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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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A B S T R A C T

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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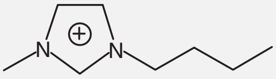
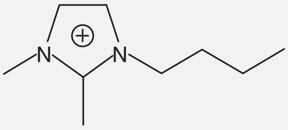
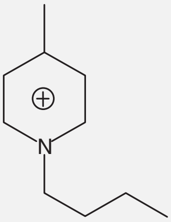
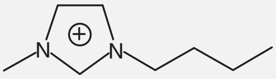
Table 1
Water content of ionic liquids.

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, 4.80–7.05 mmol) and water (33–40 mg, 1.80–2.60 mmol). The mixtures with addition of hydrofluoric acid (0.5 wt.% of a solution of 20 wt.% in water) had a composition: cyclododecanone oxime (200–215 mg, 1.00–1.10 mmol) in ionic liquid (2050–2055 mg, 6.90–9.10 mmol), HF (11.13 mg, 0.56 mmol) and water (45.2 mg, 2.51 mmol). Finally, the reaction mixture for experiments carried out with the addition of BF_3 contained: cyclododecanone oxime (200–215 mg, 1.00–1.10 mmol) in ionic liquid (2000–2055 mg, 6.90–9.10 mmol), BF_3 (10 wt.%, 270 mg, 0.4 mmol). Similar experimental set up was used to heat the ionic liquid with its own water content at 130 °C under N_2 atmosphere for 2 h before the addition of cyclododecanone oxime (about 10 wt.%); then, the mixture was heated again at 130 °C for 2 h.

At the end of the reaction, the dissolved species were extracted with diethyl ether (3 × 5 ml), and the organic solution was concentrated under vacuum. The residue was weighted and analyzed by GC, and another portion dissolved in pyridine-d_6 and analyzed by ^{1}H, ^{13}C, ^{19}F, ^{11}B and ^{31}P NMR spectroscopy.

2.4. 'In situ' solid-state NMR catalytic experiments

Approximately 30 mg of cyclododecanone oxime were introduced into a rotor glass insert (from Wilmad Glass Company) sealed to a 5-mm pyrex tube, and then 43 mg of 1-Butyl-3-methylimidazolium hexafluorophosphate were added using a syringe. The resulting mixture, with an oxime: IL molar ratio of 1:1, was homogenized within an ultrasonic bath for about 20 min. The glass tube was then connected to a stopcock using stainless steel fittings, and the ensemble to a vacuum line through O-ring joints. The mixture was degassed at room temperature for about 15 min to reach a final pressure of 3×10^{-3} mbar. The insert was sealed with a high temperature torch using a lathe rotating at about 5–10 s^{-1}, while keeping the sample in liquid nitrogen. The glass ampoules were fitted into the rotor to measure the MAS NMR spectra at room temperature just after the sample preparation and after subsequent heating at increasing temperatures. ^{15}N cross polarization (CP) under magic angle spinning (MAS) and ^{31}P MAS NMR were recorded in a Bruker AV 400 MHz WB spectrometer using a BL7 probe, with the sample spinning at 5 kHz. The ^{1}H/^{15}N CP MAS NMR spectra were recorded with a $\pi/2$ rad pulse for ^{1}H of 8 µs, a contact time of 5 ms and a recycle delay of 3 s. The ^{31}P MAS NMR spectra were acquired with a pulse of 4.5 µs to flip the magnetization $\pi/3$ rad and a recycle delay of 10 s.

3. Results and discussion

Table 2 collects conversion and selectivity to ω-laurolactam obtained after heating at 130 °C for 2 h the mixture of cyclododecanone oxime and each of the four ionic liquids studied here. The results show that $[C_4mim]^+PF_6^-$ and $[C_4mpyr]^+PF_6^-$ give practically 100% oxime conversion with high selectivity to the lactam, while $[C_4mim]^+BF_4^-$ and $[C_4m_2im]^+PF_6^-$ give no oxime conversion. The null activity of $[C_4m_2im]^+PF_6^-$ would be consistent with the absence of an acidic H2 proton in the cationic ring, while the good performance on $[C_4mim]^+PF_6^-$ could be related to the presence of that acidic proton. However, what made us to question the above interpretation was the observation that the same cation than above, i.e. $[C_4mim]^+$, when compensated by the tetrafluoroborate anion ($[C_4mim]^+BF_4^-$), does not give any activity for the Beckmann rearrangement, and $[C_4mpyr]^+PF_6^-$ gives a very high activity and good selectivity to the lactam despite the 1-butyl-4-methylpyridinium has not the acid H2 in the cationic ring. Thus, in order to understand the experimental results summarized in Table 2, we studied the Beckmann rearrangement reaction of cyclododecanone oxime into ω-laurolactam in ionic liquids by performing catalytic experiments using an 'in situ' multinuclear solid-state NMR spectroscopic technique [29–32]. For doing that, 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4mim]^+PF_6^-$, which was active for the reaction, was selected and reacted with a (^{15}N-cyclododecanone oxime)/($[C_4mim]^+PF_6^-$) molar ratio of 1. For this experiment, ^{15}N labelled oxime was used. Results in Fig. 1a show the ^{15}N CP MAS NMR spectra of the reaction mixture as prepared and after heating at 50 °C during 5 or 20 min. At zero reaction time, the ^{15}N spectrum consists of a unique peak at −45 ppm of the free ^{15}N-oxime, while after heating at 50 °C for 5 min, a new intense resonance emerges at −258 ppm characteristic of the ^{15}N-ω-laurolactam [29–32]. The peak of ^{15}N-lactam dominates the spectrum recorded after reaction at 50 °C for 20 min, while only a very weak signal of ^{15}N-oxime remains. Therefore, the results displayed in Fig. 1 indicate that, under our experimental conditions, the Beckmann rearrangement reaction already occurs at 50 °C. With respect to ^{19}F MAS NMR, all spectra of the reaction mixture, at room temperature and after heating at 50 °C, show a doublet with $\delta(^{19}F) = -72.2$ ppm and the J coupling $J(^{31}P\ ^{19}F) = 708$ Hz of the PF_6^- anion [33]. After heating at 50 °C (5 min or 20 min), the spectrum shows also a very weak doublet at $\delta(^{19}F) = -82.9$ ppm with $J(^{19}F\ ^{31}P) = 960$ Hz corresponding to the anion $[PO_2F_2]^-$ [33]. The formation of this species is supported by ^{31}P NMR spectroscopy. As illustrated in Fig. 1b, a signal at $\delta(^{31}P) = -16.1$ ppm of $PO_2F_2^-$ appears in the spectra recorded after reaction (5 min and 20 min) besides the septuplet of the PF_6^- centred at $\delta(^{31}P) = -144.3$ ppm, $J(^{31}P\ ^{19}F) = 708$ Hz [33].

The presence of the $PO_2F_2^-$ anion in the medium after reaction at 50 °C during the 'in situ' NMR experiment points out that the PF_6^- has been hydrolyzed according to reactions (1) and (2), indicating that some water remained in the medium even after evacuating the reaction mixture at room temperature. The hydrolysis of the hexafluorophosphate anion has been described by reactions (1), and, according to reaction (4), the PO_3F^{2-} anion has been suggested to be involved in equilibrium with $(HO)PO_2F^-$ [33].

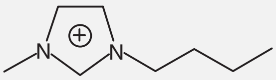
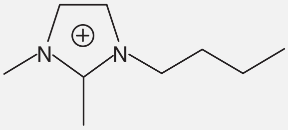
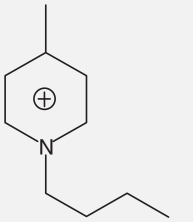
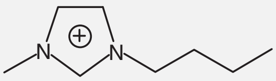
$$PF_6^- + H_2O \rightarrow POF_4^- + 2HF \tag{1}$$

$$POF_4^- + H_2O \rightarrow PO_2F_2^- + 2HF \tag{2}$$

$$PO_2F_2^- + H_2O \rightarrow HF + PO_3F^{2-} + H^+ \tag{3}$$

$$PO_3F^{2-} + H^+ \leftrightarrow (HO)PO_2F^- \tag{4}$$

Table 2
Oxime conversion (X, %) and lactam selectivity (S_{lact}, %) in the Beckmann rearrangement reaction of cyclododecanone oxime to ω-laurolactam at 130 °C during 2 h. The ionic liquids used in the reaction contained the water indicated in Table 1. The concentration of HF was determined at the end of the reaction. nd: not detected.

Ionic liquid		X (%)	S_{lact} (%)	HF (ppm)
	PF_6^-	99.9	99.5	3194
	PF_6^-	0	0	nd
	PF_6^-	100	95.8	5338
	BF_4^-	0	0	nd

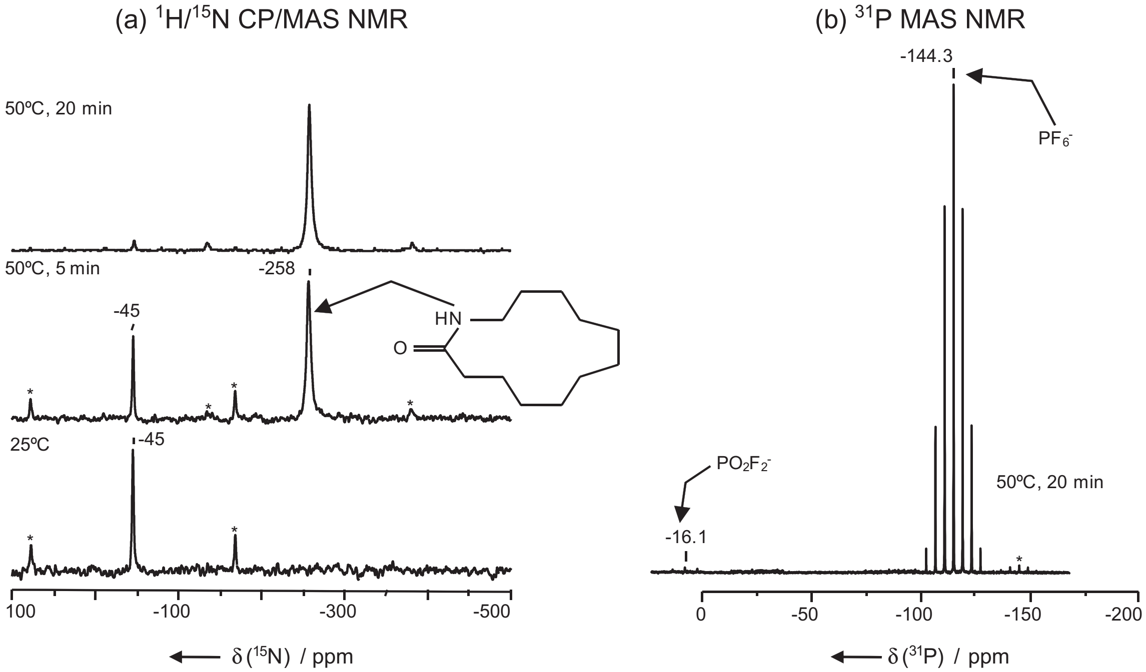


Fig. 1. (a) ^{15}N CP MAS NMR spectra of the reaction mixture as prepared and after heating at 50 °C for 5 and 20 min and (b) ^{31}P MAS NMR spectrum of the reaction mixture after heating at 50 °C for 20 min.

No signal of hydrogen fluoride was detected by 'in situ' solid-state ^{19}F NMR spectroscopy. However, according to reactions (1) and (2), the hydrolysis of PF_6^- involves the formation of HF, which can act as catalyst for the Beckmann rearrangement reaction. Hydrolysis of PF_6^- may also occur when the reaction in the ionic liquid is carried out in the glass flask reactor, and then, the HF evolved will be responsible for the catalytic results summarized in Table 2.

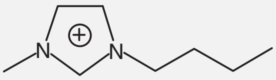
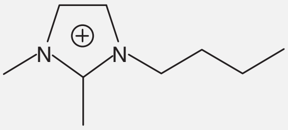
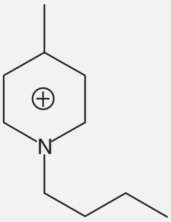
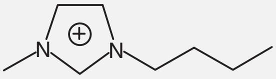
In order to determine whether hexafluorophosphate PF_6^- anions have been hydrolyzed during the heat treatment in the conventional reaction experiments, we have analyzed by ^{31}P NMR spectroscopy the reactant mixture dissolved in pyridine-d_6 at the end of the reaction. The ^{31}P NMR signal characteristic of $PO_2F_2^-$ was observed after the reaction of cyclododecanone oxime in 1-butyl-3-methylimidazolium ($[C_4mim]^+PF_6^-$) and 1-butyl-4-methyl-pyridinium hexafluorophosphates ($[C_4mpyr]^+PF_6^-$). However, $PO_2F_2^-$ or any product which could come from the hydrolysis of the BF_4^- were not detected after heating the oxime together with 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim]^+BF_4^-$) and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ($[C_4m_2im]^+PF_6^-$), which do not give any oxime conversion. The HF evolved in the lapse of the reaction in $[C_4mim]^+PF_6^-$ and $[C_4mpyr]^+PF_6^-$ listed in Table 2 was estimated from the stoichiometry of reactions (1)–(3) and the quantification of the ^{31}P NMR signal of $PO_2F_2^-$. The molecular balance between HF and H_2O was close to 80% in all experiments. We must note, however, that in some cases, we encountered difficulties to balance the amounts of HF (and then of $PO_2F_2^-$) and water.

According to Table 1, all ionic liquids contain water. Nevertheless, we added 2.3–3.0 wt.% water to the reaction mixtures to check whether a higher water concentration would help to hydrolyze the BF_4^- and PF_6^- of $[C_4mim]^+BF_4^-$ and $[C_4m_2im]^+PF_6^-$ ILs. The oxime conversions and lactam selectivities were measured by gas chromatography, and the hydrolysis of the ionic liquids was studied by ^{31}P NMR spectroscopy with a solution of the reactant mixture after the heat treatment. The results, summarized in Table 3, show that cyclododecanone oxime is converted in $[C_4mpyr]^+PF_6^-$ and $[C_4mim]^+PF_6^-$, and the corresponding ^{31}P NMR spectra show the triplet of $PO_2F_2^-$ ($\delta = -17.7$ ppm, $J(^{31}P\ ^{19}F) = 951$ Hz), and a doublet at $\delta = -8.26$ ppm $s^{31}P\ ^{19}F) = 918$ Hz attributed to PO_3F^{2-}, indicating the hydrolysis of PF_6^-. Again, no conversion occurs in $[C_4m_2im]^+PF_6^-$ and $[C_4mim]^+BF_4^-$, and in these two cases, the ^{31}P and ^{11}B NMR spectra of the reaction mixture showed only the signals of $[PF_6]^-$ and $[BF_4^-]$, respectively. Therefore, despite the deliberated addition of water, the anions of $[C_4m_2im]^+PF_6^-$ and $[C_4mim]^+BF_4^-$ are not hydrolyzed and the oxime is not converted at 130 °C.

In order to check the reactivity with water, ILs without the oxime were heated at 130 °C for 2 h and the resulting mixture analyzed by NMR. As summarized in Table 3, no hydrolysis product was observed by ^{31}P NMR for the two inactive and non hydrolyzed ILs, 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim]^+BF_4^-$) and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ($[C_4m_2im]^+PF_6^-$). Meanwhile, when a similar experiment was carried out with 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim]^+PF_6^-$), the anion was hydrolyzed giving a relatively high content on HF (see Table 3). The ulterior addition of cyclododecanone oxime and further heating under the same conditions gave practically complete oxime conversion with very high selectivity to the lactam, which is very similar to the results obtained without previous heating of the ionic liquid, as depicted in Table 3. Therefore, the reaction of the ionic liquid with water does not changed drastically regardless the presence or not of oxime.

We have carried out additional experiments in order to further prove that HF is the actual catalyst for the Beckmann reaction of cyclododecanone oxime in $[C_4mim]^+PF_6^-$ and $[C_4mpyr]^+PF_6^-$. Indeed, if the above is true, then the absence of water in the reaction medium would inhibit the hydrolysis of the hexafluorophosphate of $[C_4mim]^+PF_6^-$ and $[C_4mpyr]^+PF_6^-$, and therefore the oxime transformation should not occur. Accordingly, we have dried the $[C_4mim]^+PF_6^-$ ionic liquid by heating at 75 °C for 12 h under dynamic vacuum, and subsequently carried out the reaction under an inert atmosphere. Despite the treatment, a certain amount of water remained, as shown in Table 4, which was enough to

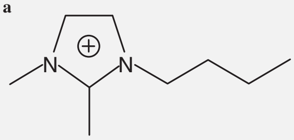
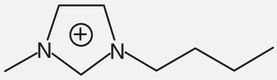
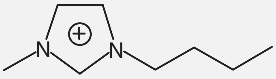
Table 3
Oxime conversion (X, %) and lactam selectivity (S_{lact}, %) in the Beckmann rearrangement reaction of cyclododecanone oxime to ω-laurolactam at 130 °C, 2 h. nd: not detected.

Ionic liquid		Addition of water to the reaction mixture[a]				Previous heating of ionic liquid[b]		
		H_2O (ppm)	X (%)	S_{lact} (%)	HF (ppm)	HF (ppm)	X (%)	S_{lact} (%)
	PF_6^-	29,152	100	78.0	63,357	–	–	–
	PF_6^-	22,433	0.3	nd	nd	nd	0	0
	PF_6^-	24,937	100	84.0	54,049	11,088	100	97.3
	BF_4^-	28,437	1.5	68.0	nd	nd	0	0

[a] 2–2.8 wt.% water was added to the reaction medium, and the HF concentration was determined at the end of the reaction.
[b] The ionic liquid contained the water indicated in Table 1, and the amount of HF was measured after pre-heating at 130 °C, before the addition of the oxime.

hydrolyze the PF_6^-, as indicated by the presence of $PO_2F_2^-$ in the ^{31}P NMR spectrum. The low concentration of hydrogen fluoride in the medium is able to rearrange the cyclododecanone oxime to ω-laurolactam with excellent activity and selectivity (see Table 4). In another set of experiments, we added HF diluted with water to the reaction mixtures containing the inactive ionic liquids, $[C_4m_2im]^+PF_6^-$ and $[C_4mim]^+BF_4^-$. The results shown in Table 4 indicate that in this case, cyclododecanone oxime reacts at 130 °C for 2 h with high conversion in $[C_4m_2im]^+PF_6^-$ and $[C_4mim]^+BF_4^-$ (Table 1). Therefore, the HF diluted in the ionic liquid acts as a catalyst for the Beckmann rearrangement reaction of cyclododecanone oxime. Comparison of Tables 2–4 show that, as could be expected, the lactam selectivity decreases when the reaction is carried out with added water (Table 3) and, certainly for experiments done with the addition of a solution of HF (Table 4).

Table 4
Oxime conversion (X, %) and lactam selectivity (S_{lact}, %) in the Beckmann rearrangement reaction of cyclododecanone oxime to ω-laurolactam at 130 °C and 2 h.

Ionic liquid		H_2O (ppm)	X (%)	S_{lact} (%)	HF (ppm)
a 	PF_6^-	19,500	100	36.2	4900
a 	BF_4^-	19,500	90.9	69.9	4900
b 	PF_6^-	460	99.5	99.5	1020

[a] The reaction was carried out after the addition of 0.5 wt.% HF (using a solution of 20 wt.% HF in water).
[b] The last row reports the results obtained with the ionic liquid previously dehydrated under dynamic vacuum at 75 °C for 12 h; the water and the HF contents were measured before and after the reaction, respectively.

Then, the results presented here indicate that the presence of small amounts of hydrogen fluoride coming from partial hydrolysis of the hexafluorophosphate anion in ionic liquids, $[C_4mpyr]^+PF_6^-$ and $[C_4mim]^+PF_6^-$, is the actual catalyst for the Beckmann rearrangement. It must be noted that PF_6^- and BF_4^- are not hydrolyzed in $[C_4m_2im]^+PF_6^-$ and $[C_4mim]^+BF_4^-$ ionic liquids, respectively. The different reactivity of hexafluorophosphate anion in the two ionic liquids is difficult to explain, and it is probably related to the microscopic properties of the ionic liquid–water mixture.

Finally, the relative amount of oxime in the $[C_4mim]^+PF_6^-$ ionic liquid was increased up to 75 wt.% oxime (oxime/IL molar ratio of 2). The results obtained after the reaction at 130 °C indicate that the conversion remains 99–100% up to 50 wt.% oxime in the reaction mixture and slightly decreases to 92% when the oxime concentration further increases up to 75 wt.%, while the selectivity does not sensitively changes. So that, for a (oxime/$[C_4mim]^+PF_6^-$) molar ratio of 1.4 (50 wt.% oxime), with a water content in the ionic liquid of 1647 ppm (see Table 1), a high yield of ω-laurolactam (≈97%) is obtained after 3 h of reaction time. Moreover, when checking the reusability of the ionic liquid, the yield of ω-laurolactam did not change after using the $[C_4mim]^+PF_6^-$ ionic liquid four times under the standard reaction conditions (10 wt.% oxime, 2 h reaction at 130 °C).

As mentioned in the introduction, BF_3 and $AlCl_3$ have been tested as Lewis acid catalysts for the Beckmann rearrangement of aromatic ketoximes in a series of ionic liquids [23]. The higher reaction rate when using ILs with $[PF_6]^-$ as anion led the authors to point out the possibility that the hexafluorophosphate would be hydrolyzed giving HF, and that this acid could be the real catalyst for the Beckmann rearrangement in the reaction system [23]. Since the use of BF_3 and $AlCl_3$ is not uncommon in industrial process, we decided to check whether the addition of BF_3 acids to the non-active ILs $[C_4m_2im]^+PF_6^-$ and $[C_4mim]^+BF_4^-$ would make possible to use them for the Beckmann rearrangement reaction. So that, the reaction was performed with addition of BF_3 (10 wt.%), and a 100% oxime conversion and 99% selectivity to the lactam in the $[C_4m_2im]^+PF_6^-/BF_3$ system, and 64% oxime conversion and 98% selectivity in the $[C_4mim]^+BF_4/BF_3$ system were obtained. Following the same methodology described above, the NMR spectra of the mixture was recorded at the end of the reaction, and the signals of $PO_2F_2^-$ in $[C_4m_2im]^+PF_6^-$ were observed, indicating the hydrolysis of the anion and consequently the formation of HF. The ^{11}B NMR signal of boric acid which could indicate the hydrolysis of BF_3 is not observed in either of the two ionic liquids, $[C_4m_2im]^+PF_6^-$ and $[C_4mim]^+BF_4^-$. These results suggest that the higher activity achieved in the $[C_4m_2im]^+PF_6^-$ IL is due to the presence of HF. It is worth noting that the addition of BF_3 into the reaction mixture of cyclododecanone oxime in $[C_4m_2im]^+PF_6^-$ induces a sharp modification in the reactivity of the ionic liquid with water, enabling the hydrolysis of the hexafluorophosphate anion. This is a proof of the complex chemistry of ionic liquids since their properties and reactivity can dramatically change when they are mixed with other substances, even at the level of ppm.

What we believe can be of interest is the fact that a very low concentration of HF in the ionic liquid is able to perform the Beckmann rearrangement of cyclododecanone oxime, which is now being carried out using large amounts of oleum. It must be remarked that while an alternative heterogeneous catalytic process to the one that uses H_2SO_4 or oleum has been found for the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam for producing Nylon-6, there is not, today, any alternative to H_2SO_4 for manufacturing ω-laurolactam used for the production of Nylon-12. The results presented here prove that just the residual water present in dry ionic liquids can hydrolyze PF_6^- of $[C_4mim]^+PF_6^-$ and $[C_4mpyr]^+PF_6^-$ ILs producing HF, and the presence of HF at the level of ppm is already able to catalyze the Beckmann rearrangement of cyclododecanone oxime to ω-laurolactam with good activity and selectivity. The advantage of using an ionic liquid as a source of HF is that avoids the use of this acid diluted with water which decreases the lactam selectivity, or the use of relatively larger amounts of BF_3. If one takes into account that the reactants are not perfectly dry and that in some cases [34] small amounts of water are also added deliberately, a process involving the active liquid acids described above could be considered [35].

The results obtained in the present work also show that attention must be paid when using ILs for organic reaction that can be catalyzed by HF. In those cases, where anion hydrolysis can occur and HF could be formed, one should be aware of that for catalyst activity.

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