



Identification of ionic liquid breakdown products in an advanced oxidation system

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ABSTRACT

Commonly used alkylimidazolium ionic liquids are poorly to negligibly biodegradable, and some are toxic, with the potential to poison typical biological test systems. Therefore, when ionic liquids are present in technological wastewaters they could break through classical wastewater treatment systems into natural waters and become potentially persistent pollutants. A recent study investigating different advanced oxidation processes found that the H₂O₂/UV system degraded dissolved imidazolium ionic liquids with the greatest efficiency. In the present study, high performance liquid chromatography was coupled with electrospray mass spectrometry to separate, analyse and identify degradation products following the treatment of ionic liquid solutions with H₂O₂ in the presence of UV irradiation. It was found that hydroxylation in short-chain entities occurred mainly within the ring moiety, whereas in the case of longer alkylated cations, oxidation of the alkyl chain yielded several products. The potential transformation products were identified structurally by MS/MS analysis and are discussed in the light of their putative toxicity and biodegradability.

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1. Introduction

Ionic liquids are often uncritically regarded as inherently 'green' because of their negligible vapor pressure. Hence, they are thought to be a good alternative to the emissions of toxic vapors from conventional molecular organic solvents. A low vapor pressure, however, is generally not sufficient to justify calling a process or even a whole technology 'greener' [1].

In view of the broad applicability of ionic liquids, especially in synthesis, extraction and as alternative lubricants [2], certain amounts of ionic liquids will soon be present in technological wastewaters. The broad applicability of ionic liquids force us to answer a question: what will happen when IL will get through the environment? Their low vapor pressure guarantees the air protection from the emissions of toxic vapors, but from the other hand their stability make them dangerous for water and soil [3–6].

The potential of ionic liquids to break through classical treatment systems into natural waters and become persistent pollutants requires that further strategies be developed to improve the

degradability of these recalcitrant compounds. In the few studies available investigating the biodegradability of ionic liquids cations a high resistance toward microbial degradation was found, particular for the most common imidazolium based compounds [7–9].

The resistance of persistent chemicals to conventional wastewater treatment systems has hastened the development of advanced oxidation processes (AOPs), new methods that employ a combination of several oxidising agents. The main task of AOPs is to promote free radical formation in aqueous solutions. Hydroxyl radicals are generated through different combinations of oxidants as well as a whole range of photocatalytic systems [10–12]. One of the most frequently used AOPs is based on the UV photolysis of hydrogen peroxide (H₂O₂/UV), where radiation below 400 nm is capable of photolysing the H₂O₂ molecule.

A recent study of ours showed that employing the H₂O₂/UV system offers the greatest degradation efficiency for imidazolium cation residues in water. Degradability in this system decreases in the order BMIM < HMIM < OMIM < EEIM and depends on the length of the alkyl chain substituted at position 1 of the 1-alkyl-3-methylimidazolium ring [13].

This was a preliminary study, however, and the identification of the breakdown products occurring in this oxidation system was

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not one of its objectives. Obviously, possible degradation products are important, and further studies must be undertaken in order to identify them if one is to gain an understanding of the overall consequences of the presence of ionic liquids in the environment. There are already known results of alkyimidazolium ionic liquids degradation in Fenton-like system [14,15], and in $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ aqueous medium with the presence of ultrasonic chemical irradiation [16]. For identification degradation products, GC–MS system was used. Recently, the extent of degradation of imidazolium and pyrrolidinium ionic liquids in electrochemical processing and their possible breakdown products were predicted using quantum chemical calculations and confirmed experimentally [17]. In other studies the radiochemical stability [18] and influence of gamma irradiation on ionic liquids [19] were also studied.

The aim of the present study was therefore to identify the decomposition products occurring in the advanced oxidation system using high performance liquids chromatography coupled to electrospray mass spectrometry, and to discuss the putative biodegradability and toxicity of these products. In general, light-induced processes initiated by reactive oxygen species ($\cdot\text{OH}$, O_3 , and $^1\text{O}_2$) represent an important abiotic degradation path of organic compounds in surface waters, even if the concentration of $\cdot\text{OH}$ radicals is much lower than in AOP systems. However, the degradation products formed should be similar, and the data presented here may add to our knowledge of the hazard assessment of ionic liquids.

2. Materials and methods

2.1. Ionic liquids and reagents

The ionic liquids selected for these studies – 1-ethyl-, 1-butyl-, 1-hexyl- and 1-octyl-3-methylimidazolium chlorides – were obtained from Merck KGaA. Used as received without any additional pre-treatment, they were dissolved in water to obtain 100 mM stock solutions for further treatment. For the better dissolution of 1-octyl-3-methylimidazolium chloride 0.05% (v:v) methanol (Riedel-de Haën GmbH) was added. Hydrogen peroxide (35% solution) was purchased from Merck KGaA.

2.2. Irradiation conditions

Degradation reactions were carried out at atmospheric pressure in a 0.25 L cylindrical batch reactor equipped with a magnetic stirrer and a CAMAG UV Lamp 254/366 nm 3×20 W. Ionic liquid solutions (1 mM) were irradiated in the presence of H_2O_2 (0.2%). After 2 h of degradation, 1 mL samples of wastewater were taken for HPLC–MS analysis.

2.3. Analytical method

Details of the analytical procedures for ionic liquids can be found in several recent papers published by our team [20–22].

All samples were subjected to HPLC–MS analyses on a liquid chromatograph (Agilent 1100 series, Agilent) coupled to a Bruker-Esquire LC electrospray ionisation mass detector (Bruker-Daltonic GmbH). Additionally, the HPLC instrument was equipped with a variable wavelength detector (210 nm). Chromatographic separations. All analyses were performed on a MonoChrom 5MS column 150 mm \times 3 mm (Varian Inc.) (flow rate = 0.5 mL min^{-1} ; injection volume = 5 μL ; mobile phase – 70% acetonitrile solution (Riedel-de Haën GmbH)/5 mM ammonium acetate in 0.1% acetic acid (Merck KGaA)). Mass spectra of the compounds analysed were acquired in the positive ion mode in the m/z 50–400 scan range. Capillary exit, trap drive and skimmer voltages were 81.9, 27.6 and 15 V,

respectively. For most of the acquired molecular ions the MS/MS technique was further applied in order to identify the structure of the degradation product.

3. Results and discussion

As outlined in the introduction, the most effective advanced oxidation process (AOP) applied to imidazolium ionic liquids is the system based on the UV photolysis of H_2O_2 . Application of this method to solutions of imidazolium ionic liquids leads to very effective oxidation, but it also gives rise to several degradation products. In this experiment we have applied exactly the same oxidation conditions as in our previous paper [13] and monitored degradation products with high performance liquids chromatography coupled to electrospray mass spectrometry. We have selected only those samples, that were characterized by the highest intensity of degradation products' signals in order to undoubtedly elucidate their structures. Comparison of the chromatograms for these samples shows clearly that the longer the alkyl chain in the imidazolium ionic liquid molecule, the more degradation products occur in the solution (Figs. 1–4). Not all breakdown products were effectively separated within applied chromatographic system due to a very similar (sometimes near identical) polarities of obtained oxidation products. Therefore, we have applied selective ion monitoring mode to confirm formed compounds due to their molecular ion masses. Each breakdown product underwent further fragmentation in MS/MS mode enabling structure elucidation by its fragmentation pathway.

The principal products expected were compounds containing additional hydroxyl or carbonyl functional groups bound to the alkyl chains of ionic liquid cations. This would produce ions of $[\text{M}+(n \times 16)]^+$ or $[\text{M}+(n \times 14)]^+$, respectively (M – mass of the 1-

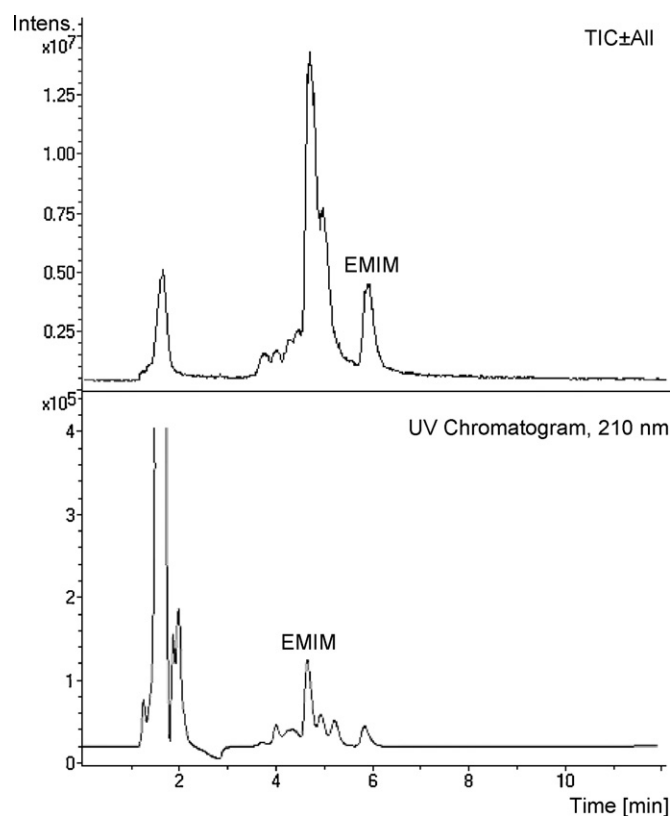


Fig. 1. Exemplary chromatograms of 1-ethyl-3-methylimidazolium entity and its degradation products simultaneously registered in UV and TIC mode.

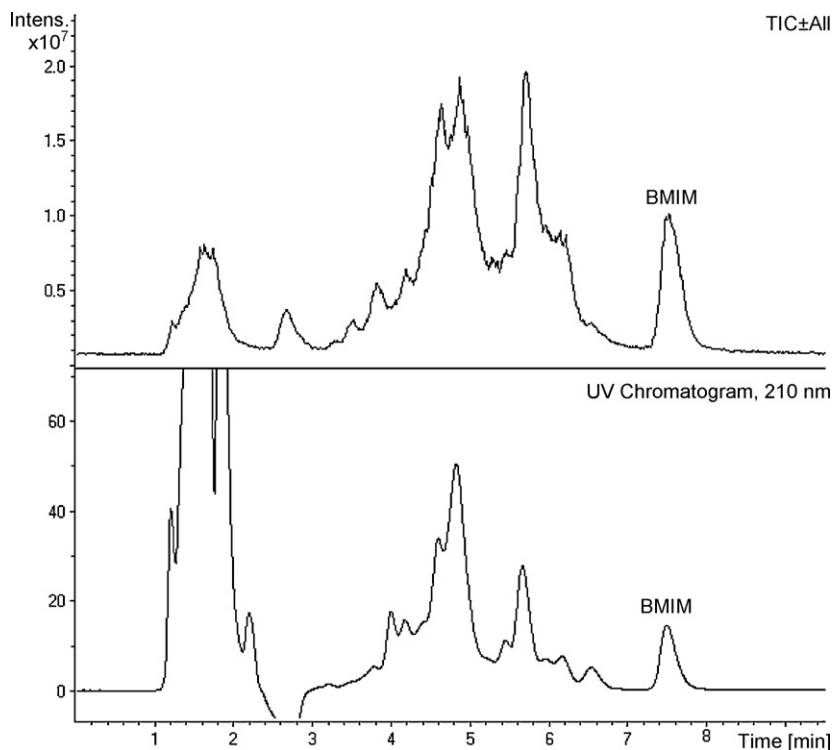


Fig. 2. Exemplary chromatograms of 1-butyl-3-methylimidazolium entity and its degradation products simultaneously registered in UV and TIC mode.

alkyl-3-methylimidazolium cation). However, degradation of all four cations yielded the product $[M+34]^+$, which is most likely $[M+(2 \times 17)]^+$. This means that modification (at least in the first stage of oxidation) occurs in the imidazolium ring, not in the alkyl chain of the molecule. Preliminary variation of oxidation parameters in the system did not let us to recognize the order or a preferred position for oxidation.

The $[M+34]^+$ signal was only observed on the total ion current chromatogram (not on UV absorption chromatogram) which likely

means that molecule has lost its aromatic properties, thus ring had opened.

MS/MS fragmentation of the $[M+34]^+$ ion, regardless of the alkyl chain length, always led to the formation of m/z 72 and $[(M+34)-59]^+$ ions (Fig. 5). Both fragments are likely to be products of the cleaved imidazolium ring, as outlined in Fig. 6.

Two or more compounds with the same mass but slightly different retention times were frequently observed during a single chromatographic run; this probably indicates different substitution

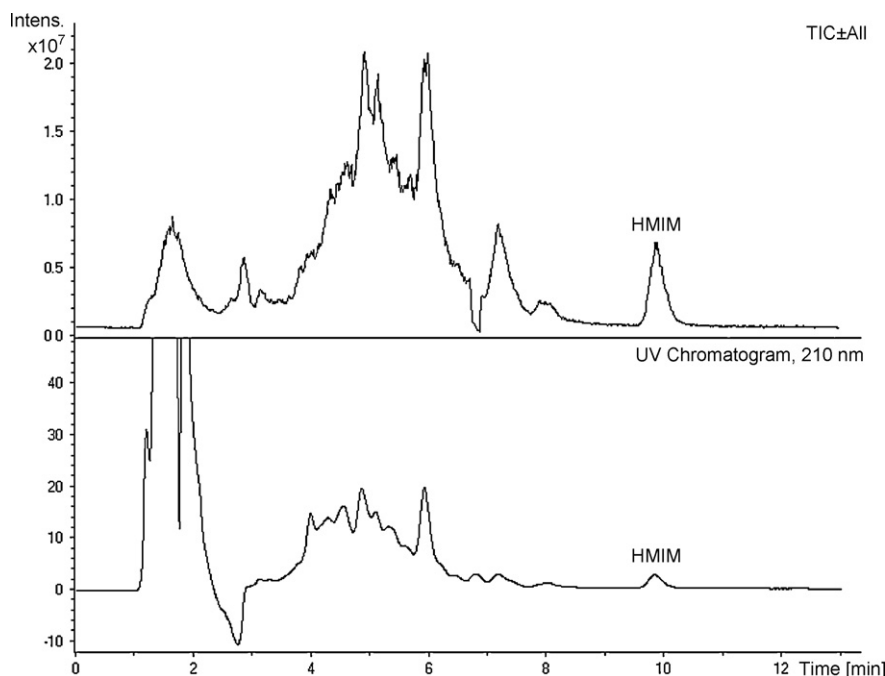


Fig. 3. Exemplary chromatograms of 1-hexyl-3-methylimidazolium entity and its degradation products simultaneously registered in UV and TIC mode.

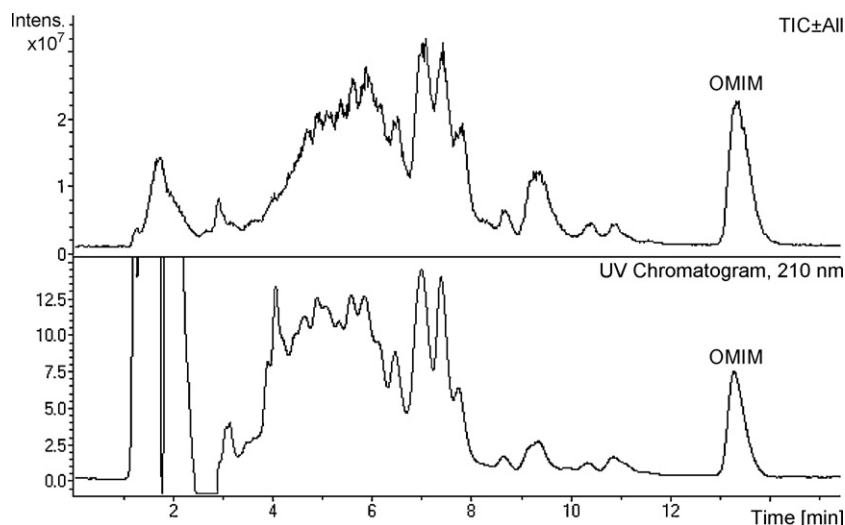


Fig. 4. Exemplary chromatograms of 1-octyl-3-methylimidazolium entity and its degradation products simultaneously registered in UV and TIC mode.

positions with hydroxyl or carbonyl functional groups on the alkyl chain. The number of possible structures increases with increasing alkyl chain length in the ionic liquid cation. If one traces the main bases of fragmentation, in several cases one can distinguish products with the same m/z . From the 1-ethyl-3-methylimidazolium cation three degradation products were obtained with m/z 177 (two hydroxyl groups instead of hydrogens in the alkyl chain and oxidation with opening of the imidazolium ring). In these ions two hydroxyl groups are in the alkyl chains but in different positions, and all have different MS/MS spectra. In the first MS/MS spectra we can see $[(M+34+(2 \times 16))-18]^+$. This peak is most noticeable in the spectra of primary alcohols. In the case of diols, privileged fragmentation occurs between two hydroxyl substituted carbon atoms. Such fragments were also observed in one of the MS/MS spectra (Fig. 7).

In the case of ion m/z 231 obtained after the oxidation of 1-hexyl-3-methylimidazolium chloride, the situation appears to be different. This m/z corresponds to $[M+(4 \times 16)]^+$, which could mean four hydroxyl groups instead of hydrogens in the alkyl chain or $[M+34+(1 \times 16)+(1 \times 14)]^+$, which likely means two carbonyl groups in opened imidazolium ring, one hydroxyl and one carbonyl group instead of hydrogens in the alkyl chain.

If there are hydroxyl groups only in the alkyl chains, m/z equals 83 (3-methylimidazolium cation) in the MS/MS mass spectrum, but if there are two additional carbonyl groups in opened imidazolium ring, m/z equals 72. The fragmentation of imidazolium cations with long alkyl chains is much more complicated, and the interpretation of their mass spectra is more difficult because of the appearance of many isomers and the McLafferty rearrangement.

Our results correspond with those obtained after degradation of ionic liquids in Fenton-like system [15] as well as those after biodegradation process [23]. Compounds identified in our study are similar to those found in these processes. In the current literature there are only a few reports discussing the possible degradation products of imidazolium ionic liquids. Recently, the decomposition of these compounds during electrochemical processing and the possible breakdown products were predicted using quantum chemical calculations. The results were confirmed experimentally [17]. It was found that in these processes, 1-butyl-3-methylimidazolium radicals are formed by the abstraction of hydrogen from the imidazolium ring. They can react further with each other in a radical–radical coupling reaction or in a disproportionation reaction. Nevertheless, this also confirms that in the

presence of hydroxyl radicals (as in our case), hydroxylation occurs, especially in the imidazolium ring. Other studies attempting to identify the gamma radiolysis products of imidazolium ionic liquids have indicated the privileged formation of a methylimidazolium cation radical arising from the rupture of the butyl chain at position $N-1$ in the imidazolium ring. 1-Butyl-3-methylimidazolium radicals are formed either by the loss of hydrogen from the ring or the alkyl chain in the alpha position [18]. This was also predicted theoretically in the cytochrome P-450 oxidation system, where the formation of the 1-butyl-3-methylimidazolium radical by the abstraction of the hydrogen in the alpha position of the alkyl chain is energetically the most favourable [24].

As regards the biodegradability of the identified products, only very limited data sets are available. Recently, the aerobic primary biodegradation for a set of ionic liquids containing, *inter alia*, hydroxyl groups was investigated using activated sludge from a wastewater treatment plant as an inoculum [23]. For example, comparison of the biodegradabilities of OMIM and OMIM–OH (here a terminal hydroxyl group was introduced into the octyl chain) showed the OMIM–OH compound to have a better biodegradability than the OMIM. For OMIM–OH different degradation products were found, related to the β -oxidation degradation pathway of the chain. Nevertheless, multiple hydroxylated side chains can be counterproductive for this mechanism. For an EMIM with a terminal hydroxylated ethyl chain, no primary biodegradation has been ascertained.

However, the main transformation products formed in the AOP applied are related to the imidazolium core. This N -substituted head group in particular is known to be poorly biodegradable [25], but the introduction of hydroxyl/carbonyl groups associated with a ring-opening reaction or the removal of aromaticity are very promising attempts to increase biodegradability. The products formed (amines, imines, aldehydes, and ketones) can undergo further chemical or enzymatic reactions.

In general, it is known that the introduction of hydroxyl groups into the side chain of ionic liquid cations results in a clearly decreased acute toxicity toward rat cell lines [26], bacteria (*Vibrio fischeri*), duckweed (*Lemna minor*) and algae (*Scenedesmus vacuolatus*) [27] compared to the alkyl compounds. However, it has to be borne in mind that the reactive intermediates formed may still cause toxic effects in the chronic scale. For a final assessment of the utility of the AOP applied here to remove ionic liquid cations in an environmentally compatible manner, further analy-

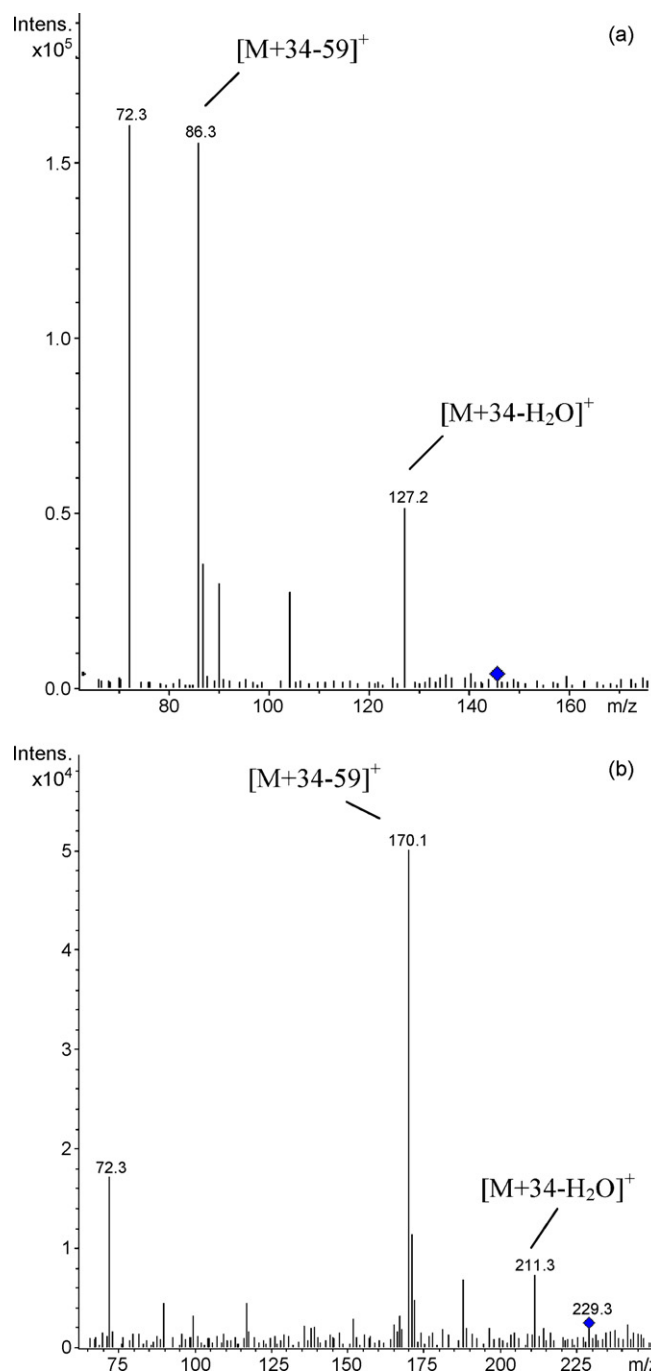


Fig. 5. MS/MS mass spectra of $[M+34]^+$ obtained after degradation of: (a) EMIM and (b) OMIM.

ses of the biodegradability and toxicity of the solutions formed are necessary.

Since ionic liquids are salts anionic part of the compound should also be considered if toxicity is discussed. Recent studies indicate, however, that influence of anion on biological responses of various test systems is not as distinct as in the case of cationic moiety side chain modifications such as its length or introduction of different functionalities [28,29].

For a final assessment of the utility of the used AOP to remove ionic liquids cations environmentally compatible further investigation are necessary analyzing the biodegradability and toxicity of the formed solutions.

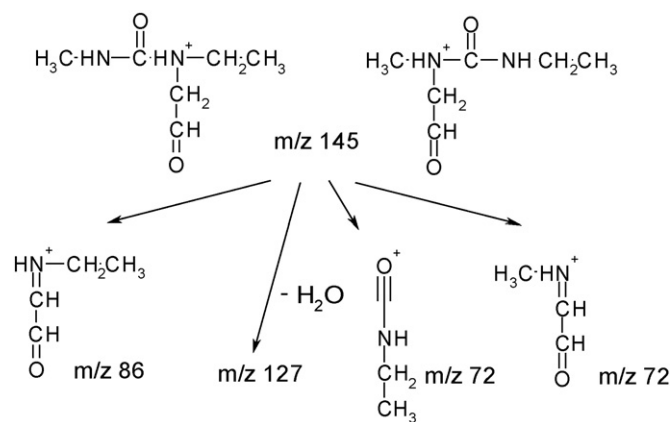


Fig. 6. Fragmentation pathways of most abundant degradation products of 1-ethyl-3-methylimidazolium cation (m/z 145).

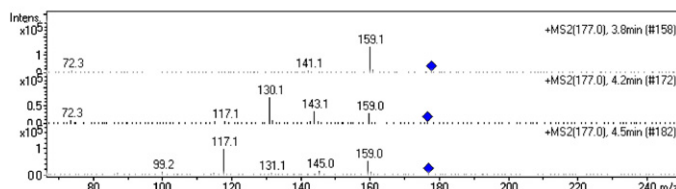
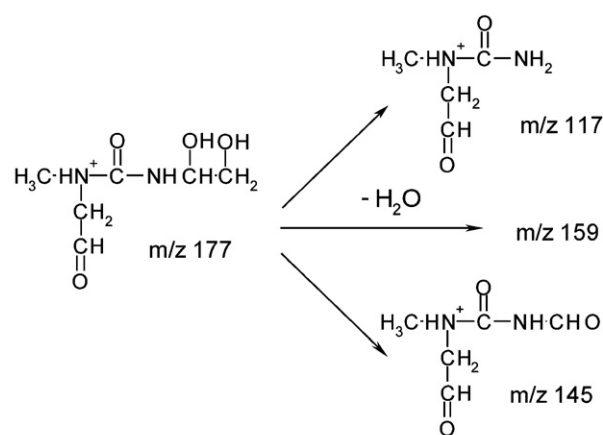


Fig. 7. Deduction of one of the fragmentation pathways based on MS/MS spectra of three different degradation products of m/z 177.

4. Conclusions

In conclusion, applying the H_2O_2/UV system to solutions of imidazolium ionic liquids is a very effective oxidation method, but it gives rise to a number of degradation products. One of the main breakdown products is formed via the substitution of two hydroxyl groups in the imidazolium ring. Also identified were products with two carboxyl groups instead of two methyl groups in the alkyl chains, a carbonyl group in the alkyl chain, and various numbers of hydroxyl groups instead of hydrogen atoms in the alkyl chain. During a single chromatographic run, two or more compounds with the same mass but slightly different retention times were also observed; these probably represent compounds substituted with the same number of hydroxyl or carbonyl functional groups but in different positions of the alkyl chain. Future studies shall cover identification of particular degradation products in various oxidation rates in order to follow the most, and the least privileged oxidation patterns. The toxicity and biodegradability of the degradation products still need to be analysed in further studies; on the basis of existing data sets, however, the prospects are very promising.

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