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## Photochemistry of imidazolium cations. Water addition to methylimidazolium ring induced by UV radiation in aqueous solution



Gabriela P. Sarmiento<sup>a</sup>, Andrés Zelcer<sup>b,c</sup>, Mariela S. Espinosa<sup>a</sup>, Paola A. Babay<sup>a</sup>,  
Martin Miranda<sup>a,b,d,\*</sup>

<sup>a</sup> Gerencia Química, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, B1650KNA San Martín, Buenos Aires, Argentina

<sup>b</sup> CONICET, Av. Rivadavia 1917, C1033AAJ Buenos Aires, Argentina

<sup>c</sup> ECyT-UNSAM, 25 de Mayo y Francia, C.P.: 1650 San Martín, Buenos Aires, Argentina

<sup>d</sup> Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pab. II, C1428EHA, Buenos Aires, Argentina

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### ABSTRACT

The UV-C induced photoaddition of water to *N*-alkyl-*N'*-methylimidazolium cations was studied. The main photoreaction products exhibit chemical additions of a proton and a hydroxyl group to either positions 4 or 5 of the imidazolium ring. For unsymmetrical imidazolium cations, two positional isomers were obtained as products. In these cases, the most abundant isomer is the one in which the hydroxyl group adds at the side of the ring having the longer alkyl substituent. Experiments performed in D<sub>2</sub>O solutions reveal that the additions of proton and hydroxyl group never take place at the same carbon atom, in a reaction that produces equal amounts of diastereoisomers. Moreover, the formation of diastereoisomers at equal proportions suggests that the reaction proceeds in an unconcerted fashion.

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### 1. Introduction

Methylimidazolium cations are one of the most common constituents of ionic liquids (ILs), a newfangled kind of organic salts that melt near or below 100 °C [1–4]. The distinctive physicochemical properties of these compounds—low flammability, tunable chemical solubility, low vapor pressure and high thermal stability, among others—make them interesting alternatives to common volatile organic solvents in many areas such as catalysis [5,6], organic synthesis [7,8], nanotechnology [9,10], and nuclear technology [11,12].

ILs were assiduously proposed as solvents for applications in green technologies since their negligible vapor pressure avoids air pollution due to evaporation and volatilization processes. However, most of them have a significant solubility in water, the most likely medium through which they would be eventually released into the environment [13]. In recent years, some research groups have succeeded in analyzing different mechanisms of degradation of methylimidazolium cations in water, since the latter are not normally considered as readily biodegradable compounds [14].

The degradation methods proposed in the literature include: (a) chemical degradation by ozonation and Fenton and Fenton like reactions, (b) electrochemical degradation and, (c) photochemical degradation by UV, UV/TiO<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub> and ultrasound/H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COOH [15]. In many cases, not only is the efficiency of degradation process the important issue. The chemical nature of the degradation products is also relevant in order to evaluate if these compounds are environmentally friendlier than their precursors. Siedlecka et al. [16] and more recently Muñoz et al. [17] showed that the main degradation products of methylimidazolium cations in aqueous solutions under Fenton oxidation are imidazolones. On the other hand, Czerwicka et al. [18] showed that the photochemical treatment of methylimidazolium cations in solution with UV/H<sub>2</sub>O<sub>2</sub> yields main degradation products with two hydroxyl groups at the imidazolium ring. While different degradation processes may lead to a variety of products, all of them have in common the oxidation, at least to some degree, of the imidazolium ring. The incorporation of oxygen atoms in the form of hydroxyl, aldehyde or carboxylic groups is interesting, since these functional groups represent possible sites for attack by oxygenases [19]. It is important to note that, although ten years ago Stepnowski and Zaleska [20] reported a pioneering work on the degradation of imidazolium ILs under UV light, they failed to inform the chemical products obtained in that process.

\* Corresponding author.

E-mail address: [miranda@cnea.gov.ar](mailto:miranda@cnea.gov.ar) (M. Miranda).

The subject of the interaction of methylimidazolium compounds with UV radiation itself also constitutes a relevant topic in photochemistry. These compounds are used as solvents in photocatalysis [21], photoisomerizations [22], photoinduced charge-transfer processes [23], and in dye sensitized solar cells [24,25], since they are optically transparent in a sizeable fraction of the UV-vis spectrum [26,27]. Although the photophysical characteristics of the methylimidazolium ionic liquids (ImILs) have been analyzed in several publications [28–30], none of them have focused on the photochemical effects produced by the irradiation of these compounds in the UV-C region, where they absorb.

The present work is focused on the photochemical reactions that occur when methylimidazolium cations are exposed to UV radiation in aqueous medium. The experiments were performed on three different *N*-alkyl-*N'*-methylimidazolium chlorides, varying the lengths of the alkyl substituent chains of the reactants in a systematic way. The separation and identification of the main reaction products were performed using a variety of techniques including chromatography, mass spectrometry and single and multidimensional NMR. The results show that all methylimidazolium cations have similar photochemical behaviors, whereas isotopic substitution experiments provide additional insights about mechanistic aspects of the photoreaction.

## 2. Materials and methods

### 2.1. Sample preparation

1-Butyl-3-methylimidazolium chloride (BMIMCl) was obtained by chemical synthesis in our laboratories following standard procedures [8]. Freshly distilled 1-chlorobutane (Merck-Reagent for synthesis) was added dropwise to distilled 1-methylimidazole (Merck-Reagent for synthesis) (1.3:1 mole proportion) under vigorous stirring. The mixture was kept at 50 °C for 5 days under continuous stirring, in a N<sub>2</sub> atmosphere, and subsequently purified by recrystallization from acetonitrile-ethyl acetate mixtures. <sup>1</sup>H NMR: (500 MHz, D<sub>2</sub>O, δ in ppm) 8.70 (s. n. r., 1H-C<sub>(2)</sub>), 7.47 (s. n. r., 1H-C<sub>(5)</sub>), 7.42 (s. n. r., 1H-C<sub>(4)</sub>), 4.19 (t, 2H-C<sub>(7)</sub>), 3.88 (s, 3H-C<sub>(6)</sub>), 1.84 (m, 2H-C<sub>(8)</sub>), 1.31 (m, 2H-C<sub>(9)</sub>), 0.91 (t, 2H-C<sub>(10)</sub>). <sup>13</sup>C NMR: (500 MHz, D<sub>2</sub>O, δ in ppm) 135.79 (C<sub>(2)</sub>), 123.42 (C<sub>(4)</sub>), 122.17 (C<sub>(5)</sub>), 49.24 (C<sub>(7)</sub>), 35.57 (C<sub>(6)</sub>), 31.22 (C<sub>(8)</sub>), 18.70 (C<sub>(9)</sub>), 12.57 (C<sub>(10)</sub>).

1-Etyl-3-methylimidazolium chloride (EMIMCl) was purchased from Aldrich (Purity 98%) and was used as received. <sup>1</sup>H NMR: (500 MHz, D<sub>2</sub>O, δ in ppm) 8.70 (s, 1H-C<sub>(2)</sub>), 7.48 (d, 1H-C<sub>(5)</sub>, *J* = 1.8 Hz), 7.41 (d, 1H-C<sub>(4)</sub>, *J* = 1.8 Hz), 4.23 (q, 2H-C<sub>(7)</sub>), 3.88 (s, 3H-C<sub>(6)</sub>), 1.49 (t, 3H-C<sub>(8)</sub>). <sup>13</sup>C NMR: (500 MHz, D<sub>2</sub>O, δ in ppm) 135.48 (C<sub>(2)</sub>), 123.39 (C<sub>(4)</sub>), 121.81 (C<sub>(5)</sub>), 44.73 (C<sub>(7)</sub>), 35.55 (C<sub>(6)</sub>), 14.45 (C<sub>(8)</sub>).

1,3-Dimethylimidazolium chloride (MMIMCl) was obtained by chemical synthesis in our laboratories. 1.7 mL of iodomethane (Merck-Reagent for synthesis) was added dropwise to 2 mL of distilled 1-methylimidazole (Merck-Reagent for synthesis) (1.08:1 mole proportion) under vigorous stirring at 0 °C for 3 h.

The mixture was then kept at room temperature and maintained under stirring for 6 days. The excess of iodomethane was removed by distillation and captured in an ammonium hydroxide solution. After distillation, a viscous yellow liquid of MMIMI was obtained. In order to replace iodide by chloride anions, MMIMI was passed through an ion exchange resin (Aldrich, Dorwex 1 × 4 chloride form). The complete exchange of iodide anion was confirmed by the absence of the UV signal at 226 nm on eluted aliquots. The excess of water was removed by evaporation under reduced pressure, yielding a colorless solid of MMIMCl. <sup>1</sup>H NMR: (500 MHz, D<sub>2</sub>O, δ in ppm) 8.64 (s, 1H-C<sub>(2)</sub>), 7.41 (s, 2H-C<sub>(4-5)</sub>), 3.88 (s, 6H-C<sub>(6-7)</sub>). <sup>13</sup>C NMR: (500 MHz, D<sub>2</sub>O, δ in ppm) 136.49 (C<sub>(2)</sub>), 123.35 (C<sub>(4-5)</sub>), 35.57 (C<sub>(6-7)</sub>). The Scheme 1 shows the chemical structures of three ionic liquids used for the experiments.

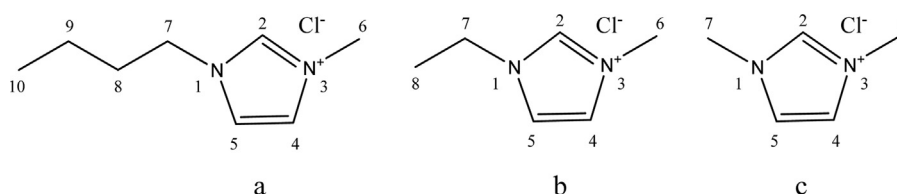
Deionized water (18 MΩ × cm), used for solution preparation, was obtained from a Milli-Q system. Water solutions of ILs were prepared by weighing, one hour before irradiation experiments. Studies were carried out under normal atmospheric air conditions, since control experiments performed under CO<sub>2</sub> and N<sub>2</sub> atmospheres did not show different results, compared with the former ones.

### 2.2. UV irradiation

A deuterium lamp (Oriol 6316 STD D<sub>2</sub>-30W) placed inside an air-cooled housing was used for the broadband irradiation of the samples. In order to obtain the photon irradiance between 190 and 235 nm, where BMIMCl absorbs, first it was determined the irradiance between 320 and 400 nm, *E* = 100 μWatts/cm<sup>2</sup>, using a Spectroline™ DM-365XA radiometer from Spectronic Corporation. With this information and, taking into account the spectral irradiance of the lamp provided by the manufacturers, it was estimated a photon irradiance amount basis [31] *E*<sub>n,p</sub> = 17 μEinstein m<sup>-2</sup> s<sup>-1</sup>. The irradiation spot was large enough (~1 cm<sup>2</sup>) to avoid small irradiation volumes. No temperature changes were registered in the sample during the irradiation. In order to ensure that the photolysis was produced by UV light, control experiments were performed using a narrow band excitation, using a commercial PTI-Spectrofluorometer provided with a Xenon lamp and monochromators. The excitation wavelength was fixed at 211 nm with a narrow excitation slit of ~1 nm. The results obtained in these experiments were the same as those recorded using broadband illumination. However, the latter alternative was chosen since it required shorter irradiation times.

### 2.3. HPLC and NMR measurements

Three different equipments were used for HPLC runs for the following purposes: equipment 1 was used for the separation and identification of the main components of the photoreaction mixtures; equipment 2 was used with the only purpose to determine the high resolution mass spectra of reactants and products and, equipment 3 was used for the isolation and



**Scheme 1.** Chemical structures of ionic liquids used for the experiments: (a) BMIMCl, (b) EMIMCl and (c) MMIMCl.

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