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In situ multinuclear solid-state NMR spectroscopy study of Beckmann rearrangement of cyclododecanone oxime in ionic liquids: The nature of catalytic sites

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ABSTRACT

The Beckmann rearrangement of cyclododecanone oxime into ω-laurolactam has been investigated in four ionic liquids: 1-butyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate ($[C_4mim]^+PF_6^-$, $[C_4mim]^+BF_4^-$), and 1-butyl-2,3-dimethylimidazolium and 1-butyl-4-methylpyridinium hexafluorophosphates ($[C_4mpyr]^+PF_6^-$, $[C_4m_2im]^+PF_6^-$), in a batch reactor as well as by 'in situ' multinuclear solid-state NMR spectroscopy. The Beckmann rearrangement reaction of cyclododecanone oxime takes place in $[C_4mim]^+PF_6^-$ and $[C_4mpyr]^+PF_6^-$ with excellent activity and selectivity, while practically null activity is observed in $[C_4m_2im]^+PF_6^-$ and $[C_4mim]^+BF_4^-$. The results obtained indicate that a very low level of hydrolysis of the PF_6^- anion in $[C_4mim]^+PF_6^-$ and $[C_4mpyr]^+PF_6^-$ occurs under reaction conditions (130 °C), and the HF formed at the level of ppm acts as catalyst in the Beckmann rearrangement with excellent conversion and selectivity.

1. Introduction

Ionic liquids have attracted the interest of scientists working in different fields such as electrochemistry, nanotechnology, analytical chemistry, separation and catalysis, being the subject of a growing number of publications during the last two decades [1–4]. These compounds are formed by an organic cation compensated by an organic or inorganic anion, with the peculiarity that many of them are liquid at temperatures close to ambient. Then, the most accepted definition of ionic liquid (IL) corresponds to organic salts with melting points below 100 °C. The low volatility and easily recyclability of ILs make them very attractive as alternative solvents to substitute the usual volatile organic compounds used many times in industrial chemistry [1–4]. In the field of catalysis, they have been used as solvent but also as catalysts after proper functionalization [1,3,4].

Most popular ionic liquids consist of 1-alkyl-3-methylimidazolium (abbreviated $[C_nmim]^+$ being n the number of carbon atoms of the alkyl chain) or N-alkylpyridinium (accordingly abbreviated $[C_npy]^+$) cations combined with anions such as halides, hexafluorophosphate or tetrafluoroborate, amongst others (see Table 1) [1–4]. ILs display high thermal and chemical stability, although it has been reported that PF_6^- and BF_4^- anions may release HF in the presence of moisture [4–7]. Ionic liquids are usually considered just as "homogeneous" solvents, but their properties differ from those of classical solvents and, indeed, it is recognised that imidazolium ionic liquids form polymeric hydrogen bonded structures or clusters, always involving the most acidic hydrogen atom H2 bonded to the C2 of the cation ring [7–9]. This carbon is positively charged owing to the electron deficiency in the C=N bond, resulting in a higher acidity of the hydrogen atom [8,9].

The Beckmann rearrangement reaction of oximes into amides is a reaction of industrial interest because of its application for the production of ε-caprolactam and ω-laurolactam, which are the monomers for manufacturing plastic and fibres [10–12]. The classical industrial process uses sulphuric acid or oleum as catalyst, producing large amounts of ammonium sulphate as secondary product. The requirements for cleaner and more environmentally friendly processes have motivated the investigation of heterogeneous

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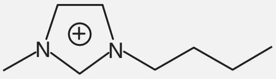
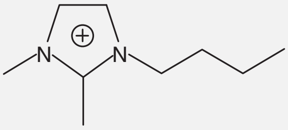
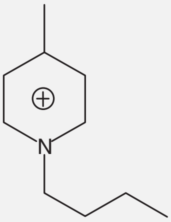
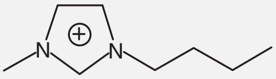
Table 1
Water content of ionic liquids.

Ionic liquid			H_2O (ppm)
$[C_4mim]^+PF_6^-$ (1-butyl-3-methylimidazolium hexafluorophosphate)		PF_6^-	1647
$[C_4dmim]^+PF_6^-$ (1-butyl-2,3-dimethylimidazolium hexafluorophosphate)		PF_6^-	2468
$[C_4mpyr]^+PF_6^-$ (1-butyl-4-methylpyridinium hexafluorophosphate)		PF_6^-	4068
$[C_4mim]^+BF_4^-$ (1-butyl-3-methylimidazolium tetrafluoroborate)		BF_4^-	1986

systems using solid catalysts [10–15]. The use of solids with weakly acidic silanol instead of strong Brønsted acid groups as active sites improves the selectivity to lactams, which has allowed the commercialization of an industrial process for the production of ε-caprolactam using a high silica medium pore zeolite as catalyst [16]. However, this catalytic system fails to catalyze the Beckmann rearrangement of cyclododecanone oxime to ω-laurolactam, which is the monomer to produce Nylon-12, and H_2SO_4 or oleum is still the catalyst for the process.

Imidazolium- and pyridinium-based ionic liquids have been used as reaction media for the Beckmann rearrangement of several oximes, using phosphorated compounds (PCl_5, $POCl_3$, P_2O_5) [17–19] or metaboric acid [20] as catalysts. Brønsted acidic ionic liquids consisting of gemini dicationic carrying two SO_3H groups at the cation moiety-mediated zinc chloride ILs-$ZnCl_2$ catalytic system have also been tested [21,22]. Recently, Lewis acid catalysts ($AlCl_3$, $TiCl_4$, $SnCl_4$, BF_3) in a large variety of ionic liquids have been reported to be able to perform the Beckmann rearrangements of several ketoximes with high levels of conversion and selectivity [23]. Brønsted acidic ionic liquids functionalized with sulfonyl chloride [24,25] and caprolactamium-based ionic liquids with BF_4^-, NO_3^- and CF_3COO^- as anions [26] have given satisfactory results when used as both reaction media and catalysts for the Beckmann rearrangement of several oximes. Interestingly, investigations into the reaction mechanism of the rearrangement of cyclohexanone oxime into caprolactam in oleum have shown that, indeed, this is the largest scale industrial technology using for decades an ionic liquid, caprolactamium hydrogen sulphate, as the reaction medium [27].

The present work was originally aimed to test whether the H2 hydrogen atom of the 1-alkyl-3-methylimidazolium ($[C_nmim]^+$) ring is acidic enough to catalyze the Beckmann rearrangement of cyclododecanone oxime into ω-laurolactam, acting the ionic liquid as both reaction media and catalyst. With this purpose, we tested two ionic liquids containing the cation 1-butyl-3-methylimidazolium with the above-mentioned acidic H2 hydrogen, and hexafluorophosphate ($[C_4mim]^+PF_6^-$) and tetrafluoroborate as counterions ($[C_4mim]^+BF_4^-$). For comparison, we also studied the ionic liquids 1-butyl-4-methylpyridinium ($[C_4mpyr]^+PF_6^-$) and 1-butyl-2,3-dimethylimidazolium ($[C_4m_2im]^+PF_6^-$) hexafluorophosphates, whose cations do not contain the above-mentioned acidic hydrogen. The results obtained show, however, that the water present in hexafluorophosphate-based ionic liquid can partially hydrolyze the anion and produce hydrogen fluoride which, at the level of ppms, is able to catalyze the Beckmann rearrangement of cyclododecanone oxime to ω-laurolactam with excellent activities and selectivities. The amount of HF can be controlled by selecting the appropriate ionic liquid and the water content for hydrolysis at the ppm levels.

2. Materials and methods

2.1. Materials

Cyclododecanone oxime was prepared by reaction of the corresponding ketone with hydroxylamine hydrochloride in a mixture of ethanol and pyridine at 85 °C, according to the procedure described in Ref. [28]. The ^{15}N enriched oxime was synthesized using ^{15}N-hydroxylamine hydrochloride (85%; Cambridge Isotope Laboratories). The purity of the oxime (99%) was confirmed by gas chromatography (GC), and ^1H and ^{13}C NMR spectroscopy.

Hydrofluoric acid (48 wt.%) was purchased to Scharlau, and before use was diluted to 20 wt.% in water. The ionic liquids were commercially available (98%; Solvent Innovation) and used without further purification. The water content of each ionic liquid was determined using a volumetric Karl–Fisher titrator (Metler Toledo, DL 31), and the results expressed in ppm are summarized in Table 1. For $[C_4mim]^+PF_6^-$ and $[C_4mim]^+BF_4^-$, the amount of water was also measured by ^1H NMR, using 5-mm NMR tubes equipped with a coaxial capillary tube containing DMSO-d_6, with tetramethylsilane (TMS) as internal chemical shift reference. The water content in $[C_4mim]^+PF_6^-$ and $[C_4mim]^+BF_4^-$ ILs determined by the two methods agree within 5%.

2.2. Characterization

The ^1H, ^{13}C, ^{31}P, ^{11}B and ^{19}F NMR spectra were recorded on a Bruker 300 MHz instrument using a 5-mm PABBO probe. Ionic liquids (about 50 mg) were dissolved in acetone-d_6 (1 ml) for NMR measurements. Pyridine-d_6 was used as solvent to analyze the reaction mixtures as the use of more common solvents (acetonitrile, chloroform or DMSO) gave inhomogeneous solutions with two or more phases. Routine one pulse sequence was used to measure ^{31}P and ^{19}F NMR, and with proton decoupling for ^{13}C and ^{11}B NMR.

Gas chromatographic (GC) analysis was done with a Varian 3900 instrument, using a flame ionization detector with the following flow rates: hydrogen, 30 ml/min; air, 300 ml/min; and helium, 1 ml/min. A HP-5 (5%-phenyl)-methylpolysiloxane (L = 30 m, D = 0.25 mm, film = 0.25 μm) column was used, the injection temperature was 250 °C and the temperature regime of analysis was as follows: starting temperature 50 °C for 3 min, then 20 °C/min up to 300 °C, and a final temperature of 300 °C for 10 min.

2.3. General procedure for the Beckmann rearrangement reaction

Typically, a mixture of about 10 wt.% of cyclododecanone oxime (150–245 mg, 0.75–1.25 mmol) in ionic liquid (1520–2410 mg, 5.15–9.75 mmol) was charged into a magnetically stirred 10-ml glass flask and heated at 130 °C for 2 h. Experiments with addition of water, hydrofluoric acid or BF_3 were done in a magnetically stirred Teflon-lined autoclave (volume 15 ml), sealed and then pressurized with N_2 until a final pressure of 1 bar. The composition of the reaction mixture for experiments carried out with deliberated addition of water (2.2–2.8 wt.%) was as follows: cyclododecanone oxime (140–176 mg, 0.70–0.90 mmol), ionic liquid (1520–1760 mg,