopicity (Figure 1). These data reveal that approximately half of the water uptake occurs within the first 2 min. After 14 min the hydration was virtually complete. The drop was then collected and the water content was found to be 13.5% by Karl Fischer titration.

Elemental analysis (CHNF) is complicated by the hygroscopic nature of the compound; however, the data indicated a water content between 1.5 and 2.1 mol. The lower water content (1.5 mol, 14.4%) is consistent with the Karl Fischer measurements at saturation. The higher value of 2.1 mol corresponds to 19% water, which might be explained by water absorption over a longer period of time. Consideration of all of the data obtained suggests the best value of x to be 1.5−1.6 HF.

The complete absence of solvents and the nontoxic starting materials (except HF) and byproducts, combined with the circumvention of halide contamination, no need for purification, and a quantitative yield in the last reaction step, make this synthetic approach attractive. The presence of some water in this IL is irrelevant for biomass dissolution because of the ubiquitous presence of water in the feedstock. Nevertheless, uncertainties in the exact composition of the IL and the delicacy of handling liquid HF might hinder large-scale applicability of fluoride-based ILs in biomass application.

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Experimental Section

Ethylimidazole (2). Imidazole (10.0 g, 147 mmol), KO*t*Bu (18.2 g, 162 mmol), and tetrabutylammonium bromide (TBAB, 0.82 g, 2.94 mmol, 2 mol %) were mixed and submerged in an ultrasonic bath for 15 min. The solid mixture was cooled to 0 °C, 22.9 g (147 mmol) of ethyl iodide was added, and the reaction was stirred for 3 h while being allowed to reach room temperature. A new liquid phase formed. Distillation from the reaction mixture afforded the product, which was dried under high vacuum to remove traces of *t*BuOH. A fractionated distillation was done to purify the compound. Yield: 5.83 g (60 mmol), 41%.

^{1}H NMR (360 MHz, DMSO) δ 7.62 (s, 1H), 7.17 (s, 1H), 6.87 (s, 1H), 3.97 (q, 2H, J = 7.3 Hz), 1.31 (t, 3H, J = 7.3 Hz); ^{13}C NMR (90 MHz, DMSO) δ 16.1, 40.6, 118.6, 128.1, 136.5.

1-Ethyl-3-methylimidazoliumcarboxylate (4). Ethylimidazole (5.8 g, 60 mmol) and dimethyl carbonate (21.6 g, 240 mmol) were put into a glass pressure tube and sealed tightly. The tube was heated in an oven for 7 days at 70 °C. The reaction mixture was cooled to room temperature and the solvent removed under a stream of nitrogen. Colorless crystals of product precipitated from a brown solution. Washing with dry acetone yielded off-white crystals. Yield: 2.66 g (17 mmol), 29%.

^{1}H NMR [1-ethyl-3-methylimidazolium hydrogen carbonate (major product in CD_3OD)] (360 MHz, CD_3OD) δ 7.66 (d, 1H, J = 1.9 Hz), 7.58 (d, 1H, J = 1.9 Hz), 4.27 (q, 2H, J = 7.3 Hz), 3.93 (s, 3H), 1.53 (t, 3H, J = 7.3 Hz); ^{13}C NMR (90 MHz, MeOD) δ 15.7, 36.5, 46.1, 123.4, 124.5, 161.5.

^{1}H NMR (360 MHz, DMSO) δ 9.47 (s, 1H), 7.82 (s, 1H), 7.73 (s, 1H), 4.20 (q, 2H, J = 7.3 Hz), 3.86 (s, 3H), 1.40 (t, 3H, J = 7.3 Hz); ^{13}C NMR (90 MHz, DMSO) δ 15.1, 35.6, 44.1, 122.0, 123.5.

^{1}H NMR [1-ethyl-3-methylimidazolium-2-carboxylate **4** (major product in DMSO)] (360 MHz, CD_3OD) δ 7.56 (d, 1H, J = 2.0 Hz), 7.49 (d, 1H, J = 1.9 Hz), 4.57 (q, 2H, J = 7.2 Hz), 4.07 (s, 3H), 1.48 (t, 3H, J = 7.2 Hz); ^{13}C NMR (90 MHz, MeOD) δ 16.5, 37,9, 46.6, 122.6, 125.1.

^{1}H NMR (360 MHz, DMSO) δ 7.65 (d, 1H, J = 2.0 Hz), 7.58 (d, 1H, J = 1.9 Hz), 4.46 (q, 2H, J = 7.2 Hz), 3.95 (s, 3H), 1.33 (t, 3H, J = 7.2 Hz); ^{13}C NMR (90 MHz, DMSO) δ 15.9, 36.4, 44.0, 120.4, 122.5, 141.8, 154.1.

[C_2mim][F]·*x*HF (6). 1-Ethyl-3-methylimidazoliumcarboxylate (0.22 g, 1.43 mmol) was three times evacuated and put under inert gas atmosphere within a glovebox. The droplets dried out during this procedure leaving an off-white solid, which was then transferred into a PFA reactor and weighted. The reactor was cooled to −195 °C with liquid nitrogen and an excess of HF was condensed into the tube, which was allowed to reach room temperature during 1 h. The excess of HF was removed and the sample was dried under high vacuum overnight. The product was a free flowing liquid. Yield: 100%.

^{1}H NMR (360 MHz, DMSO) δ 13.72 (s, 1.4 H), 9.17 (s, 1H), 7.78 (s, 1H), 7.70 (s, 1H), 4.18 (q, 2H, J = 7.3 Hz), 3.84 (s, 3H), 1.41 (t, 3H, J = 7.3 Hz); ^{13}C NMR (90 MHz, MeOD) δ 15.8, 36.6, 46.1, 123.4, 125.1, 126.4; ^{19}F NMR (470 MHz, DMSO) δ −70.95, −69.44. CHNF elemental Anal. Calcd for [C_2mim][F]·1.5HF·1.5H_2O: C 38.5, H 8.4, N 15.0, F 25.4. Calcd for [C_2mim][F]·1.6HF·2.1H_2O: C 36.0, H 8.5, N 14.0, F 24.7; Found: C 36.0, H 6.2, N 13.5, F 24.9.

Acknowledgment. This work was supported by BASF, North America. We would like to thank Dr. Alfred Waterfeld and Ms. Monica Khural for the use of the HF equipment and Dr. David Cordes for the crystallographic data.

Supporting Information Available: TGA and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO800578B