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Hydrophobic Bis(trifluoromethylsulfonyl)imide-Based Ionic Liquids Pyrolysis: Through the Window of the Ultrasonic Reactor

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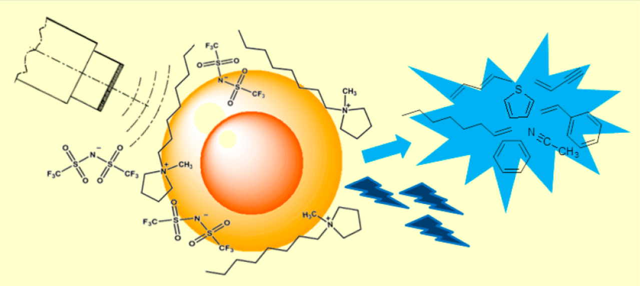
Supporting Information



ABSTRACT: There are typically signs of light degradation of ionic liquids by pyrolysis when used in electrochemistry or when submitted to high heat or to ultrasound irradiation for chemical reactions. Cavitation observed through sonoluminescence from dry hydrophobic ionic liquids under sonication leads to degradation by pyrolysis at the level of traces. The degradation products can hinder recycling ionic liquids and, in turn, hinder the beneficial of their use and development of efficient large-scale processes. Unfortunately, various experimental limitations have prevented structural determination. The problems include the following: ionic liquids are almost non-volatile, which excludes the use of classical analytical techniques, and degradation products are produced at very low concentrations, which complicates extraction and analysis. Reported here is the first structural determination of the degradation products of a hydrophobic bis(trifluoromethylsulfonyl)imide-based ionic liquid under ultrasonic irradiation.

KEYWORDS: *Ionic liquids, Ultrasound, Sonoluminescence, Degradation, Catalysts recycling, Pyrolysis*

■ INTRODUCTION

In recent years, chemical reactions using ionic liquids associated to power ultrasound as an activation method have attracted much attention.[1−3] Ionic liquids as a reaction medium have been shown to allow for easier separation of catalyst and easier recycling. In a previous work, we demonstrated the importance of using the original and unique combination of a bis(trifluoromethylsulfonyl)imide (NTf_2^-)-based ionic liquid with ultrasound for the efficient epoxidation of olefins.[4] We demonstrated a peculiar contribution of ultrasound through the first enantioselective epoxidation in an achiral ionic liquid medium.[5] However, problems encountered with recycling the catalytic system at the end of the reaction led us to suspect a modification of the ionic liquid structure, impossible to identify using the classical analytical tools for structure determination such as ^{1}H NMR, ^{13}C NMR, FTIR, or MS. Yet, a darkening of the ionic liquid from colorless to amber let us suspect some thermal decomposition. Although ionic liquids have been touted as being thermally stable to very high temperatures, Baranyai et al. showed that ionic liquids based on the imidazolium cation degrade, yielding volatile degradation products, at temperatures significantly lower than usually reported.[6] In a more recent work, Burrell et al. highlighted the limited thermal stability of imidazolium- and pyrrolidinium-based ionic liquids.[7] In their study, colored impurities, readily detected by an increase in fluorescence, were shown to be formed by heating at temperatures above 150 °C, well below the onset temperature for decomposition of 400 °C determined by TGA.

The complete study of these typical signs of slight degradation of ionic liquids by pyrolysis when used in sonochemistry and that prevent their recycling represents a crucial issue for the development of viable processes based the ionic liquids use. This work describes a complete investigation of the sonochemical degradation of a pyrrolidinium-based ionic liquid used in our previous work[4,5] and proposes the development of a process to reduce the impact of ultrasound on this hydrophobic ionic liquid.

More than eight decades after their discovery, ultrasound-induced chemical processes,[8−10] also known as sonochemistry, remain a subject of intense research.[11,12] It is generally accepted that the chemical effects of ultrasound result from the

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phenomenon of acoustic cavitation. Sound waves with frequencies higher than 16 kHz traveling through a liquid can force the nucleation, growth, and implosive collapse of microbubbles in response to the motion of expansion and compression waves. The primary chemical effects occur during and immediately after collapse of the cavity of the bubble as a result of the transient high pressures and temperatures. For instance, when water is used as a solvent, water vapor filling the cavities undergoes a thermal dissociation affording hydrogen and hydroxyl radicals ($H^\bullet$ and $^\bullet OH$).[13,14] Solutes present in the vicinity of the bubble/liquid interface can undergo thermal decomposition. Secondary reactions take place in the liquid phase between solute molecules and sonolysis products, mainly $^\bullet OH$ in the case of saturated aqueous solution.

The first important breakthrough in modern organic sonochemistry can be attributed to Luche et al. who studied the sonochemical preparation of organolithium compounds and their use as reagents for a Barbier coupling with carbonyl derivatives.[15] Since this early work, many examples have shown the efficiency of ultrasound in organic chemistry for the synthesis of heterocycles, coupling reactions, alkylation reactions, condensation reactions, substitution reactions, etc.[11] Ultrasound is shown to improve yields and reaction times, and in some specific cases, different selectivities are observed under sonication due to more specific effects of cavitation that may even lead to mechanism switching.[16]

Whatever the case, whether calibration or scaling, the acoustic power dissipated by the ultrasonic wave into the bulk of a solution is a key parameter required to express the efficiency of a sonochemical reactor and is also considered to have the main contribution on the sonochemical yield.[17,18] The easiest and probably most general way to measure the acoustic power is calorimetry.

Recently, we determined for the first time the absorbed acoustic power at a frequency of 20 kHz (low frequency) of a panel of hydrophobic bis(trifluoromethylsulfonyl)imide-based ionic liquids associated with methylbutylpyrrolidinium ([C_4mpyrr][NTf_2]), ethyloctylpiperidinium ([C_8epip][NTf_2]), methyloctylimidazolium ([C_8mim][NTf_2]), octylpyridinium ([C_8py][NTf_2]), and methyloctylpyrrolidinium ([C_8mpyrr][NTf_2]) cations.[19] These data allow to compare the behavior of ionic liquids and water when they are submitted to ultrasonic irradiation; the results show that ionic liquids heat up almost three times faster than water, which can be very interesting when ionic liquids are used as solvents for organic reactions, leading to interesting effects when used as solvents for organic reactions.

In this work, we focus on the study of the effects of acoustic cavitation on methyloctylpyrrolidinium-based ionic liquid ([C_8mpyrr][NTf_2]) that was shown to be very efficient for epoxidation of olefins.[4,5] We report for the first time the sonochemical and sonoluminescent properties of a pyrrolidinium based ionic liquid and the structural identification of its degradation products for which mechanisms of formation are proposed. These degradation products trapped in the bulk of the ionic liquid may then harm the efficiency of a catalytic system from the recycled ionic liquid. This could explain the large decrease in catalytic activity encountered when using a recycled ionic liquid and a catalyst under the conditions previously described.[5] In this work, we simulated 10 cycles of recycling by submitting the ionic liquid to an ultrasonic irradiation time of 10 h.

■ EXPERIMENTAL SECTION

Selected ionic liquids were synthesized as described previously.[5] All ionic liquids were characterized by ^{1}H NMR, ^{13}C NMR, FTIR, HRMS, and cyclic voltammetry. Multibubble sonoluminescence spectra of [C_8mpyrr][NTf_2] and [C_8epip][NTf_2] were recorded using a spectrometer (SP 2356i, Roper Scientific) coupled to a liquid nitrogen-cooled CCD camera (SPEC10-100BR with UV coating, Roper Scientific). Water content of [C_8mpyrr][NTf_2] (39 ± 12 ppm for the dry sample and 9970 ± 77 ppm for the water saturated one) and [C_8epip][NTf_2] (65 ± 15 ppm for the dry sample) were determined by Karl Fischer coulometric titration (Metrohm 831KF coulometer) using Hydranal 34843 Coulomat AG-H (Fluka) as titrant. Ionic liquids were deoxygenated and dried by bubbling of Ar dried through P_2O_5.

Complementary information about the used ultrasonic system and the designed reactor and all analyses spectra are available in the Supporting Information.

■ RESULTS AND DISCUSSION

Sonications were carried out at 20 kHz at ~500−700 $W.L^{-1}$ (acoustic power absorbed by ionic liquids) for 1, 3, and 10 h using 3 mL of neat ionic liquids (H_2O content <50 ppm) at 25 °C. Figure 1 shows the coloration of [C_8mpyrr][NTf_2], which was almost brown after 10 h of ultrasonic irradiation. Similar results were obtained for all studied ionic liquids, whether aromatic or not. Yet, the FTIR, ^{1}H NMR, ^{13}C NMR, and mass spectra (ESI$^+$ and ESI$^-$) as well as the viscosity of the ionic liquids studied did not differ significantly after sonication (Supporting Information). This is probably due to a lack of sensitivity of these methods whose detection limits are not low enough to detect compounds at trace level. In addition, no detectable mass loss was observed in the sonicated samples. Interestingly, the sonication of [C_8mpyrr][NTf_2] for 3 h with air bubbling caused a more significant change in the UV−visible spectrum compared with a dry argon bubbling. Thus, even if the collapse of bubbles is considered to be more efficient in a monatomic gas rather than in polyatomic one,[20] we suggest that the presence of oxygen increases the ionic liquid degradation at the temperatures of the bubble's collapse.

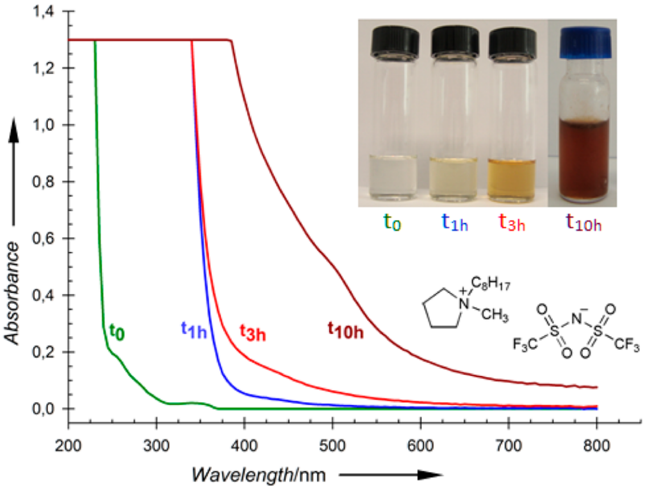


Figure 1. UV−visible spectrum of [C_8mpyrr][NTf_2] ionic liquid degraded under ultrasound after different sonication times (1, 3, and 10 h).

In our case, the bulk temperature of sonicated ionic liquids did not exceed 25 °C. However, it is well established that the collapse of acoustic cavitation bubbles produces intense local heating (about 5000 K).[21,22] This so called hot spot theory is the one generally proposed for explaining the origin of sonochemistry and sonoluminescence. Kinetic studies carried out by Suslick et al. revealed a two-site model in a cavitating liquid.[23,24] Thus, the sonochemical reaction can take place in the gaseous phase inside the bubble, in the limit shell around the bubble, or in the bulk solution. The temperature in the limit shell is estimated between 800 and 2000 K.[25]

Sonoluminescence of Ionic Liquids. Like sonochemistry, sonoluminescence (SL: bubble implosive collapse generating a huge pulse of energy, which leads to the emission of photons) derives from acoustic cavitation. A means to probe the effect of ultrasound on ionic liquids is to measure their SL spectra. To date, the only report dealing with SL of an imidazolium-based ionic liquid has been published by Suslick et al.[26,27] In addition, in this latter work, GC-MS analyses of the head-gas over each sonication indicated that not only were the imidazolium-based ionic liquids decomposed under sonication but also the products of their primary sonolysis are *N*-alkylimidazoles and 1-alkylhalides.

In our work, we studied the multibubble sonoluminescence (MBSL) of two ionic liquids, [C_8mpyrr][NTf_2] and [C_8epip][NTf_2], in a stainless steel reactor specially and specifically designed for the sonoluminescence (SL) measurements of small volumes of liquid. Spectra were recorded using a spectrometer coupled to a liquid nitrogen-cooled charge-coupled device camera (CCD camera: details in Supporting Information). The MBSL spectra of nonaromatic ionic liquids such as [C_8mpyrr][NTf_2] (Figure 2) or [C_8epip][NTf_2] (Supporting Information) contained the usual SL continuum and molecular emissions from excited states of CN and C_2. The lines at 386 and 415 nm are attributed to the transitions of excited CN* molecules,[28] and the peaks displayed at 469, 515, 560, and 600 nm correspond to C_2* Swan bands.[29,30] For [C_8mpyrr][NTf_2], both the continuum and the line intensities decrease with increasing sonication time, and the lines almost become indistinguishable from the continuum (Table 1). The decrease in continuum can be shown by an increase of UV—visible absorption by the medium with irriadation time (Figure 1).

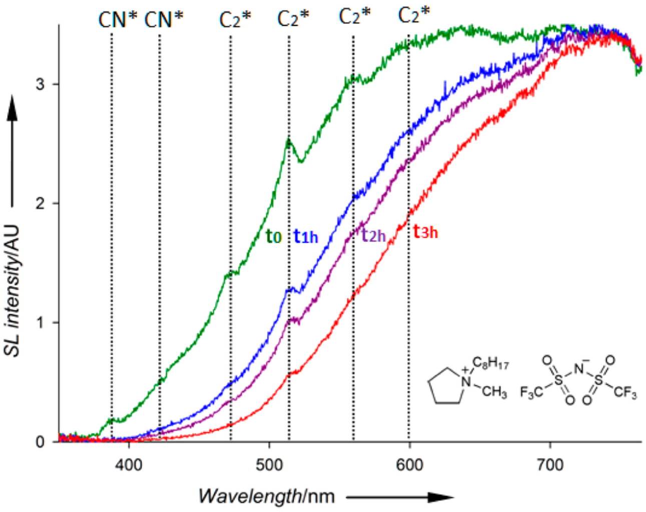


Figure 2. MBSL spectra of [C_8mpyrr][NTf_2] ionic liquid as a function of sonication time.

Table 1. | Evolution with Sonication Time of the Continuum Represented by MBSL Intensity at 585 nm

$t_{sonication}$	0	1 h	2 h	3 h	5 h
$I_{SL(585\ nm)}$	3.233	2.462	2.122	1.628	0.832

Products of Sonochemical Degradation. With their negligible vapor pressure, ionic liquids should have very little susceptibility to sonochemical degradation, and the selected hydrophobic ionic liquids cannot lead to substantial •OH production during sonication because of their negligible water content. Thus, we have identified the main products of degradation in order to understand the behavior of ionic liquids under low frequency ultrasound and ascertain the degradation mechanisms. Indeed, in our work, the primary and secondary sonolysis products of the [C_8mpyrr][NTf_2] have been identified through three methods: online detection of gaseous organic products in the head-gas over the sonication, quantification of sulfur ions, and analysis of volatile impurities trapped in degraded ionic liquid due to headspace technology.

The head-gas over each sonicated ionic liquid, [C_8mpyrr][NTf_2] and [C_8epip][NTf_2], was sampled and analyzed by a mass spectrometer (MS) directly connected to the gas output of the reactor during sonication. Table 2 displays the main head-gas components observed during sonication of [C_8mpyrr][NTf_2] and [C_8epip][NTf_2], namely, dihydrogen and trace amounts of light hydrocarbons (methane, acetylene) and nitriles (acetonitrile, butyronitrile) originating from the decomposition of the cations. Sulfur dioxide traces are due to the degradation of the anion NTf_2^-. No fluoride-containing species were detected.

Table 2. Proportion of Gases Observed in the Head during Sonication of [C_8mpyrr][NTf_2] and [C_8epip][NTf_2] Ionic Liquids

gas	[C_8mpyrr][NTf_2]	[C_8epip][NTf_2]
H_2	51%[a]	47%[b]
CH_4	26%	34%
acetylene	18%	14%
CO_2	2%	2%
acetonitrile	2%	3%
SO_2	0.5%	0.2%
others[c]	traces	traces

[a] Measured flow rate [H_2] = 5.6.10^{-5} mol L^{-1} min^{-1}. [b] Measured flow rate [H_2] = 5.1.10^{-5} mol L^{-1} min^{-1}. [c] Traces of H_2O, propene, and butyronitrile were also observed.

Analyses of sulfur ions in the [C_8mpyrr][NTf_2] ionic liquid revealed the formation of sulfates (70.0 ppm) after 3 h of ultrasonic irradiation and the formation of sulfite (15.2 ppm) and thiocyanate (17.0 ppm) after 10 h of irradiation. These results confirm the slight degradation of the anion under ultrasound. Notice that these sulfur compounds were not present in the ionic liquid before degradation by ultrasound.

After sonication, volatile compounds trapped in degraded [C_8mpyrr][NTf_2] ionic liquid were desorbed by headspace technique, and then separated and identified by GC-MS analyses.

Some irradiation durations of 3 and 10 h were used to simulate the aging of the ionic liquid under ultrasonic irradiation and to concentrate the degradation products generated that could harm the efficiency of catalytic system.

Differences between the chromatograms after 3 and 10 h of irradiation clearly show the significant formation of impurities (Figure 3). Table 3 gives the main volatile degradation products identified in samples after 3 and 10 h of ultrasonic irradiation. It is worth noting that degradation of [C$_8$mpyrr][NTf$_2$] after 3 h is very slight, and the identified volatile species are traces of solvents (acetone and dichloromethane) or degradation products from traces of the remaining first generation ionic liquid ([C$_8$mpyrr][Br]), less thermally stable than [C$_8$mpyrr][NTf$_2$], which degraded in 1-octene and brominated species (bromomethane and 1-bromooctane).

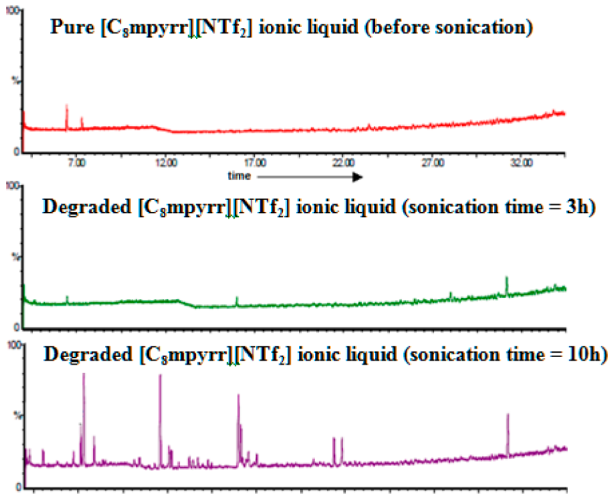
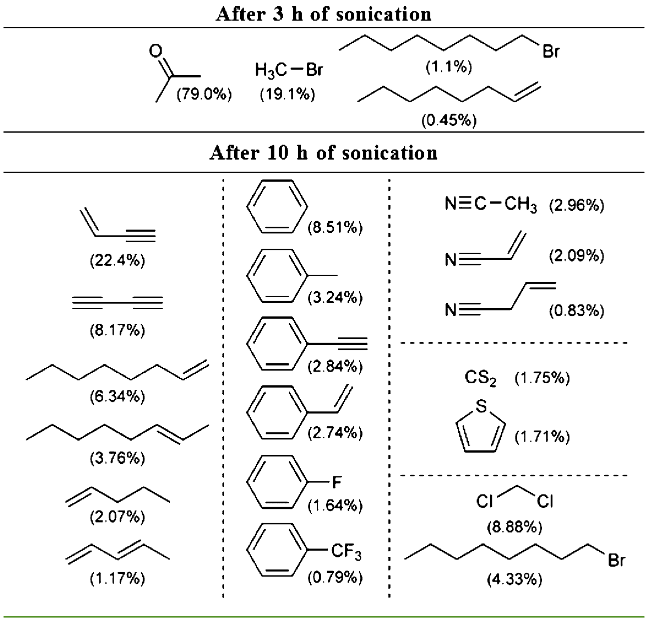


Figure 3. GC chromatograms of [C$_8$mpyrr][NTf$_2$] ionic liquid showing the formation of degradation products as a function of sonication duration.

Table 3. Degradation products of [C$_8$mpyrr][NTf$_2$] identified after 3 and 10 h sonication



Mechanisms of Sonochemical Degradation. Degradation products of [C$_8$mpyrr][NTf$_2$] identified after 10 h of sonication are mainly compounds directly produced by the pyrolysis of the octyl chain of the ionic liquid (44%), benzene derivates obtained through reforming mechanisms (20%), derivates of acrylonitrile obtained from ammoxidation of propene under air (6%), and sulfur-containing compounds resulting from the degradation of the NTf$_2^-$ anion (3%) (Figure 4).

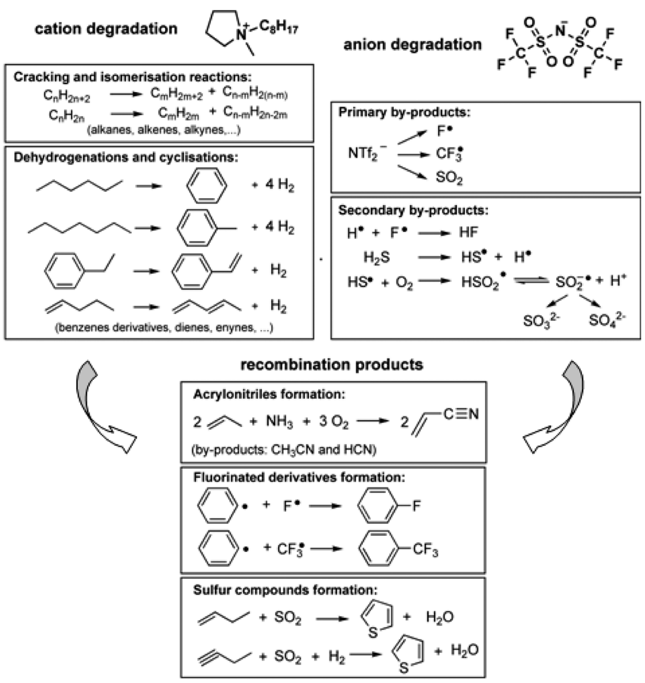


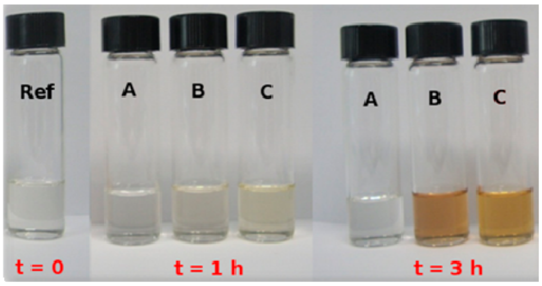
Figure 4. Mechanistic trajectories proposed for the formation of the [C$_8$mpyrr][NTf$_2$] degradation products observed.

The elementary processes involved during the pyrolysis of alkanes are conventionally initiation, propagation, and termination reactions. This mechanism involves radical species that rearrange by recombination, dismutation, and β-scission reactions. It mainly leads to the formation of alkanes, alkenes, and alkynes. Cracking and isomerization reactions are usually carried out at the industrial scale at about 775 K with an acid as catalyst.[31,32] Here, degradation is probably catalyzed by HF issuing from anion degradation. Another hypothesis would involve titanium particules[33] arising from erosion of the ultrasonic immersion probe, which may act as a catalyst for the degradation reactions. However, no turbidity of the medium was observed on visible spectra after sonication. A third hypothesis would involve the ionic liquid, which may act as cocatalyst in degradation reactions, like in the Dimersol process used for the dimerization of alkenes. In this case, the activity of the catalyst is shown to be much higher in the ionic liquid than in the solvent-free system and in the conventional solvent system.[34,35]

Derivatives of acrylonitrile are produced by reactions of ammonia with alkenes under air.[36] Indeed, the formation of ammonia according to eq 1 has a negligible reaction rate under conventional conditions, but it is possible at temperatures at 775 K and above, which are reached during cavitation collapse.

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{1}$$

At last, the degradation of the anion leads to the production of a sulfur source. The produced SO$_2$ and H$_2$S may react with olefins and alkynes to form, respectively, thiophenes[37] and radical species leading under O$_2$ to sulfate and sulfite anions.[38] The first case explains the most significant color change of



A: ionic liquid/water (4:1); B: saturated with water ionic liquid; C: dry ionic liquid

Figure 5. Coloration of different $[C_8mpyrr][NTf_2]$ solutions after 1 and 3 h sonication.

irradiated ionic liquid under air bubbling instead of dry argon bubbling.

The degradation products of hydrophobic $[C_8mpyrr][NTf_2]$ ionic liquid and associated mechanisms can only be explained by pyrolysis of the anion and cation. No product of oxidation by $^{\bullet}OH$ radicals was detected. The observed products are similar to those observed for the degradation of ionic liquids by thermolysis,[6,39] photolysis,[40] and radiolysis;[41,42] the mechanisms of degradation have been almost always studied for imidazolium-based ionic liquids.

A Way To Reduce the Impact of Ultrasound on Ionic Liquids. We finally compared three types of $[C_8mpyrr][NTf_2]$ solutions: the biphasic system $[C_8mpyrr][NTf_2]$/water (4:1), the water-saturated $[C_8mpyrr][NTf_2]$ (content of water = 10,000 ppm), and the dry $[C_8mpyrr][NTf_2]$ (content of water <50 ppm). The influence of water content on the coloration of $[C_8mpyrr][NTf_2]$ when it is sonicated is clear (Figure 5); in the biphasic system, the ionic liquid is almost not degraded. On the contrary, the water saturated ionic liquid and the dry one display important color changes. These results were confirmed by UV−visible analyses (Supporting Information).

More striking is that the analysis of the head-gas over sonication of each sample showed that the amount of gases arising from the ionic liquid sonochemical degradation decreases by a factor of two when the ionic liquid is saturated with water and is 20 times less important in a water/ionic liquid biphasic system (Figure 6).

We thus pointed out a practical and simple method to reduce the impact of low-frequency ultrasound on hydrophobic ionic liquids. We propose that hot spots occur preferentially in water rather than in the ionic liquid essentially because of the difference of viscosities and vapor pressures. Indeed, cavitation highly depends on the viscosity of the medium,[43] but as Toma et al. showed, it is difficult to explain the energy dissipation in organic solvents by looking at only a particular physical property.[18] Thus, addition of water "protects" the ionic liquid from degradation by pyrolysis, while maintaining desired mechanical effect,[44] ensuring the micromixing needed for the chemical reaction; this was observed in our previous work.[4]

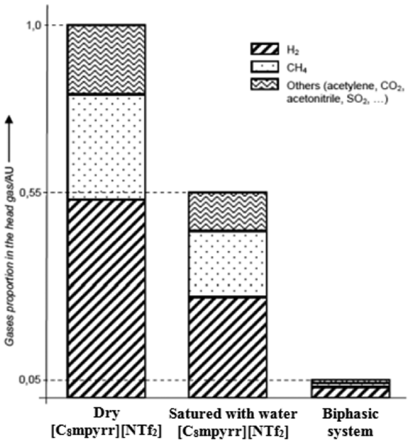


Figure 6. Gas amount in the head-gas of different $[C_8mpyrr][NTf_2]$/water systems during sonication.

■ CONCLUSION

In conclusion, we have shown that hydrophobic bis(trifluoromethylsulfonyl)imide-based ionic liquids decompose under ultrasonic irradiation in traces of degradation products. Although the proportions of these degradation products are limited, they are sufficient to prevent the reuse of ionic liquids. The sonoluminescence spectra confirmed that cavitation occurs in pyrrolidinium- and piperidinium-based ionic liquids. The identification of various organic products in the head-gas and of volatile compounds contained in the degraded ionic liquid allowed us to propose mechanisms for the degradation of ionic liquids under ultrasound. All degradation products result from pyrolysis reactions at the collapse of the cavitation bubbles and not from oxidation reactions involving $^{\bullet}OH$ radicals. Indeed, the amount of $^{\bullet}OH$ is negligible in the absence of water in these hydrophobic ionic liquids. Because of these observations, we are in a position to propose a practical method to reduce the impact of cavitation on ionic liquids by switching to a biphasic ionic liquid/water system.

Finally, the structure of degradation products observed under ultrasonic irradiation of a NTf_2-based methyloctylpyrrolidinium ($[C_8mpyrr][NTf_2]$) ionic liquid may be similar to the degradation products induced by submitting it to high temperature or to an oxidation potential close to the limits of its electrochemical window; this work may be be useful for a large number of chemical applications involving a $[C_8mpyrr][NTf_2]$ ionic liquid, such as in organic chemistry, sonochemistry, catalysis, electrochemistry, etc.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information on reagents, apparatus (designed ultrasonic reactor), and analyses. All spectra of multibubble sonoluminescence measurements, ^1H NMR, ^{13}C NMR, FTIR, MS, and UV−visible of degraded ionic liquids. Spectra of identified volatile compounds contained in the ionic liquid degraded under ultrasound. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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