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



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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 D₂O 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/TiO₂, UV/H₂O₂ and ultrasound/H₂O₂/CH₃COOH [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/H₂O₂ 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.

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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 N₂ atmosphere, and subsequently purified by recrystallization from acetonitrile-ethyl acetate mixtures. ¹H NMR: (500 MHz, D₂O, δ in ppm) 8.70 (s. n. r., 1H-C₍₂₎), 7.47 (s. n. r., 1H-C₍₅₎), 7.42 (s. n. r., 1H-C₍₄₎), 4.19 (t, 2H-C₍₇₎), 3.88 (s, 3H-C₍₆₎), 1.84 (m, 2H-C₍₈₎), 1.31 (m, 2H-C₍₉₎), 0.91 (t, 2H-C₍₁₀₎). ¹³C NMR: (500 MHz, D₂O, δ in ppm) 135.79 (C₍₂₎), 123.42 (C₍₄₎), 122.17 (C₍₅₎), 49.24 (C₍₇₎), 35.57 (C₍₆₎), 31.22 (C₍₈₎), 18.70 (C₍₉₎), 12.57 (C₍₁₀₎).

1-Etyl-3-methylimidazolium chloride (EMIMCl) was purchased from Aldrich (Purity 98%) and was used as received. ¹H NMR: (500 MHz, D₂O, δ in ppm) 8.70 (s, 1H-C₍₂₎), 7.48 (d, 1H-C₍₅₎, *J* = 1.8 Hz), 7.41 (d, 1H-C₍₄₎, *J* = 1.8 Hz), 4.23 (q, 2H-C₍₇₎), 3.88 (s, 3H-C₍₆₎), 1.49 (t, 3H-C₍₈₎). ¹³C NMR: (500 MHz, D₂O, δ in ppm) 135.48 (C₍₂₎), 123.39 (C₍₄₎), 121.81 (C₍₅₎), 44.73 (C₍₇₎), 35.55 (C₍₆₎), 14.45 (C₍₈₎).

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, Dorex 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. ¹H NMR: (500 MHz, D₂O, δ in ppm) 8.64 (s, 1H-C₍₂₎), 7.41 (s, 2H-C₍₄₋₅₎), 3.88 (s, 6H-C₍₆₋₇₎). ¹³C NMR: (500 MHz, D₂O, δ in ppm) 136.49 (C₍₂₎), 123.35 (C₍₄₋₅₎), 35.57 (C₍₆₋₇₎). The Scheme 1 shows the chemical structures of three ionic liquids used for the experiments.

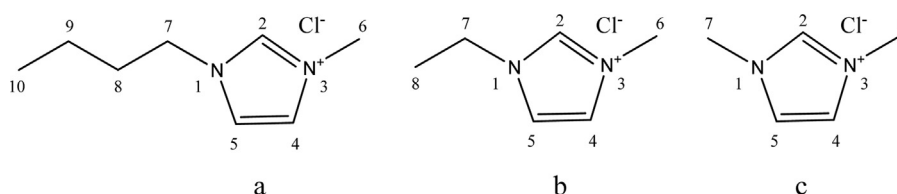
Deionized water (18 MΩ × cm), used for solution preparation, was obtained from a Milli-Q system. Water solutions of ILs were prepared by weighing, one hour before irradiation experiments. Studies were carried out under normal atmospheric air conditions, since control experiments performed under CO₂ and N₂ atmospheres did not show different results, compared with the former ones.

2.2. UV irradiation

A deuterium lamp (Oriel 6316 STD D₂-30W) 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/cm², 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*_{n,p} = 17 μEinstein m⁻² s⁻¹. The irradiation spot was large enough (~1 cm²) 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.

subsequent chemical characterization of the main photoreaction products. Pure water and diluted acidic solutions were tested as mobile phases, in order to find the best experimental run conditions. The diluted acidic solutions were finally preferred because they yield the chromatograms with the narrowest peaks.

Equipment 1 was a Shimadzu 2020 LC-PDA-ESI-MS instrument. ESI was in positive mode under the following conditions: scan range $15 < m/z < 1000$; ESI voltage 2.5 kV; desolvation line (DL) temperature 100°C ; heated block temperature 200°C ; DL voltage +80 V; Q-array DC voltage +10 V; Q-array RF voltage 60 V; nebulizing gas flow rate 1.5 L/min; drying gas flow rate 18 L/min. Chromatographic and PDA conditions were: Gemini-NX C-18 column (Phenomenex), $3\ \mu\text{m}$, $150 \times 4.6\ \text{mm}$; column temperature 25°C ; PDA range 200–350 nm; PDA flow-cell temperature 25°C ; injection volume $20\ \mu\text{L}$. A flow rate of 1 mL/min was established with a flow reduction down to 0.2 mL/min at the ESI entrance. A washing step with methanol was included between runs.

Equipment 2 was a Bruker micrOTOF-Q instrument. ESI was operated in positive mode under the following conditions: scan range $50 < m/z < 950$; capillary voltage 4.5 kV; end plate offset $-500\ \text{V}$; collision cell RF 100.0 VPP, nebulizing gas pressure 3.5 bar; drying heater temperature 200°C ; drying gas flow rate 7 L/min. Chromatographic and PDA conditions were: Luna C-18 column (Phenomenex), $3\ \mu\text{m}$, $100 \times 2\ \text{mm}$; injection volume $10\ \mu\text{L}$; column temperature 25°C ; PDA range 200–350 nm; PDA flow-cell temperature 25°C . Elution with 0.1% aqueous formic acid was employed at a flow rate of 0.2 mL/min; a linear solvent program for methanol to clean the column was as follows: 0 min 5%, 6 min 30%, 12 min 55%, 18 min 80%, 20 min 5%.

Equipment 3 was used to separate the photoproducts to be used in the subsequent ^1H NMR and HSQC measurements. It consisted of a Gemini-NX C-18 column (Phenomenex), $3\ \mu\text{m}$, $150 \times 4.6\ \text{mm}$, a binary pump (Thermo Spectra series P200, USA), a UV-vis detector (Thermo UV 100, USA) set at 220 nm, and a manual valve (Rheodyne 2895, USA) for fraction collection. Elution was carried out isocratically with 0.0025% acetic acid/water mixture at a flow rate of 1 mL/min. A washing step with methanol was included between runs.

To separate and characterize the main reaction products, $\sim 1 \times 10^{-4}\ \text{M}$ of BMIMCl, EMIMCl and MMIMCl water solutions were irradiated during 1 h and injected into equipments 1 and 2.

For the NMR measurements, $1 \times 10^{-2}\ \text{M}$ ImILs solutions in either D_2O or H_2O were irradiated during 22 h and injected into equipment 3. Different elution volumes per run were collected for the narrower peaks corresponding to reactant and products. The collected fractions were frozen, freeze-dried and re-dissolved in 0.6 mL of D_2O for NMR measurements.

NMR spectra were recorded on a Bruker Avance II 500, using D_2O and water/ D_2O as solvents. Measurements include ^1H NMR, ^{13}C NMR, COSY, HSQC and NOESY experiments.

3. Results and discussion

3.1. Separation of photoproducts from the reaction media

BMIMCl, EMIMCl and MMIMCl aqueous solutions were exposed to UV radiation. The irradiated solutions were injected into a HPLC-PDA-ESI-MS (see Section 2.3 for details). Fig. 1 shows the chromatograms of the three irradiated solutions, obtained by monitoring the UV absorption at two different wavelengths: (i) at 211 nm, where the imidazolium cation has an absorption maximum and, (ii) at 230 nm, where the imidazolium cation does not appreciably absorb. The figure also includes the mass spectra at some selected retention times.

BMIM⁺ chromatogram (Fig. 1a) shows three well-resolved peaks at 3.96, 4.53 and 5.32 min. The peak at 5.32 min is associated with a mass spectrum containing a single signal at $m/z = 139^+$. This peak is assigned to unreacted BMIM⁺, as it was confirmed by independent runs performed with non-irradiated solutions of pure ILs. In the same chromatogram two peaks are observed at shorter retention times, 3.96 and 4.53 min. The mass spectra associated with both peaks show single signals at $m/z = 157^+$. The differences observed in: (i) the retention times, (ii) the m/z ratios and (iii) the absorption characteristics of these compounds compared with the reactants, clearly indicate the presence and the effective separation of, at least, two photoreaction products.

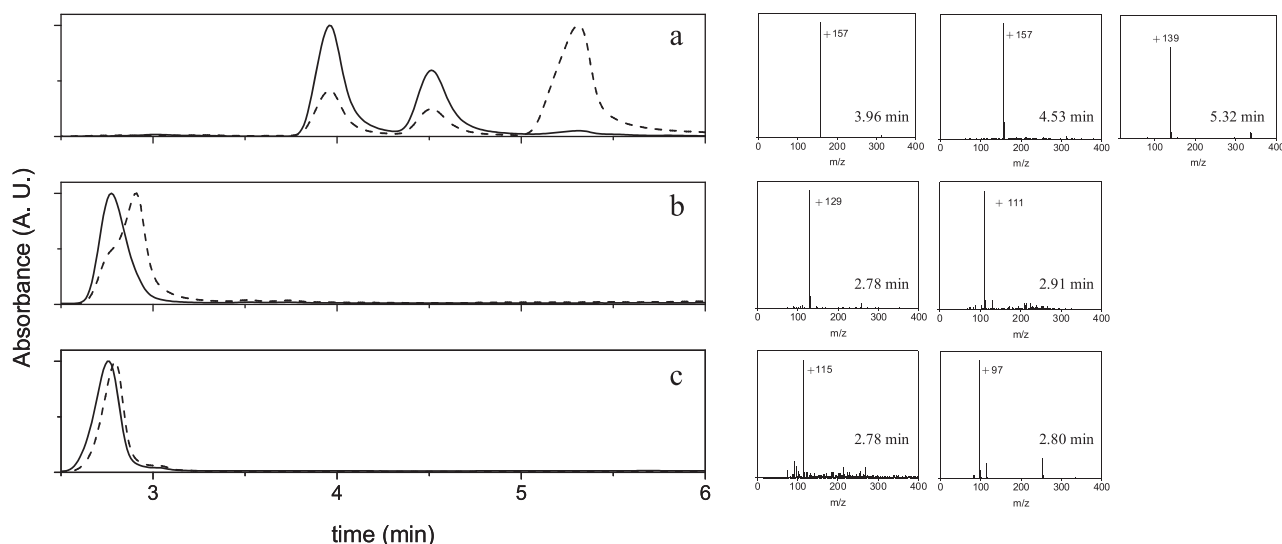


Fig. 1. HPLC chromatograms of irradiated solutions of: (a) BMIMCl, (b) EMIMCl and, (c) MMIMCl, obtained in a C18 column. The detection was performed at 211 nm, where the imidazolium cation has an absorption maximum (dashed line) and at 230 nm where the imidazolium cation does not appreciably absorb (full line). Mass spectra were obtained at the selected retention times in the chromatogram.

EMIM⁺ chromatogram (Fig. 1b) shows similar features, although with less resolved peaks. At $t = 2.91$ min a peak with an associated mass of $m/z = 111^+$ is found. This peak corresponds to unreacted EMIM⁺. The shorter retention time of EMIM⁺ in C18 column compared to BMIM⁺ is consistent with the shorter ethyl chain that confers a major polarity to the reactant. In the same figure, a peak at 2.78 min with a mass spectrum showing a single signal at $m/z = 129^+$ is also observed. This signal confirms the presence of, at least, one reaction product.

Finally, MMIM⁺ chromatogram is presented in Fig. 1c. It can be observed a peak at 2.80 min associated to a mass spectrum with a single signal at $m/z = 97^+$ that corresponds to MMIM⁺. This reagent exhibits the shortest retention time of the three methylimidazolium cations, since the presence of a methyl group turns it into the reagent with highest polarity. As in the two previous cases, the presence of a peak with a shorter retention time than the reactive, at 2.78 min, is also observed. This feature is associated to a mass spectrum with a single signal at $m/z = 115^+$.

In the three cases, the retention times of products are always less than those of the corresponding reagents. Furthermore, the m/z ratio of the products is related to that of the reactants according to the following simple expression: $m/z_{\text{prod}} = m/z_{\text{react}} + 18$, suggesting the

addition of a water molecule to the reactant. Considering that the relationship between the isotopic abundances of Cl³⁷ and Cl³⁵ is $24.23/75.77 \approx 1/3$, the absence of mass signals at $[(m/z) + 2]$ in the mass spectra (positive mode) of the irradiated samples provides clear evidence of the absence of chlorine atoms in the photoproducts of the reaction. On the other hand, the high resolution mass spectra of the products reveals molecular formulas of the type $C_5H_{11}N_2O-(CH_2)_n^+$ with $n = 0, 1$ or 3 for MMIM⁺, EMIM⁺ and BMIM⁺ respectively, confirming the addition of a water molecule to each methylimidazolium reactant. The incorporation of an oxygen functional group leads to products with higher polarities than reactants and justifies the lower retention times observed in the chromatograms.

Table 1 summarizes the main characteristics of reactants and products: retention times, m/z ratios, molecular formulas and UV spectra. It is remarkable that all products show similar UV spectra with absorption maxima around 230 nm. In particular, the two products of BMIM⁺ photolysis have the same absorption spectra. These photoproducts absorption spectra, in turn, present different absorption bands than reagents, which show absorption maxima around 210 nm. The addition of water has a significant effect on the chromophoric unit of the original reactant.

Table 1
HPLC retention times, m/z ratios, molecular formulas and UV spectra of reactants and products.

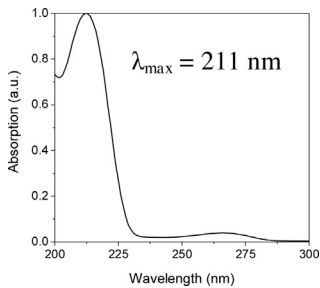
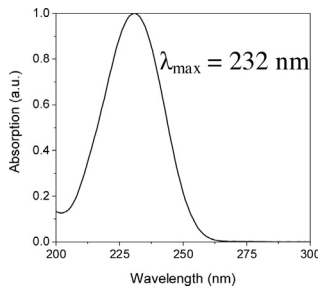
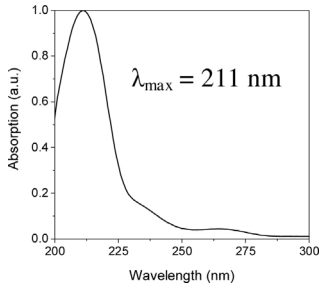
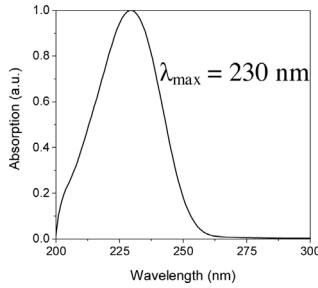
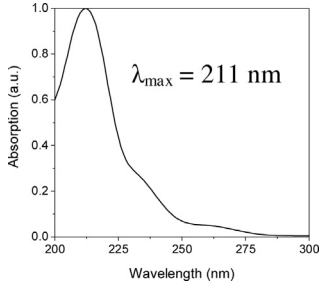
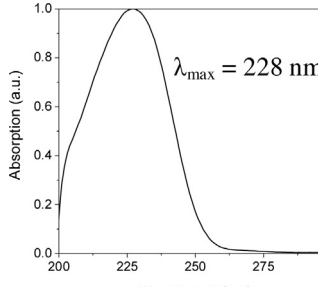
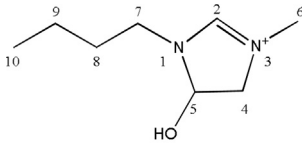
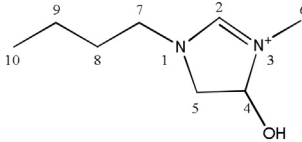
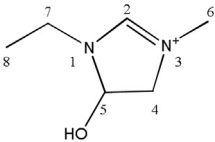
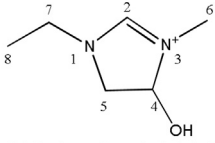
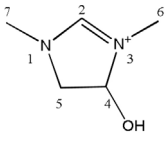
Reactant			Product		
R_t /min	m/z molecular formula	Absorption spectrum	R_t /min	m/z molecular formula	Absorption spectrum
5.32	139.123 $C_8H_{15}N_2^+$		3.96	157.134	
			4.53	157.134	
2.91	111.092 $C_6H_{11}N_2^+$		2.78	129.102	
			2.78	129.102	
2.80	97.076 $C_5H_9N_2^+$		2.78	115.087 $C_5H_{11}N_2O^+$	

Table 2
Chemical structures and ^1H NMR and ^{13}C NMR signals of the photoreaction products.

Molecule	^1H RMN			^{13}C from HSQC	
	Atom	Signal type	δ	Atom	δ
 1-butyl-5-hydroxy-3-methyl-4,5-dihydro-imidazolium	H-C(2)	s	8.20	C(2)	156.53
	H-C(5)	dd ($J=4$ and 9)	5.74	C(5)	83.11
	H-C(4)	dd ($J=9$ and 14)	4.09	C(4)	57.53
	H-C(4)	dd ($J=4$ and 14)	3.69	C(6)	34.32
	H ₃ -C(6)	s	3.20	C(7)	44.14
	H ₂ -C(7)	t ($J=7$)	3.52	C(8)	29.34
	H ₂ -C(8)	q ($J=7$)	1.66	C(9)	18.98
	H ₂ -C(9)	sex ($J=7$)	1.33	C(10)	12.75
	H ₃ -C(10)	t ($J=7$)	0.91		
 1-butyl-4-hydroxy-3-methyl-4,5-dihydro-imidazolium	H-C(2)	s	8.20	C(2)	156.45
	H-C(4)	dd ($J=4$ and 9)	5.65	C(4)	84.13
	H-C(5)	dd ($J=9$ and 14)	4.11	C(5)	55.52
	H-C(5)	dd ($J=4$ and 14)	3.72	C(6)	31.59
	H ₃ -C(6)	s	3.18	C(7)	47.73
	H ₂ -C(7)	t ($J=7$)	3.53	C(8)	28.53
	H ₂ -C(8)	q ($J=7$)	1.64	C(9)	19.01
	H ₂ -C(9)	sex ($J=7$)	1.32	C(10)	12.75
	H ₃ -C(10)	t ($J=7$)	0.91		
 1-ethyl-5-hydroxy-3-methyl-4,5-dihydro-imidazolium	H-C(2)	s	8.10	C(2)	156.16
	H-C(5)	dd ($J=4$ and 9)	5.66	C(5)	83.04
	H-C(4)	dd ($J=9$ and 14)	3.99	C(4)	57.60
	H-C(4)	dd ($J=4$ and 14)	3.59	C(6)	34.25
	H ₃ -C(6)	s	3.11	C(7)	43.09
	H ₂ -C(7)	q ($J=7$)	3.46	C(8)	12.84
	H ₃ -C(8)	t ($J=7$)	1.20		
 1-ethyl-4-hydroxy-3-methyl-4,5-dihydro-imidazolium	H-C(2)	s	8.09	C(2)	156.16
	H-C(4)	dd ($J=4$ and 9)	5.55	C(5)	55.39
	H-C(5)	dd ($J=9$ and 14)	4.02	C(4)	84.20
	H-C(5)	dd ($J=4$ and 14)	3.62	C(6)	31.98
	H ₃ -C(6)	s	3.08	C(7)	45.08
	H ₂ -C(7)	q ($J=7$)	3.38	C(8)	12.12
	H ₃ -C(8)	t ($J=7$)	1.18		
 4-hydroxy-1,3-dimethyl-4,5-dihydro-imidazolium	H-C(2)	s	8.03	C(2)	157.07
	H-C(5)	dd ($J=4$ and 14)	3.59	C(4)	84.41
	H-C(5)	dd ($J=9$ and 14)	3.99	C(5)	57.52
	H-C(4)	dd ($J=4$ and 9)	5.55	C(6)	30.48
	H ₃ -C(6)	s	3.08	C(7)	34.25
	H ₃ -C(7)	s	3.10		

3.2. Chemical structures of photoproducts

The products of the three photoreactions were separated from each reaction medium by HPLC. Once isolated, they were frozen, freeze-dried and analyzed by single and multidimensional NMR (see Section 2.3 for details).

In the case of BMIM⁺, one product was isolated from each chromatogram peak. The chemical structures of these products were obtained by combining information provided by mass and NMR spectra, including isotopic substitution experiments (*vide infra*). Unfortunately, the peaks in EMIM⁺ and MMIM⁺ chromatograms could not be properly resolved; in particular, the product peak in the case of EMIM⁺ stands an unresolved peak. Nevertheless, in the latter case, the NMR spectra can be understood as a combination of just two products structurally similar to those obtained in the BMIM⁺ photolysis.

^1H NMR spectra of the products show clear differences when compared to reactants. In particular, it is noticeable the simultaneous disappearance of the signals corresponding to the hydrogens located at positions 4 and 5 of the imidazolium ring and the growth of three new hydrogen signals with gem, syn and anti coupling between 3.6 and 5.8 ppm. These features imply that the hydroxyl and proton additions take place at either positions 4 (next to the methyl group) or 5 (next to the alkyl chain) on the imidazolium ring, leading to two positional isomers. Table 2 summarizes the NMR signals and the proposed chemical structures of the products.

Once the spectra of the reaction products were identified, the next step in the analysis involved the consideration of coupling signals in NOESY spectra, in order to assign NMR spectra to each positional isomer. As an example, the particular case of EMIM⁺ will be analyzed, although similar considerations apply for the case of BMIM⁺. Fig. 2 shows a selected region of NOESY spectrum of EMIM⁺

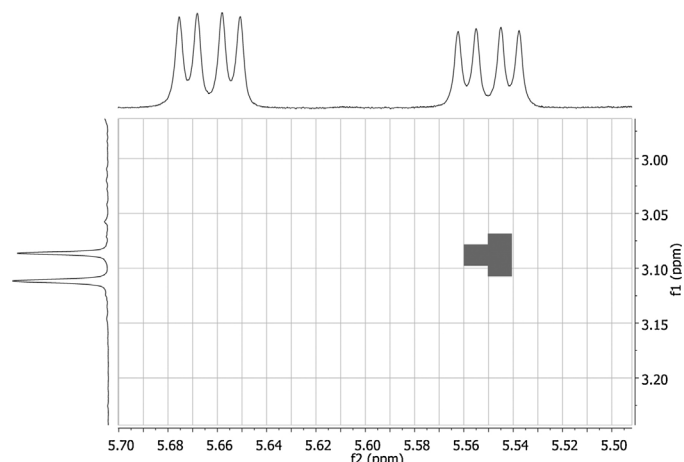


Fig. 2. Selected region of NOESY spectrum of EMIMCl irradiation products.

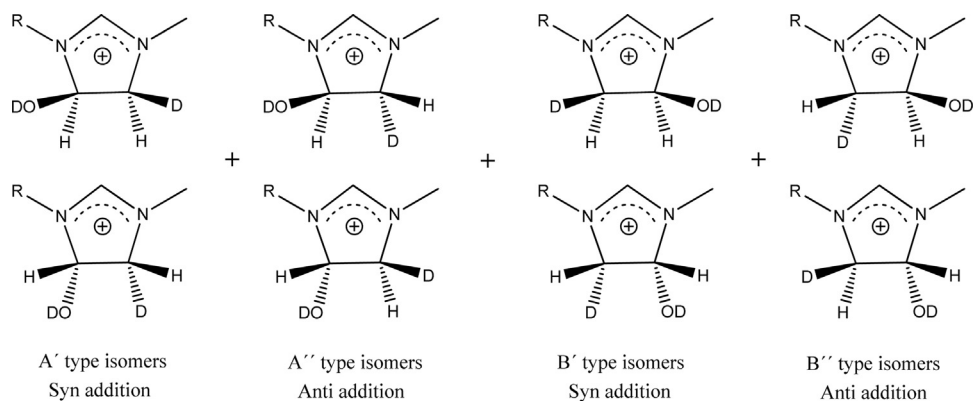
products. It can be seen that the signal of the hydrogen located at the hydroxylated carbon (5.55 ppm) couples to those of hydrogens at methyl position (3.08 ppm) only for the isomer that show hydroxyl addition to C4 position. Thereby, it was possible to assign each spectrum with their respective isomer.

To facilitate the following discussion, it will be useful to denote the isomers with the hydroxyl group at the position 5 as of the “A” type, whereas those with the hydroxyl group at the position 4 as of the “B” type. A/B ratios are far from unit for the Bmim⁺ and Emim⁺ reactions, whereas the symmetry of the MMIM⁺ cation precludes the existence of two positional isomers. This magnitude can be calculated in each case by integrating ¹H NMR signals of the reaction mixtures corresponding to the hydrogens at position 5 in A isomers and at position 4 in B isomers. The calculations yield A/B = 1.50 and A/B = 1.12 ratios for R = Butyl and R = Ethyl products respectively. In all cases, A isomers are more abundant, suggesting that the addition is not driven by steric effects. As such, it may be possible that the stability of an eventual intermediate dictates the position of the substitution, but further experiment should be performed in order to confirm this hypothesis.

The analysis of ¹H NMR spectra of the reaction mixtures before and after irradiation shows that the total number of hydrogen atoms in A and B isomers accounts approximately for half the number of imidazolium hydrogens that have reacted—which are roughly estimated in ~25 % of the total reactant—(data non

shown). Consequently, the products formed by addition of water to the imidazolium ring constitute about 50% of the total products and, evidently, represent the principal reaction products. The existence of other reaction products with very high retention times in HPLC experiments has also been observed. Additional irradiation experiments were performed on aqueous solutions of HPLC isolated A and B isomers, in order to evaluate the hypothesis that these unidentified products could derive from further photodegradation of the hydroxylated products. The results of these experiments showed that no photochemical degradation was observed for these compounds, at least at the irradiation wavelengths at which they absorb. These results confirm that unidentified compounds are originated from the direct irradiation of imidazolium cations in aqueous solution. The separation and chemical characterization of these photoproducts, due to their lower concentration and complex structure, deserve a separate treatment that is beyond the scope of this paper.

Since the chloride anions are not present as part of the photoproducts, an interesting question arises concerning whether they might intervene at any stage in the reaction. The absorption spectrum of the chloride anion in aqueous solution shows a maximum in 175 nm ($\epsilon_{\lambda=175\text{nm}} = 160 \text{ M}^{-1} \text{ cm}^{-1}$) extending up to 190 nm [32]. In the experiments performed on diluted solutions with a narrow bandwidth excitation of $211 \pm 1 \text{ nm}$, the fraction of light absorbed by this species is negligible compared to the one of



Scheme 2. Different isomers feasible to be obtained by irradiation of unsymmetrical methylimidazolium cations in D₂O.

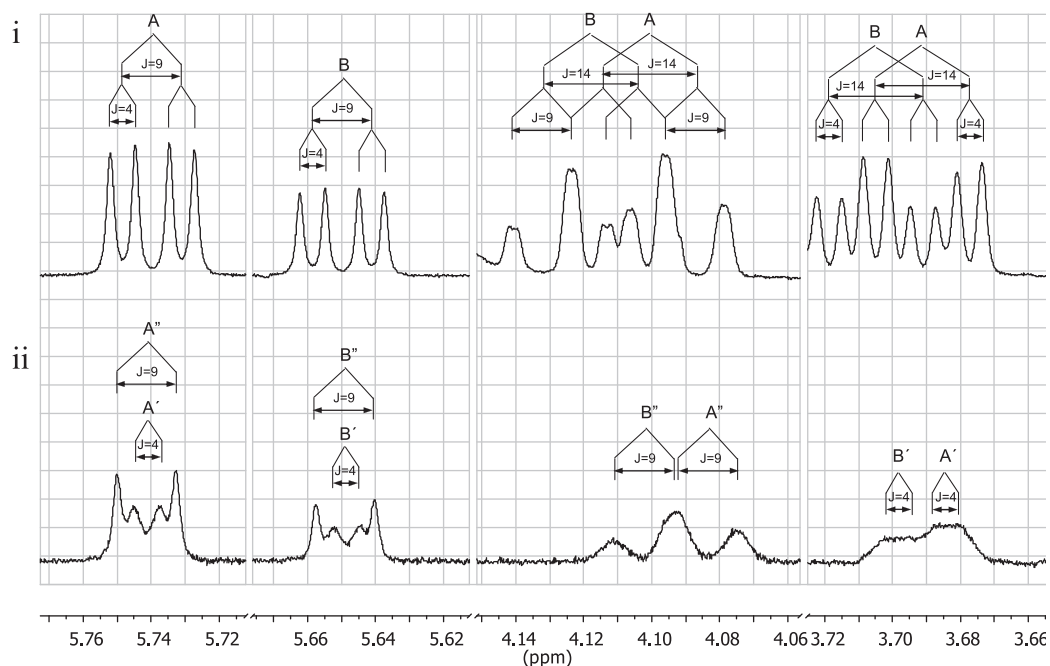


Fig. 3. ^1H NMR signals of the hydrogens located at positions 4 and 5 of the BMIM^+ photoreaction products in: (i) aqueous solution, (ii) D_2O solution.

the imidazolium cations. In order to experimentally confirm that chloride anions do not play any relevant role in the reaction, additional irradiation experiments were performed by adding NaCl to diluted solutions of BMIMCl. No differences in the formation of the photoproducts were observed for different chloride concentrations.

The same line of reasoning used for the chloride case can be applied to the hydroxyl anion. The molar absorption coefficient of the hydroxyl anion at 211 nm is $\sim 300 \text{ M}^{-1} \text{ cm}^{-1}$ [33]. In neutral solutions, the lower concentration of hydroxyl ions makes the fraction of light absorbed by this specie at 211 nm also negligible. Experiments performed by adding NaOH to BMIMCl solutions do not show changes in the formation of photoproducts.

3.3. Stereochemistry of the photoreaction

In order to study the stereochemistry of the photoreaction, isotopic substitution experiments were performed by irradiating methylimidazolium cations in D_2O . The reaction of unsymmetrical methylimidazolium cations in D_2O yields eight different isomers, some of them indistinguishable by conventional ^1H NMR spectroscopy. Scheme 2 shows the chemical structures of these isomers. The two A isomers exhibiting *syn* addition are indistinguishable by ^1H NMR because they are enantiomers, and will be referred hereinafter as A' . On the other hand, the two A isomers showing *anti* addition are also enantiomers and will be referred as AA' and A'' isomers are diastereoisomers. A similar description

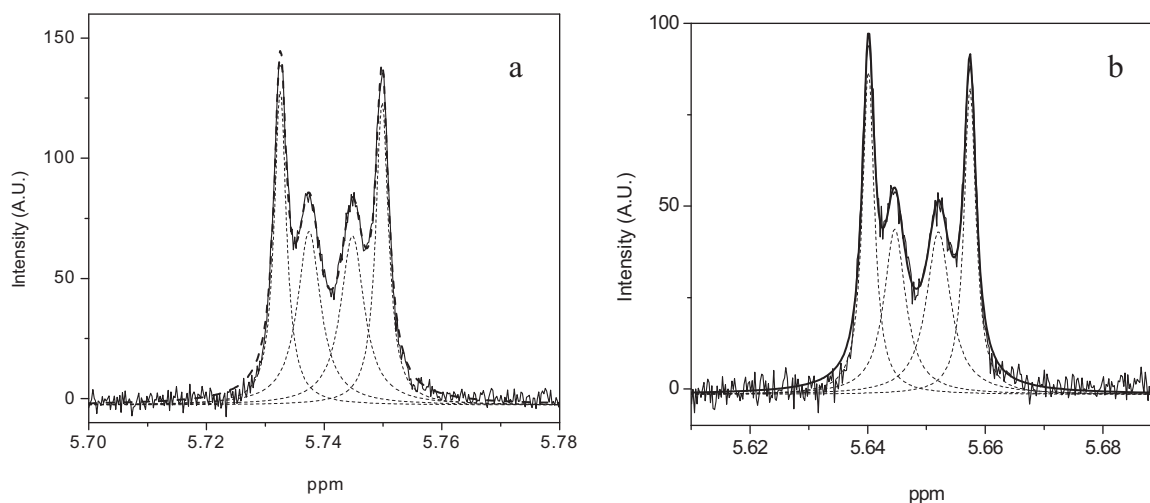


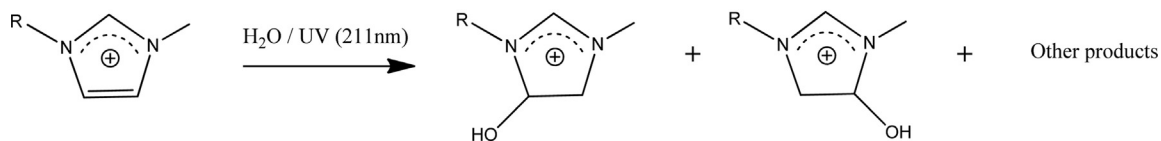
Fig. 4. ^1H NMR signals of hydrogens at position: (a) C5 for A-type isomer and, (b) C4 for B-type isomer, obtained by irradiation of a D_2O solution of BMIMCl at 211 nm. The dotted lines represent the Lorentzian functions used for the convolution and the dashed line indicates the sum of all contributions.

Table 3

Peak position and Lorentzian functions areas used for the reproduction of the ^1H NMR spectra of the hydrogens at the positions: (a) C5 for A-type isomer and, (b) C4 for B-type isomer, obtained by irradiation of D_2O solution of BMIM^+ at 211 nm.

Type-A isomers			Type-B isomers		
Lorentzian	Area	Center	Lorentzian	Area	Center
1	0.51	5.732	1	0.34	5.640
2	0.54	5.737	2	0.31	5.645
3	0.53	5.745	3	0.34	5.652
4	0.52	5.750	4	0.32	5.657

applies for B isomers. The two B isomers with addition *syn* will be referred to as B' , while the two B isomers with addition *anti* will be



Scheme 3. Photochemical reaction of methylimidazole cations in aqueous solution under UV-C radiation.

referred to as B'' . The following analysis, performed for stereochemistry characterization of the photoreactions, was carried out on NMR spectra of reaction mixtures instead of NMR of individual compounds since they provide extra information about A'/A'' and B'/B'' ratios, as will be shown in the next paragraphs.

Fig. 3 shows ^1H NMR signals related with the two products of the BMIM^+ photoreaction in: (i) aqueous solution and, (ii) D_2O solution. In each case, the selected signals correspond to hydrogens at positions 4 and 5: three for A isomers and three for B isomers. The hydrogen signals of the products obtained in water show three different coupling constants: $J_{\text{gem}} = 14$, $J_{\text{cis}} = 9$ and $J_{\text{trans}} = 4$. On the other hand, the signals of the products obtained in D_2O show the disappearance of the large ^1H - ^1H *gem* coupling ($J_{\text{gem}} = 14$). The absence of this coupling confirms that the addition of deuterium atom always occurs on the carbon that is not hydroxylated. In other words, the results indicate that the addition of D and OD never takes place at the same carbon.

Although small shifts and widening are evident—most likely as a result from hydrogen and deuterium coupling—none of the above mentioned signals fully disappear. It is note that if the addition had proceeded completely either in a *syn* or *anti* manner, some of the signals of the hydrogens attached to un-hydroxylated carbon in the aqueous mixture (C4 for A isomer or C5 for B isomer) should have disappeared. The fact that this is not observed indicates that the addition does not occur exclusively with a *syn* or *anti* stereochemistry, but proceeds in the two ways simultaneously.

The signal at 5.74 in Fig. 3ii can be interpreted as a sum of the two signals corresponding to *syn* and *anti* additions. The different dihedral angles in each isomer yield different coupling constants— $J_{\text{cis}} = 9$ and $J_{\text{trans}} = 4$ —[34], leading to two distinguishable doublets. As such, it is possible to quantitatively measure the relative abundance of *syn* and *anti* additions by evaluating the contribution of each doublet signal to the total signal intensity. The same line of reasoning can be applied for the signal at 5.65 ppm. Fig. 4 shows the decomposition of these signals as a sum of several Lorentzian functions. The corresponding maxima and areas of each curve are listed in Table 3. It is noteworthy that the areas of the four functions are similar, indicating that both diastereoisomers contribute to the total intensity in equal form. This result reveals

the presence of *syn* and *anti* additions in equal proportions, suggesting that the reaction proceeds in an unconcerted fashion.

Spectral analysis of the mixtures obtained by irradiation of EMIMCl and MMIMCl in D_2O shows similar results (data not shown), indicating the formation of diastereoisomers in the same proportion for all cases.

4. Conclusions

In this work, photochemical reactions of methylimidazolium cations induced by UV-C radiation in aqueous solution have been investigated. The main result can be summarized by the following reaction Scheme 3:

The principal products of the photochemical reaction are the result of the chemical addition of a proton and a hydroxyl group to

the imidazolium ring, which comprise $\sim 50\%$ of the total reaction products. The addition of the hydroxyl group takes place either at positions 4 or 5 of the imidazolium ring, leading the formation of two positional isomers. For MMIM^+ only one substitution product is obtained, due to the symmetry of the molecular ion. The ratios between isomer populations depend on the lengths of the alkyl chains bonded to the nitrogen atoms. The most abundant isomers correspond to those that show the addition of the hydroxyl group at the ring side having the longer alkyl substituent.

Results from experiments performed in D_2O solutions reveal that the addition of hydrogen and hydroxyl group: (i) takes place at different carbon atoms on the imidazolium ring and, (ii) produce equal amounts of *syn* and *anti* additions.

The formation of diastereoisomers at equal proportions could be a strong indication that the reaction does not proceed via a mechanism that involves a single step. In principle, a concerted attack on the double bond should promote a preferential *syn* or *anti* addition. As such, further experiments should be performed in the future to establish the mechanism of the photochemical reaction.

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