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Characterization of the ionic liquid obtained by chlorosulfonation of 1-methylimidazole: 1-methyl-3-sulfonic acid imidazolium chloride, 1-methylimidazolium chlorosulfate or a zwitterionic salt?

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ABSTRACT

A great number of organic reactions catalyzed by the ionic liquid product of chlorosulfonation of 1-methylimidazole have been reported recently. At the same time controversial assumptions have appeared on the real structure of the catalyst. In the present report the primarily formed chlorosulfonation product is proved to be 1-methylimidazolium chlorosulfate ($[HMim]^+[SO_3Cl]^-$) instead of 1-methyl-3-sulfonic acid imidazolium chloride, reported previously. The former structure is confirmed by X-ray crystallography and NMR spectroscopy, including ^{1}H-, ^{13}C-, ^{17}O- and ^{15}N–^{1}H HSQC measurements. ^{1}H and ^{17}O NMR experiments support fast hydrolysis of [HMim] $[SO_3Cl]$ resulting in the formation of $[HMim][HSO_4]$ in the presence of traces of water.

1. Introduction

Acid-catalyzed reactions involve one of the most important technologies applied in the chemical industry. The most common catalysts are mineral acids, used in homogeneous phase reactions. Although they usually show high catalytic activity, they often suffer from some drawbacks, such as the problems of side reactions, large amounts of acidic wastes and corrosion of the equipment. Isolation of the products can also be tedious, which can cause environmental problems. As a result, great efforts have been devoted to the development of new catalysts. One possibility is the application of solid acids which, as non-volatile materials, are less harmful than traditional liquid acids [1]. However, these heterogeneous systems often show an inferior activity when compared to their homogeneous counterpart. As another approach, increasing attention has been paid to the application of task specific ionic liquids as catalysts [2]. Especially acidic ionic liquids were found to be useful and even recyclable alternatives to conventional Brønsted or Lewis acid catalysts [3]. Among them, ionic liquids (ILs) incorporating imidazolium cations with *N*-alkyl sulfonic groups serve as efficient Brønsted acids in a great variety of organic transformations [4]. Furthermore, they can be converted into $–SO_3H$ functionalized dual Brønsted–Lewis acidic ILs possessing complex metal halide anions as the Lewis acidic site [5]. The first example for a Brønsted acidic IL with an SO_3H moiety attached directly to imidazolium nitrogen, 1-methyl-3-sulfonic acid imidazolium chloride ([MSim]Cl, **1**, Fig. 1), was reported by Zolfigol et al. in 2010 [6]. Since then, the catalytic activity of ILs incorporating the $[Msim]^+$ cation (**1**) and different anions [7] was tested in a wide range of organic reactions. At the same time, no detailed structural data are available for these compounds. Only ^{1}H and ^{13}C NMR spectra were reported [6] that do not give sufficient information about the position of the SO_3 moiety. Recently, Shiflett et al. found that chlorosulfonation of 1-methylimidazole led to a mixture of two compounds, an overall neutral zwitterion (**2**) as the main product and another derivative that was claimed to be **1** [8]. The formation of the former was proved by crystallography but beyond that only ^{1}H and ^{13}C spectra of the mixture of the two compounds were presented. Based on ^{1}H NMR data, it was supposed that compound **2** could be converted to **1** when an equimolar amount of HCl was added [8]. It should also be mentioned that Zolfigol described the product as a viscous oil [6] while the other group obtained a solid material and they recorded a melting point of 325.8 °C for the zwitterionic component **2** [8].

As part of our ongoing interest in the application of acidic IL catalysts in ring opening of epoxides [9] as well as oligomerization of alkenes [10], we decided to explore the activity of ILs with N-SO_3H moieties. Before that the clarification of the somewhat contradictory results seemed to be necessary that prompted us to carry out a more detailed investigation of the chlorosulfonation product of 1-methylimidazole.

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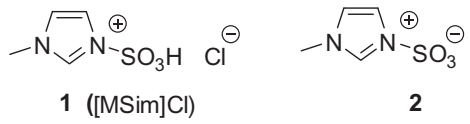


1 ([MSim]Cl) 2

Fig. 1. The stucture of the product of chlorosulfonation of 1-methylimidazole, suggested by Zolfigol et al. [6] ([MSim]Cl, **1**) and the zwitterionic structure **2** reported by Shiflett et al. [8].

2. Experimental

2.1. Computational methods

Theoretical calculations were performed with the Gaussian 09 software package [11]. Molecular geometries were optimized using the long-range corrected hybrid density functional CAM-B3LYP [12]and the standard 6–311++G** basis set. The optimizations were performed without any symmetry constraint. The vibrational analysis yielded no imaginary frequencies verifying that each of the optimized structures is a true minimum on the potential energy surface. The Gibbs free energies were refined using the CPCM solvent model (with Solvent=dichloromethane) built in the Gaussian 09 suite.

2.2. Synthetic methods

Chlorosulfonation of 1-methylimidazol was carried out based on the procedure reported by Zolfigol [6].

Method A: Chlorosulfonic acid (1.05 ml, 15.6 mmol) was added dropwise into a room temperature solution of 1-methylimidazole (1.2 ml, 15 mmol) in 150 ml dry CH_2Cl_2. The mixture was stirred overnight and then left to stand for one hour. After that the CH_2Cl_2 was decanted. The residue was washed with dry CH_2Cl_2 (3 × 50 ml) and dried in vacuum to obtain a viscous oil that solidified upon standing two weeks under strictly inert conditions.

Method B: Chlorosulfonic acid (1.05 ml, 15.6 mmol) was added dropwise into a cooled solution of 1-methylimidazole (1.2 ml, 15 mmol) in 150 ml dry CH_2Cl_2. The mixture was stirred for 20 min and left to stand a further 20 min to obtain a colorless solid precipitate. After that the CH_2Cl_2 was decanted. The residue was washed with dry CH_2Cl_2 (3 × 50 ml) and dried in vacuum.

[HMim][HSO_4] (**4**) was prepared by the reaction of 1-methylimidazole and H_2SO_4. Concentrated sulfuric acid (1.34 ml, 25.1 mmol) was added dropwise to 2 ml (25.1 mmol) 1-methylimidazole under vigorous stirring in an ice bath. After warming to room temperature it was stirred for 48 h and then was washed with 5 × 5 ml diethyl ether and was dried in vacuum at 70 °C for 10 h.

[HMim]Cl was prepared by the reaction of 1-methylimidazole and HCl. HCl was liberated from the reaction of NaCl and H_2SO_4 in a separated flask connected with the vessel containing 2 ml (25.1 mmol) 1-methylimidazole. The reaction mixture was stirred at room temperature overnight, then it was washed with 5 × 10 ml diethyl ether and was dried in vacuum at 60 °C for 10 h.

2.3. X-ray diffraction analysis

X-ray quality crystals of **3** were grown from the neat sample obtained by Method A upon standing. A suitable crystal was fixed onto a Mitegen loop using high density oil. Diffraction intensity data collection was carried out using a Bruker-D8 Venture diffractometer equipped with INCOATEC IμS 3.0 dual (Cu and Mo) sealed tube micro sources and Photon II Charge-Integrating Pixel Array detector using Mo Kα (λ = 0.71073 Å) radiation. Low temperature data collection (150 K) was applied to protect the sample from traces of moisture and also because of the low melting point. High multiplicity data collection and integration was performed using the APEX3 (Ver. 2017.3–0, Bruker AXS Inc., 2017.) software. Data reduction and multi-scan absorption correction was performed using SAINT (Ver. 8.38A, Bruker AXS Inc., 2017). The structure could be solved using direct methods and refined on F^2 using the SHELXL program [13] incorporated into APEX3 suite. Refinement was performed anisotropically for all non-hydrogen atoms. Hydrogen atoms were placed into geometric positions. The structure is stabilized by strong intermolecular N-H..O and weak C-H..O hydrogen bonds. The CIF file was manually edited using the publCIF software [14]. Results of X-ray diffraction structure determinations were very good according to the Checkcif of PLATON software [15] and structural parameters such as bond length and angle data are in the expected range. Further crystallographic and refinement details can be seen in the SI. Powder diffraction data were collected using the same instrument applying Cu Kα (λ = 1.54178 Å) radiation. Integration and background correction was performed with Bruker's DIFFRAC.EVA 4.2.2.3 software.

CCDC entry 2,023,770 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.4. NMR investigations

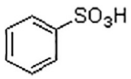
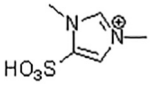
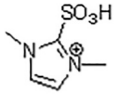
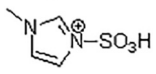
All NMR investigations were carried out on a Bruker Avance II 400 MHz spectrometer using a 5 mm BBO probe with temperature regulation. The relaxation delays applied were 1, 4 and 10 s for the ^1H, ^{13}C, and ^{15}N nuclei, respectively. The standard Bruker pulse sequences were used. 2–3000 scans were sufficient to record ^{17}O NMR spectra.

3. Results and discussion

3.1. Quantum chemical calculations

Acidities of some well-known acids and different sulfonated imidazolium ions were compared based on their dissociation free energies (Table 1). Sulfonation of imidazole derivatives is reported to take place in position four or five under usual conditions for electrophilic substitutions [16]. 2-Sulfonated imidazoles were prepared by oxidation of 2-substituted thiols [17]. These sulfonic acids were shown to exist mainly as zwitterionic compounds (Fig. 2) according to the crystallographic data [16,17]. In the present case however, the formation of a cationic species is supposed so data for the proposed [6] *N*-sulfonated

Table 1
Relative dissociation free energies for different acids in CH_2Cl_2 solvent.

Entry	AH	$\Delta G_{diss}\Delta G_{diss}$ [kJ/mol][a]
1	HCl	0
2	H_2SO_4	−34.2 (128.9)[b]
3	CF_3SO_3H	−59.4
4		−4.3
5		−80.6
6		−104.1
7		−126.7

[a] ΔG_{diss}- ΔG_{diss}(HCl).
[b] 2nd H^+ in parenthesis.

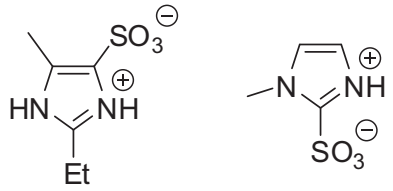


Fig. 2. Zwitterionic structures of sulfonated imidazoles [16,17].

Table 2
Gibbs free energy differences between **2** + HA and [MSim]A structures in dichloromethane[a].

Entry	Anion	ΔG [kJ/mol]
1	chloride	−85.8
2	hydrogensulfate	−75.4
3	triflate	−71.9

[a] G(**2**+HA) - G([MSim]+anion)

cation ([MSim]) (entry 7) as well as those for cationic C-4 (entry 5) and C-2 sulfonated derivatives (entry 6) were determined.

The dissociation free energies defined by eq. (1) were calculated using the cam-B3LYP density functional with the 6–311++G** basis set. The geometry optimisations and free energy calculations were performed using the conductor-like polarisable continuum model (CPCM) with CH_2Cl_2 solvent. The dissociation energy data, relative to HCl are summarized in Table 1. For the sulfonated imidazolium ions, the calculations gave surprisingly high energies (Table 1 entries 5–7) compared to the data of common acids. The value for the $[MSim]^+$ cation indicates much higher acidity of this structure than that of CF_3SO_3H.

$$AH \rightarrow A^- + H^+.$$

$$\Delta G_{diss} = G_{A-} + G_{H+} - G_{AH} \quad (1)$$

G_{A-}: Calculated Gibbs free energy for A^-.
G_{AH}: Calculated Gibbs free energy for AH.
GH_+: Gibbs free energy of H^+ ($G_{H+} = -26.28$ kJ/mol) [18]

Geometry optimizations were also performed for the *N*-sulfonated cation ($[MSim]^+$) in the presence of chloride, hydrogensulfate or triflate anions as well as for the deprotonated form (**2**) with the corresponding acid (Scheme 1, Table 2). In each case, the zwitterion **2** had much lower Gibbs free energy.

These results support the assumption that the equilibrium depicted in Scheme 1 is shifted considerably to the right side for Cl^-, HSO_4^- or OTf^- anions. That means that the *N*-sulfonated derivative may exist mainly in the zwitterionic form **2** similarly to other sulfonated derivatives (Fig. 2). In other words, hydrogen chloride is not a sufficiently strong acid to protonate zwitterion **2**, especially when they are present in equimolar amounts. It should be mentioned however that sulfuryl imidazolium salts, the ester derivatives of the proposed ILs [MSim]A, are known compounds and their synthesis and applications were reported before [19].

The presence of zwitterion **2** in the two component mixture was proved by Shiflett [8] but we felt that some more evidence was necessary to be certain about the structure of the other component. Accordingly, a more detailed investigation of the chlorosulfonation product of 1-methylimidazole was carried out. Besides the formation of the zwitterionic form **2**, a simple acid-base reaction leading to the $[HMim]^+$ cation (Scheme 2) was also taken into consideration. [HMim][SO_3Cl] (**3**) had been obtained before by the reaction of 1-methylimidazolium hydrogensulfate ([HMim][HSO_4], **4**) with $SOCl_2$ and was characterised by HRMS and ^1H NMR spectroscopy [20].

3.2. Preparation of ionic liquids

Chlorosulfonation of 1-methylimidazole was carried out based on the report of Zolfigol [6]. A careful addition of chlorosulfonic acid to the room temperature solution of 1-methylimidazole and stirring the mixture overnight (Method A) led to the formation of a highly viscous oil forming a separate phase. After the removal of the dichloromethane phase, the material solidified upon standing two weeks under strictly anhydrous conditions and even crystals suitable for X-ray investigations could be isolated. In another procedure, chlorosulfonic acid was added dropwise to a cooled solution of 1-methylimidazole in dichloromethane (Method B). In this case, a colorless solid precipitated almost immediately that was separated after stirring the mixture for 20 min.

3.3. X-ray measurements

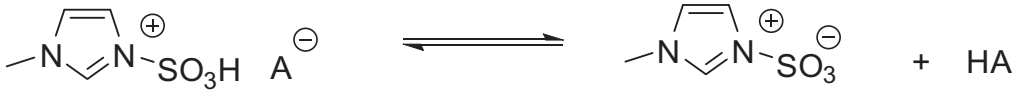
Crystals degraded rapidly upon warming so diffraction data had to be collected at low temperature (150 K). The compound crystallized in the $P2_{1/c}$ monoclinic space group. Crystallographic data are summarized in Table 3. The results revealed the formation of an imidazolium salt with a $ClSO_3^-$ anion: ([HMim][$ClSO_3$] (**3**) Scheme 2, Fig. 3). It should be mentioned that to the best of our knowledge, X-ray data for only two structures incorporating the $ClSO_3^-$ anion were reported before [21].

Comparison of the PXRD of the bulk sample shows that all the bulk crystalline material is the same as the single crystal salt structure **3** (Fig. S3).

3.4. NMR investigations

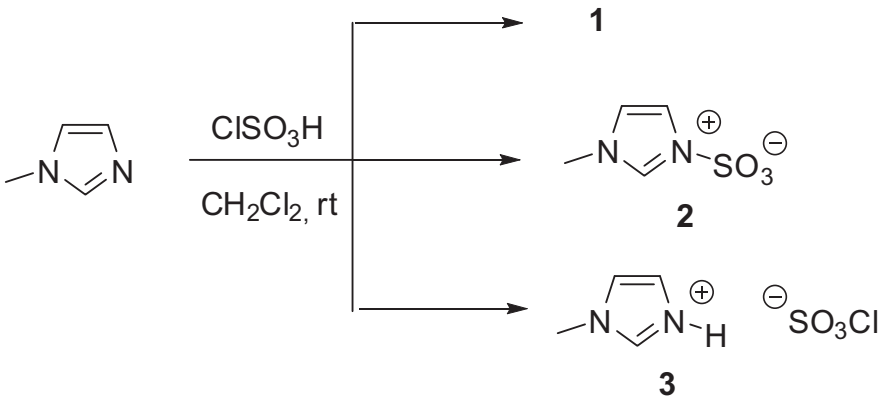
Next, detailed NMR investigations [22] of the materials obtained by the two different methods (A and B) were carried out.

NMR data of a freshly prepared neat sample of the ionic liquid obtained by Method A supported the X-ray structure and proved the formation of **3**. It is noteworthy that because of the peculiar properties, such as the extreme viscosity or high polarity or low melting point of the ionic liquids, recording and interpretation of spectra require special attention [23]. In the ^1H NMR spectrum of the neat sample (Fig. 4) a one-proton signal could be found at 12.7 ppm and three more with 1: 2: 3 integral ratios at 8.41 (2-H), 7.11 (4-H, 5-H), and 3.57 (N-CH_3)



2

Scheme 1. Possible deprotonation the *N*-sulfonated cation ($[MSim]^+$) in the presence of anions



Scheme 2. Possible products of the reaction of 1-methylimidazole with chlorosulfonic acid

ppm, respectively. Unlike the 4-H, 5-H proton signals, the corresponding carbons are clearly resolved in the $^{13}C\{^1H\}$ NMR spectrum (Fig. 5).

The high chemical shift of the NH proton (12.7 ppm) can be explained by the existence of a hydrogen bond between this proton and one of the oxygen atoms of the SO_3Cl^- anion in the neat sample, similarly to the solid structure (Fig. S2).

It should also be mentioned that another set of signals can be seen in the ^1H and $^{13}C\{^1H\}$ NMR spectra with a relative integral ratio of about 1/10 (Fig. 4) that shows the presence of some minor component(s).

The two nitrogens of the imidazole ring gave completely overlapping signals at 170.7 ppm in the inverse-gated $^{15}N\{^1H\}$ NMR spectrum (Fig. 6). It is important to notice that this experiment is not directly influenced by a protonation – deprotonation exchange [22]. pH-dependence of ^{15}N NMR shifts of 1-methylimidazole had been reported earlier [24]. While an approximately 80 ppm difference was observed between the $^{15}N_1$ and $^{15}N_3$ signals under basic conditions (corresponding to 1-methylimidazole), a single peak had been detected for the two nitrogens in acidic solutions at pH<5, where the 1-methylimidazolium cation is in excess. So the overlap of the signals in the present case, though somewhat unexpected, may provide another proof for the formation of the $[HMim]^+$ cation.

Table 3
Summary of crystallographic data for compound **3.**

Crystal data	
Chemical formula	$C_4H_7N_2 \cdot ClO_3S$
M_r	198.63
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	5.9038 (3), 18.0587 (11), 7.4778 (5)
β (°)	95.048 (2)
V (Å^3)	794.15 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.70
Crystal size (mm)	0.35 × 0.26 × 0.21
Data collection	
Diffractometer	Bruker D8 VENTURE
Absorption correction	Numerical *SADABS2016/2* - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.78, 0.87
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8179, 1487, 1427
R_{int}	0.019
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.139, 1.35
No. of reflections	1487
No. of parameters	102
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.96, −0.91

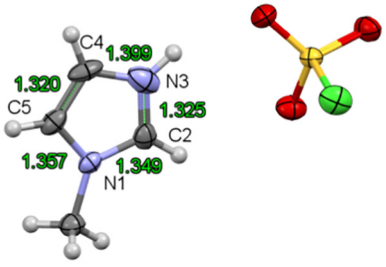


Fig. 3. X-ray structure of ionic liquid ([HMim][SO_3Cl] (**3**) with partial numbering scheme and selected bond distances. S-O distances are in the range of 1.433–1.439 Å.Thermal ellipsoids drawn at 50% probability.

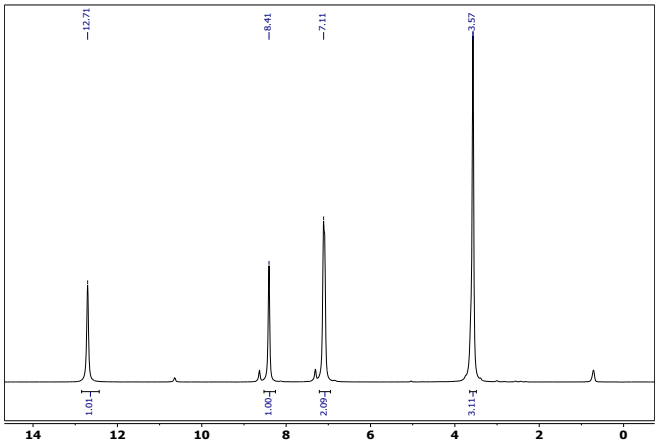


Fig. 4. ^1H-400 MHz NMR spectrum of a neat sample of compound **3** (obtained by Method A).

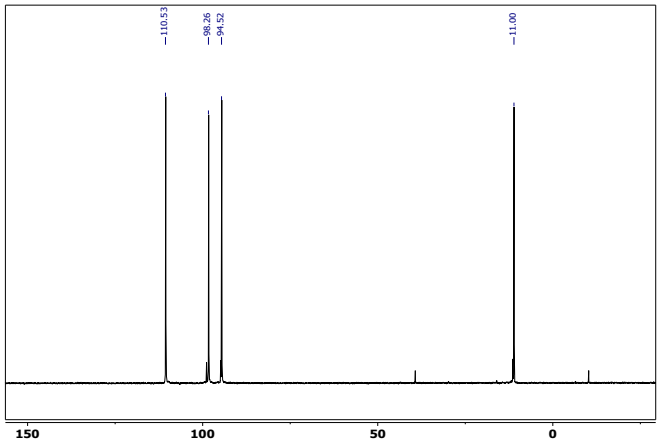


Fig. 5. $^{13}C\{^1H\}$- 100.3 MHz NMR spectrum of a neat sample of compound **3** (obtained by Method A).

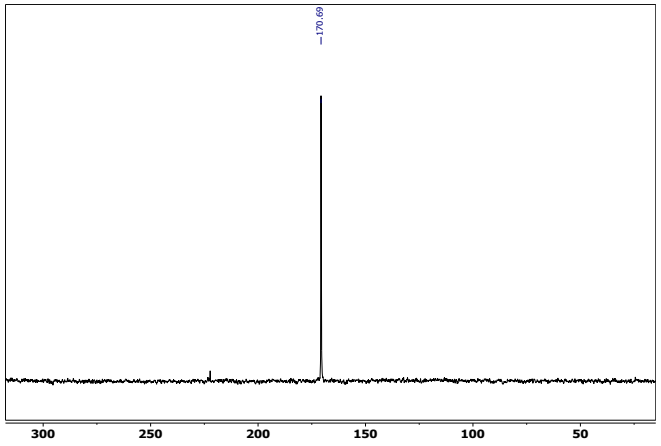


Fig. 6. $^{15}N\{^1H\}$ inverse-gated- spectrum of a neat sample of compound **3** (obtained by Method A).

The proton-detected $^{15}N–^1H$ through-bond (HSQC) experiment using a typical one-bond coupling value ([1]$J(^1H–^{15}N) = 100$ Hz) [17] exhibited an extremely strong cross peak (Fig. 7) between the 12.7 ppm proton signal and the 170.7 ppm N_3 nitrogen signal, confirming that they are directly connected. However, this correlation

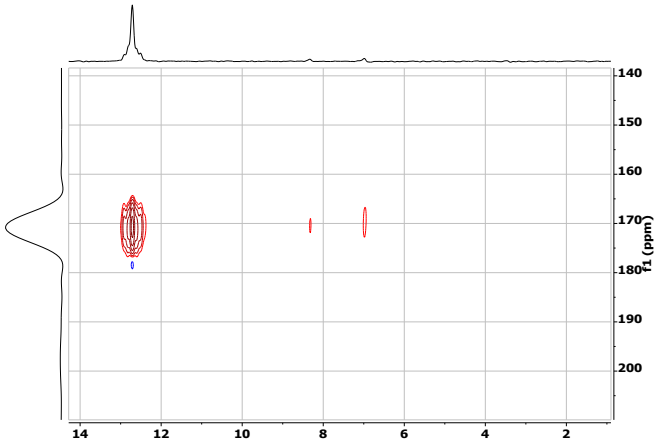


Fig. 7. Proton-detected $^{15}N–^1H$ HSQC spectrum of a neat sample of compound **3** (J= 110 Hz) (obtained by Method A).

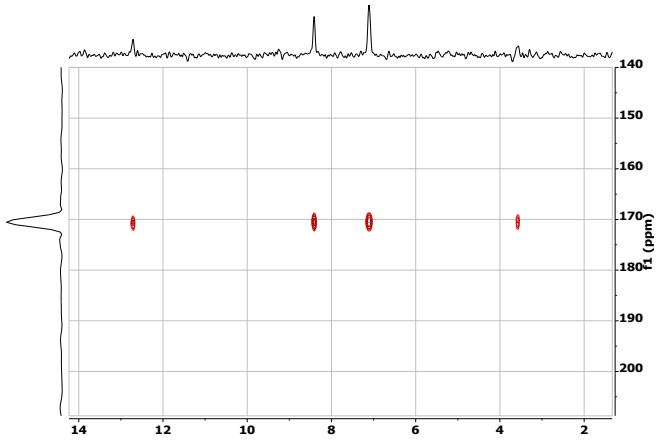


Fig. 8. Proton-detected $^{15}N–^1H$ HSQC spectrum of a neat sample of compound **3** (J=11 Hz) (obtained by Method A).

disappears, as soon as the NH protons take part in an exchange process fast on the ^1H time scale. Note that the weaker correlation seen on Fig. 8 points to the N_1 nitrogen coupled also to the 12.7 proton by a three bond coupling. These observations correspond to the presence of the $[HMim]^+$ cation.

The highly concentrated neat sample made possible also the recording of spectra of rare nuclei such as ^{17}O within reasonable accumulation time. Thus, to identify the structure of the anion, the ^{17}O NMR spectrum was also attempted at natural abundance. At room temperature it presented a broadened peak at 240.8 ppm (Fig. 9). This chemical shift can be indicative of the presence of a Cl-S-O moiety [20]. Incorporation of chlorine results in a considerable downfield shift of the ^{17}O signal Some literature examples are as follows: $CH_3SO_2OCH_3$: 170 ppm [25], CH_3SO_2Cl: 238 ppm [25], $CH_3OSO_2OCH_3$: 140 ppm [26], CH_3OSO_2Cl: 219 ppm [26]. At the same time, δ_O of sulfonic acid derivatives remains far below 200 ppm (*e.g.* 140 ppm for p-toluenesulfonic acid monohydrate [27], 171 ppm for Cys-SO_3H) [28].) Also, an increase in the negative charge on oxygens around sulfur was found to lead to deshielding (e.g. δ_O (H_2SO_4) = 140 ppm, while δ_O (SO_4^{2-}) = 167 ppm) [25a].

The sample, stored for a period of two months in a closed bottle, displayed a bit different ^1H NMR spectrum compared to the fresh material (Fig. 10). Although the signals of the $[HMim]^+$ cation remained unaltered, some increase in the integral value of the peak at 10.8 ppm was observed. Another marked feature is the disappearance of the signals of

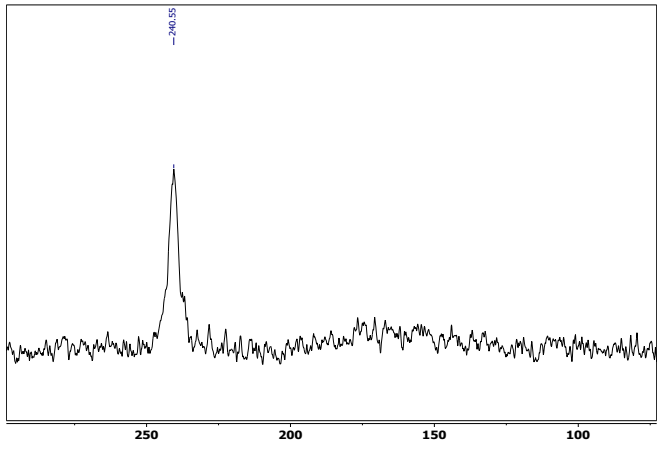


Fig. 9. ^{17}O-direct detection (zg) not-proton decoupled (linewidth ~ 300 Hz) NMR spectrum of a neat sample of compound **3** (obtained by Method A).

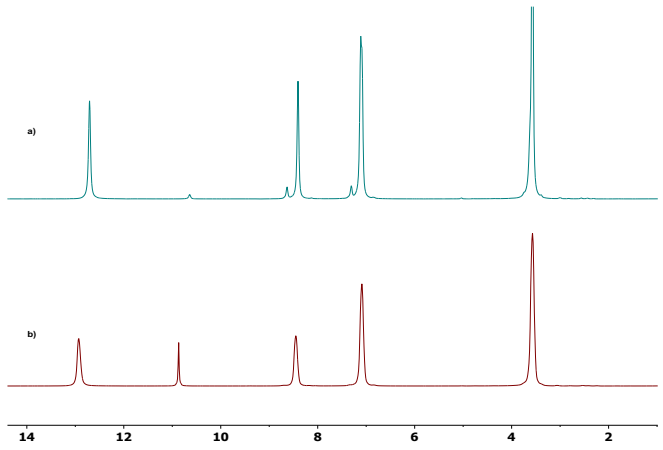


Fig. 10. a) 400 MHz ^{1}H NMR spectra of a freshly made neat sample prepared by Method B (300*K*); b) ^{1}H NMR spectrum of the same sample after a two-month storage (304 K).

the 1-methylimidazole moiety of the minor component. This proves that the proton with the peak at 10.8 ppm does not belong to the latter.

It can be assumed that ionic liquid **3** is extremely sensitive to moisture, similarly to chlorosulfonic acid [29] and the changes in the ^{1}H NMR spectrum (Fig. 10) can be attributed to partial hydrolysis. The deliberate addition of DMSO-d_6 containing traces of water to the fresh sample resulted in a considerable change in the integral value of the signal around 11 ppm (Fig. 11b). In a sample with higher dilution (Fig. 11c), signals corresponding to protons of the methyl group and the imidazole ring became sharper. Besides, two broad signals could clearly be distinguished from the narrow ones: one above 14 ppm, corresponding to approximately one proton, and another one at 7.5 ppm with a larger integral value (Fig. 11c). NOESY spectra indicate slow exchange between the two (Fig. S4).

Essentially the same spectra were obtained in DMSO-d_6 for the material prepared by Method B (Fig. S5) showing that the two methods led to the formation of the same major product. The integral value of the peak around 11 ppm decreased in the spectrum of a more concentrated sample (probably due to the lower water content) together with some downfield shift of the signal (Fig. S6). The broad singlet with the highest chemical shift moved to the other direction, in accordance with the behaviour of the other sample (Fig. 11). Signals corresponding to a minor compound incorporating the 1-methylimidazole moiety could be distinguished again in all of these spectra, similarly to the sample prepared by Method A.

A broadening of the most de-shielded two signals (~14 and ~12 ppm) was observed when the temperature was increased to 323 K and they collapsed into a single broad peak upon further heating (Fig. S7), supporting an exchange between them. These signals disappeared when D_2O was added to the mixture and a new broad H_2O peak was detected at 4.4 ppm indicating a deuterium-proton exchange (Fig. 12). It is noteworthy that the singlets corresponding to the minor component were absent from the spectrum obtained by heating this sample to 323 K. Only four signals with the ratio of 1:1:1:3 could be distinguished at 8.63 ppm, 7.40 ppm, 7.38 ppm and 3.79 ppm, respectively, supporting the presence of a single compound.

Fast hydrolysis of the chlorosulfate anion [29] of [HMim][SO_3Cl] (**3**) may lead to the formation of protons and different anions (Scheme 3).

To prove the hypothesis of the formation of HSO_4^- (or SO_4^{2-}) anions in the partially hydrolysed samples, the spectra were compared with those of [HMim][HSO_4] (**4**), prepared by the reaction of 1-methylimidazole and H_2SO_4 (Figs. S8-S10).

The signals in the ^{1}H NMR spectrum of a neat sample of [HMim][HSO_4] (**4**) (Fig. S8) is very similar to those of the main components of the partially hydrolysed samples of substances obtained by Methods A (Fig. 11b) and B (Fig. S5). An exchange between the two protons exhibiting the broad signals at 13.2 ppm and 11.0 ppm was proved by a change in the temperature of the ^{1}H NMR experiment (Fig. S10). This behaviour is also similar to that of the hydrolysed material (Fig. S7).

The presence of HSO_4^- (or SO_4^{2-}) anions in a hydrolysed sample could also be proved by ^{17}O NMR measurements. The chemical shift at 165.5 ppm observed for the substance obtained by Method B in the presence of water (and D_2O) (Fig. 13b) corresponded well to the ^{17}O signal of [Hmim][HSO_4] (**4**) (Fig. 13c), as well as to that of $KHSO_4$ (163 ppm) [30], supporting the hydrolysis of the anion of $\mathbf{3}^-$ to form HSO_4^- ions. A similar behaviour could be noticed on comparing the ^{17}O NMR spectra of chlorosulfonic acid and a chlorosulfonic acid / water mixture. The $ClSO_3^-$ ions immediately and fiercely form HSO_4^- (and HCl) and practically remove water from the mixture (see spectrum at Fig. S11).

It should also be mentioned that spectra depicted in Fig. 11a and Fig. S5 are very similar to that reported by Shiflett [8], except that a greater difference (major / minor ratio = 10 and 8, respectively) was observed between the amount of the major and minor components.

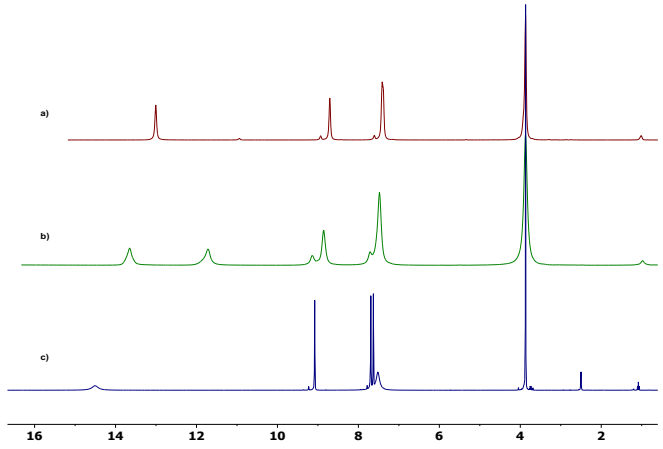


Fig. 11. a) 400 MHz ^{1}H NMR spectra of a neat sample prepared by Method A (300 K); b) ^{1}H NMR spectrum of the same sample after addition of 30% DMSO-d_6 (300 K); c) ^{1}H NMR spectrum of a diluted sample (70 mg/ 0.4 ml DMSO-d_6 (300 K) (The shift of the methyl singlet in spectrum a) is adjusted to the same signals of the spectra obtained in DMSO-d_6 b).)

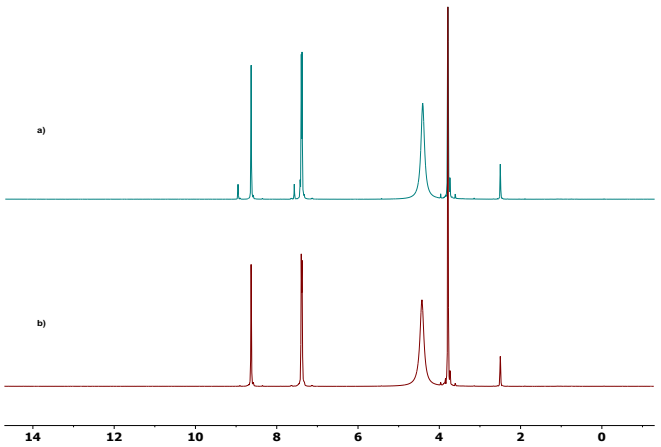
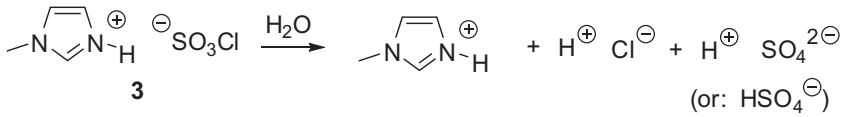


Fig. 12. 400 MHz ^{1}H NMR spectra of the material obtained by Method B in a mixture of DMSO-d_6 (0.3 ml) and D_2O (0.1 ml) a) 313 K; b) 323 K.



Scheme 3. Hydrolysis of [HMim][SO_3Cl] (**3**) in the presence of added water

Shiflett proved the formation of zwitterion **2** as one of the two products by X-ray investigations [8]. The other derivative was supposed to be [MSim]Cl (**1**), although the explanation for the appearance of two different peaks in the region of acidic protons in the ^{1}H NMR spectrum remained somewhat vague.

In our case, the integral values of the high-frequency shifted two protons (~13–14 ppm and ~11–12 ppm) suggests that they do not belong to the minor product.

Based on the above results, it can be supposed that the minor component in the substances prepared by Methods A or B is zwitterion **2**. For this compound, only signals corresponding to the methylimidazole core can be distinguished either in the ^{1}H- or in the ^{13}C NMR spectra. It was prepared before [31] by the reaction of 1-methylimidazole and SO_3 and was found to loose SO_3 in the presence of water. It was also shown that it could convert alcohols to alkyl sulfates. Consequently, its hydrolysis may result in the formation of [HMim][HSO_4] (**4**), similarly to that of the main component of the material obtained by Method A, [HMim][$ClSO_3$] (**3**) (Scheme 3). This may give an explanation for the presence of one set of signals in the region of imidazolium protons in samples contaminated with water, corresponding to the [HMim]$^+$ cation. The signal around 14 ppm can be attributed to the NH proton of the same cation, while the peak with altering intensity around 11 ppm can be assigned to the HSO_4^- anion. That means that wet samples contain mixtures of [HMim][$ClSO_3$] (**3**), [HMim][HSO_4] (**4**) and, eventually, zwitterion **2**. NMR investigations of the substance obtained by Method B (Figs. S5-S7) strongly suggest that it is also a mixture of zwitterion **2**, and ionic liquids **3** and **4**.

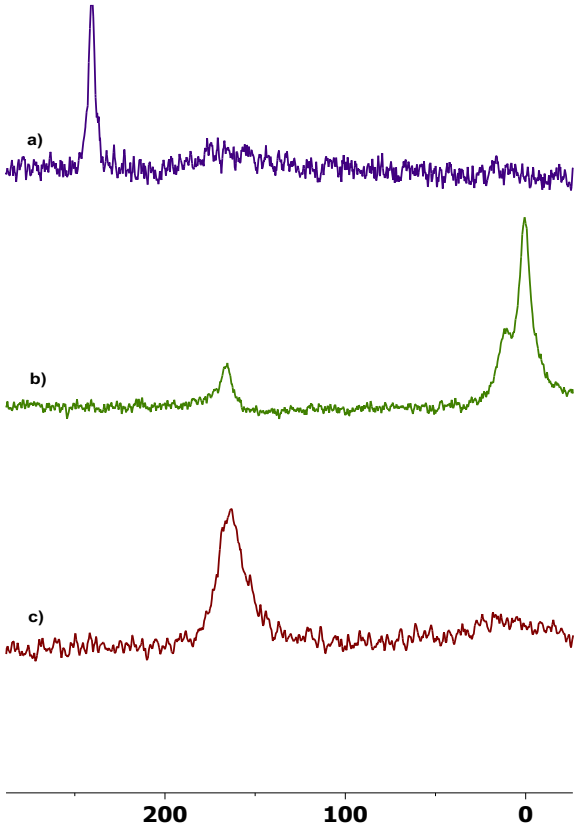


Fig. 13. 54.2 MHz ^{17}O NMR spectra without proton decoupling. a) neat [HMim][SO_3Cl] (**3**) $\delta = 240.8$ ppm, b) substance obtained by Method B in the presence of DMSO-d_6 and D_2O (50 μL D_2O, 298 K) $\delta = 165.5$ ppm (HSO_4^-), $\delta = 13.1$ ppm (DMSO), and $\delta = 0.0$ ppm (excess H_2O was added as reference) and c) [HMim][HSO_4] (**4**) in the presence of DMSO-d_6 (50 μl) $\delta = 163.6$ ppm.

It should be mentioned that the experiments discussed above prove that the zwitterion **2** is much less prone to hydrolysis than **3** and is converted to **4** only on heating (Fig. 12), or on prolonged interaction with water (Fig. 10).

It should be emphasized that high chemical shift of the NH proton of the [HMim]$^+$ cation in neat samples can be due to the existence of hydrogen bonds, e.g. between N^3H of the cation and O^1 of the anion in case of **3**, as indicated by the X-ray structure (Fig. S2). Also, the chemical shifts of NH protons of **3**, **4** and [HMim]Cl in the neat samples (Fig. S12) change in a reversed order to the acidity of the conjugate acid of the anion. This phenomenon was observed before for diethylmethylamine based protic ionic liquids with the chemical shift of NH protons ranging from 14.35 ppm to 7 ppm with increasing acid strength of the acid used during the protonation of the amine. This tendency was explained by the increase in the strength of hydrogen bond formed between the anion and the protonated base, causing a deshielding of the exchangeable proton [32].

4. Conclusions

The results presented above show that the reaction of chlorosulfonic acid and 1-methylimidazole can lead to a mixture of [HMim][SO_3Cl] (**3**) and a minor component **2** at room temperature. The primarily formed ionic liquid is very sensitive to moisture and readily hydrolyses to [HMim][HSO_4] (**4**). A slower reaction of zwitterion **2** with water leads to the same product (**4**). The formation of [MSim]Cl as a stable product of the present reaction remains to be proved. ^{1}H and ^{13}C NMR data are not sufficient for this as NH chemical shifts (and even ^{13}C and ^{15}N NMR chemical shifts [24]) of 1-methylimidazole are subject to changes depending on the conditions (dilution, pH, etc.). Also, it can be seen that the chlorosulfonation reaction is extremely sensitive not only to moisture but also to other experimental details. The original report describes the formation of a single product [6], Shiflett obtained a mixture with two components of comparable amounts [8]. The present reactions led to the same two products but in a different ratio. Chlorosulfonic acid is prepared by the reaction of SO_3 and HCl. The reaction is reversible [33], so chlorosulfonic acid may contain some SO_3 that can lead to the formation of zwitterion **2** in an amount corresponding to the SO_3 content of the reagent.

It should be mentioned that the formation of **3** cannot be due to the lack of proper inertness of our procedure as it was shown to decompose in the presence of moisture soon. At the same time, under sufficiently inert conditions it can survive a two-month long storage.

Good catalytic activity of the chlorosulfonation product is also not a proper proof for the existence of [MSim]Cl and can also be explained by the formation of ionic liquid **3**. Bao et al. investigated the acidity of [HMim][SO_3Cl] (**3**), obtained by the reaction of SO_2Cl and [Hmim][HSO_4], and showed that the ionic liquid **3** had dual Brønsted–Lewis acidity [20]. Moreover, much superior catalytic activity of the latter salt compared to that of [Hmim][HSO_4] was observed in esterification

reactions. It should be mentioned, that the great majority of the catalytic processes carried out with'[MSim]' Ils [6,7] are condensations resulting in the formation of water, so hydrolysis or partial hydrolysis may take place even under strictly inert conditions in the course of the reactions. The hydrolysis product (Scheme 3) can be considered a mixture of a protic ionic liquid and an inorganic acid. Such mixtures were shown to exert improved catalytic activity over the single components [34], that could be awaited in the present case, too.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.115276.

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