Carbenes in ionic liquids†

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Received (in Montpellier, France) 19th May 2010, Accepted 18th August 2010
DOI: 10.1039/c0nj00380h

The chemistry of 1,3-dialkylimidazolium-based ionic liquids (ILs) can easily be linked to that of N-heterocyclic carbenes (NHCs) in the presence of sufficiently basic counteranions. B3LYP/6-31+G*, B3LYP/aug-cc-pVTZ and MP2/6-311+G** studies show that increasing the basicity of the anionic component the relative stability of the ion pair and that of the hydrogen bonded complex of the corresponding free acid and NHC itself can be shifted toward the formation of NHC. In the case of the acetate anion, the ion pair and the NHC-acetic acid complex have similar stability. Photoelectron spectroscopic studies show that the vapor of EMIM-acetate is dominated by the NHC-acetic acid complex. The mass spectrum of the same compound shows the presence of both acetic acid and 1-ethyl-3-methylimidazolium-2-ylidene, in agreement with the low pressure during the MS experiment, which facilitates dissociation. The possibility of systematic and simple variation of the NHC content of the ILs facilitates the extension of carbene chemistry in ionic liquids.

Introduction

The chemistry of imidazolium derivatives has a wide variety of applications: with many anions their salts form ionic liquids (ILs)[1] which are regarded as promising solvents for different applications, due to their low volatility, non-flammability and good thermal stability. From 1,3-dialkylimidazolium cations N-heterocyclic carbenes (NHCs)[2] can be derived by a single deprotonation.[3] These compounds are of high interest as organocatalysts;[4] furthermore NHCs as ligands in transition metal complexes were shown to have excellent catalytic[5] and also medical[6] effects. This deprotonation, however, can only be achieved by superbases,[3] and accordingly 1,3-dialkylated imidazolium salts are termed non-protic ILs.

Nevertheless, it is an appealing idea to unite the chemistry of carbenes and ILs[7] and there are some scattered evidences that N-heterocyclic carbenes are present in imidazolium-based ILs. Carbene catalysed reactions were observed in these solvents (in the presence of DBU),[8] or certain palladium salts,[1i,f] furthermore carbene complexed palladium has been isolated from ionic liquids.[9,10] Besides, the known proton/deuteron exchange at the 2-position in 1,3-dialkylimidazolium salts in D_2O[11a,b] or MeOD[11c] media also suggests the involvement of the N-heterocyclic carbene. All of the above examples necessitate the removal of the proton from the imidazolium moiety, with a possible formation of the acid from the anionic part of the imidazolium salt. Such proton transfer between cation and anion in ILs is also known in the so-called protic ILs, which consist of weakly acidic (NH bonded) cation and a sufficiently basic counter anion (*e.g.* chloride).[1k] This rearrangement provides a neutral and thus volatile acid–base pair,[1k,12] resulting even in industrial application.[13]

It has been shown recently that not only protic ionic liquids but also 1,3-dialkylimidazolium salts can be evaporated,[14] raising the question if the formation of the neutral (and thus volatile) N-heterocyclic carbene (NHC)-acid pair would be responsible for this important observation. Photoelectron spectroscopic,[15] FTR-ICR[16] and line of sight mass spectroscopic[17] studies showed, however, that the evaporation of the investigated non-protic ILs proceeds *via* single ion pairs. The isolated ion pairs were also studied computationally,[18,19] and vaporization enthalpies could be reproduced with remarkable accuracy.[19b,d] The 1-butyl-3-methylimidazolium-bis(trifluoromethanesulfonyl)amide ion pair was found to be substantially (by 154.7 kJ mol^{-1} at B3LYP/TZVP) more stable than the isolated 1-butyl-3-methylimidazol-2-ylidene and bis(trifluoromethanesulfonyl)amine,[19b] in agreement with the experimental suggestions. These findings, however, are in contrast with the indirect evidences suggesting that NHCs are present in aprotic ILs. It is therefore apparent to investigate the factors influencing the carbene concentration in aprotic imidazolium ionic liquids.

Since NHCs are strong bases,[20] and the basicity of the anions (PF_6^-, BF_4^-, $CF_3SO_3^-$, $N(SO_2CF_3)_2^-$) of the hitherto investigated distillable ionic liquids[14–17] is significantly smaller, it is apparent that such anions were unable to deprotonate the imidazolium ring at the 2-position. However, anions derived from weak acids, have increased basicity; thus, it is likely that the carbene concentration of an imidazolium based ionic liquid can systematically be tuned by the basicity of its counter ion. Keeping in mind, that many ILs have recently been characterized containing rather basic anions (*e.g.* salts of amino acids[1f]

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† Electronic supplementary information (ESI) available: Geometries (in Cartesian coordinates) and total energies of the optimized structures. See DOI: 10.1039/c0nj00380h

or weak organic acids[1e,9]) the question is apparent: are there any counteranions, which increase the carbene concentration to an observable extent?

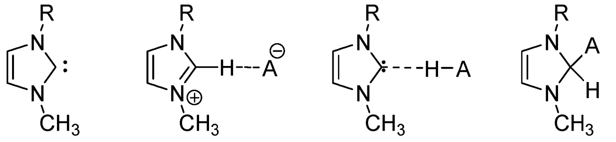
Methods

Computations have been carried out with the Gaussian 03 program package.[21] As preliminary calculations full geometry optimizations were performed for all molecules at the B3LYP/6-31+G* level with subsequent second derivative calculations. For some systems further functional (B971, MPW1K) and basis set (6-311+G**, aug-cc-pVTZ) and also MP2/6-311+G** method were applied to evaluate the accuracy of the results. For the dissociation of the isomers of MeMIM-acetate to acetic acid and the corresponding carbene counterpoise corrections were calculated at the B3LYP/6-31+G* and B3LYP/aug-cc-pVTZ level to evaluate the error caused by Basis Set Superposition Error (BSSE). Since it has been found to be negligible (<1 kcal mol^{-1}) even with the smaller 6-31+G* basis set, BSSE has not been considered in further calculations. Proton shift transition structures were characterized by a single imaginary frequency. Orbital energies were calculated at the HF/6-31+G* level on the B3LYP/6-31+G* level geometries, and ionisation energies were obtained by the OVGF/6-311++G**// B3LYP/6-31+G* method.[22] For the visualization of the optimized structures the MOLDEN program has been used.[23]

The instrument used for MS measurements was a Finnigan MAT 90 sector mass spectrometer. The sample was vaporized at 10^{-6} mbar by a TIC evaporation technique, which occurred at temperatures between 50 and 100 °C, in agreement with the literature data regarding the feasibility of distillation for non-protic ILs at 6–8 mbar at 300 °C.[14] The vapour was transferred into the spectrometer *via* a direct inlet, and ionized by 70 eV electron impact (EI) method.

The instrument used for the UPS measurements has been described earlier,[24] and has been completed with a new, 19 cm long heatable inlet. During the measurements the temperature of this inlet was set to 150 °C, to avoid the condensation of the vaporised sample prior to entering the reaction chamber. The follow-up cleaning showed no signs of condensation. The bands were calibrated to He, N_2 and MeI, while the resolution was 40 meV at the Ar $^2P_{1/2}$ and this remained unchanged during the entire measurement, again indicating that no condensation occurred in the reaction chamber of the spectrometer. The sample was gradually heated until the amount of the vapour provided a sufficiently intense spectrum, and the pressure in the spectrometer chamber reached the limiting 2 10^{-4} mbar value for the detector, which occurred at 150 °C. These conditions result in an estimated 10^{-2} mbar pressure in the ionization chamber (which is by 2–3 order of magnitude larger than at the detector).

Results and discussion



1: R = Me
5: R = Et

2: R = Me
6: R = Et

3: R = Me
7: R = Et

4: R = Me
8: R = Et

Fig. 1 The investigated isomers of 1,3-dimethylimidazolium salts.

To gain a general picture on the possibility of the proton transfer, the deprotonation energy of the chosen 1,3-dimethylimidazolinium cation model compound has been calculated. In accordance with the related experiments in the literature,[2–3,20] we investigated the removal of the hydrogen at the 2-position only, since this process leads to the most stable carbenoid structure.[25] The B3LYP/6-31+G* deprotonation energy is 268 kcal mol^{-1}, in reasonable agreement with previous computational (for **1** (Fig. 1) 259.5 kcal mol^{-1} B3LYP/6-311+G(2p,2d)[26] and 258.7 kcal mol^{-1} CBS-QB3 protonation energy was reported[27]) and experimental (for 1-ethyl-3methyl-imidazole-2-ylidene 251.3 kcal mol^{-1})[20c] data.

Accordingly, the superbase nature of the carbene[20a,20c,27] can be described at this level of the theory too, which can be used for our preliminary calculations. Since the anionic components of the ILs are also bases (see Table 1), they compete

Table 1 Protonation energies (E_{prot}) of the examined anions and dissociation energies of the 2, 3, 4 structures to 1 and the corresponding conjugate acid at the B3LYP/6-31+G* and B3LYP/aug-cc-pVTZ levels (in parenthesis), without BSSE correction in kcal mol^{-1} units

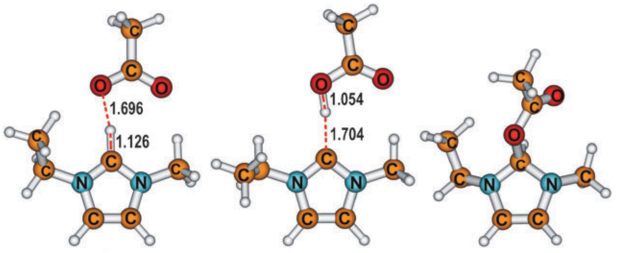
		E_{diss}		
Anion	E_{prot}	**2**	**3**	**4**
$(CF_3SO_2)_2N^-$	−297.7 (−300.2)	45.8	—	—
$CF_3SO_3^-$	−301.7 (−307.1)	46.7	—	—
Cl_3CCOO^-	−321.4 (−326.6)	31.8	—	—
Cl_2CHCOO^-	−327.8 (−333.3)	28.3	—	—
$^aCl^-$	−328.1 (−334.7)	29.6 (26.1)	—	—
$ClCH_2COO^-$	−334.9 (−339.7)	25.1	—	—
$CH_3CH_2COO^-$	−348.2 (−352.5)	18.3 (15.2)	15.9 (15.0)	8.2 (4.0)
$^bCH_3COO^-$	−349.2 (−353.6)	18.1 (14.9)	15.4 (14.3)	7.3 (6.6)
PhO^-	−350.7 (−355.5)	7.6 (4.1)^f	12.7 (11.6)^f	6.5 (1.9)^f
SH^-	−351.1 (−354.4)	9.8 (5.1)	5.6 (4.9)	—
$^cCN^-$	−353.2 (−355.7)	2.3 (2.3)	8.8 (8.5)	10.8 (8.7)
$^dF^-$	−366.0 (−372.6)	—	20.8 (18.7)	18.4 (13.1)
CH_3O^-	−384.8 (−387.8)	—	9.9 (8.9)	13.1 (8.5)
$^eOH^-$	−392.5 (−395.0)	—	10.1 (8.9)	12.9 (7.9)

MP2/6-311+G** level energies of some systems are:[a] Cl: E_{prot} = −339.3 kcal mol^{-1} E_{diss} of **2**: 23.7 kcal mol^{-1}. [b] Acetate: E_{prot} = −354.9 kcal mol^{-1} E_{diss} of **2**: 16.0 kcal mol^{-1}, **3**: 16.4 kcal mol^{-1} **4**: 10.8 kcal mol^{-1}. [c] Cyanide: E_{prot} = −356.9 kcal mol^{-1} E_{diss} of **2**: 2.5 kcal mol^{-1} **3**: 9.3 kcal mol^{-1} **4**: 15.5 kcal mol^{-1}. [d] Fluoride: E_{prot} = −376.3 kcal mol^{-1} E_{diss} of **3**: 17.9 kcal mol^{-1} **4**: 9.8 kcal mol^{-1}. [e] Hydroxide: E_{prot} = −398.0 kcal mol^{-1} E_{diss} of **3**: 10.3 kcal mol^{-1} **4**: 11.3 kcal mol^{-1}. [f] B3LYP/aug-cc-pVTZ//B3LYP/6-31+G*.

for the proton with the carbene. The result of such a competition can be a hydrogen bonded structure (like **3**),[28] which is an isomer of the hydrogen bonded ion pair **2** that was observed with certain anions as evaporation product from ionic liquids-see above. Compounds of type **4** with saturated carbon being formed after a nucleophilic attack of the anion were also considered. In the following section these isomeric structures will be investigated for different acids (HA).

The gas phase protonation energies of the investigated anions ($A^{(-)}$–see Table 1) range from about 300 to 400 kcal mol^{-1}. If the B3LYP/6-31+G* basicity of the anion is smaller than 335 kcal mol^{-1}, only structures of type **2** could be optimized, in which the anion interacts with the hydrogen at the 2-position of the imidazolium cation by forming an H-bond (Fig. 1). Dissociation of these structures to imidazole-2-ylidene (**1**) and the acid (HA) is highly endoergic (Table 1), therefore the formation of the free carbene is rather unlikely, in good agreement with the previously reported experiments,[15–17] and calculations.[19b,c]

Interestingly, in case of the moderately basic anions (-340 kcal mol^{-1} $> E_{\mathrm{prot}} >$ -360 kcal mol^{-1}) both **2** and its H-shifted isomer **3** (having the H-bond between the acid and **3**) could be optimized. The stability of these type **3** complexes is below 20 kcal mol^{-1}, making the dissociation to the carbene and acid favourable in comparison with the process yielding the separated anion and imidazolium cation.[29] Type **4** isomers of these derivatives could also be optimized with the exception of the SH^{-} compound, but in most cases they exhibit higher energy. With the most basic anions ($E_{\mathrm{prot}} < -360$ kcal mol^{-1}) type **2** structures could not be optimized, thus the carbene formation is favored, as it was found computationally for EMIM fluoride[25a] and hydroxide.[25b] Accordingly, the alkoxide anions (which belong to this group of anions) are known to produce carbenes from imidazolium salts as discussed above.[2,3] To check the reliability of the above preliminary results B3LYP/aug-cc-pVTZ and MP2/6-311+G** calculated relative stabilities are also presented in Table 1 (in parenthesis and footnotes, respectively). Using the larger basis set generally increases the protonation energy of the anion, and thus the relative stability of **3** by a few kcal mol^{-1}, while the tendencies for the different anions remaining the same.



6a **7a** **8a**

Fig. 2 Structure of the most stable conformers of each investigated 1-ethyl,3-methylimidazolium acetate ion pair isomers at the B3LYP/6-31+G* level.

The most interesting is the case of those anions, when all three structures (**2**, **3** and **4**) could be obtained, as it is shown in Fig. 2 for the acetate anion. Thus, for our further studies we have selected the practically most interesting EMIM-acetate. The relative energy of **7a** compared to that of **6a** was found to be almost identical to that for **3a** and **2a** at the B3LYP/6-31+G* level (see Table 2). Using larger basis sets, however, the relative stability of **7a** and **6a** is about the same (see Table 2). The barrier of the **6a–7a** isomerisation is only 3.6 kcal mol^{-1} (B3LYP/6-31+G*), thus our results indicate that both **7a** and **6a** can be present in the vapor phase when 1-ethyl-3-methylimidazolium-acetate is distilled. It is worth noting that the calculated dipole moment of these two isomers were found to be significantly different: 10.14 D for **6a**, and 4.94 D for **7a**; thus the energy demand of the evaporation from the ionic liquid for the latter species should be much lower. Apparently, either **6a** or **7a** is formed during distillation, after condensation the ion pairs will be formed by a reverse process due to the energetically favourable self-solvation of the ions present in the liquid phase.

Apart from the acetate case, the phenolate anion deserves special attention. From the reaction mixture of 1,3-dimesityl-imidazole-2-ylidene and 2,6-di-*tert*-butyl-4-methylphenol an ion pair (type **2** structure) could be crystallized, and structurally characterized,[28b] with a carbon-oxygen $C^{+}(\text{–H}\cdots)O^{-}$ distance of 2.752 Å. More recently some other structurally characterized phenolates were also reported as type **2** structures.[30] The reaction of the same carbene with diphenylamine (note the low acidity of the proton obtainable from the NH bond) resulted in a hydrogen bonded (type **2**) complex, with a 3.196 Å N(–H···)C distance. Thus, experimental proof is also available for the two different types of hydrogen bonding modes discussed above. Although these structures are in the crystalline phase, and are therefore not directly comparable to gas phase results, the similarity between the C(–H···)O and N(–H···)C distances is noteworthy (*cf.* with the similar distances in the **6a** and **7a** structures as discussed above).

The observation of the ion pair (**1** type structure) in the X-ray study seems to be contradictory to the computed results, which predict that **3b** is more stable for the phenolate than **2b**

Table 2 Relative energy of **7a** compared to **6a** on different computational levels in kcal mol^{-1} units. (For detailed conformation analysis see supporting information)

	6-31+G*	6-311+G**	def2-TZVPP	aug-cc-pVTZ	def2-QZVPP
B3LYP	3.0	1.1	0.4	1.0	0.7[a]
B971	2.3	0.4	−0.4	0.1	−0.1[a]
MPW1K	2.3	0.2	−0.5	0.0	−0.3[a]
MP2	4.5[b]/1.7[c]	0.3[b]/0.3[c]	—	—	—

[a] Single point energies on the geometries obtained by the corresponding DFT functional with aug-cc-pVTZ basis set. [b] Single point energies on the B3LYP/aug-cc-pVTZ level geometries. [c] Single point energies on the B3LYP/6-31+G* level geometries.

at all applied levels of theory (Table 1). This apparent disagreement can partially be attributed to steric effects, since in case of the 1,3-dimesitylimidazole-2-ylidene and 2,6-di-*tert*-butyl-4-methylphenol adducts the **2** analogue was only 1.9 kcal mol^{-1} (B3LYP/6-31+G*) higher in energy. Although the accuracy of the computational methods may also influence the deviation to the experimental results, it should be considered, that in the crystal (and also in the liquid) the coulombic interaction between the ions pairs with their neighbours stabilizes **2** with respect to the neutral **3**. Accordingly, a cluster of two MeMIM phenolate type **2** structures are more stable by 4.7 kcal mol^{-1} (B3LYP/6-31+G*) than its isomer cluster consisting of a type **2** and a type **3** structure.

Interestingly, dissociation energies of type **3** structures are quite large; thus, carbenes are apparently forming very strong H-bonds in the gas phase with R-OH functional groups.[25*b*] The stability in many cases exceeds that between two water molecules (6.4 kcal mol^{-1} 4.6 kcal mol^{-1} and 6.0 kcal mol^{-1} at the B3LYP/6-31+G*, B3LYP/aug-cc-pVTZ and MP2/6-311+G**, respectively). Although all dissociation energies are high positive values, considering the role of entropy at high distillation temperatures and low pressures, the dissociation Gibbs free energies can be lower, and the formation of the free carbene and the weak acid (*e.g.* acetic acid) is conceivable.

To observe the mechanism of vaporization experimentally, a sample of 1-ethyl-3-methylimidazolium-acetate was gradually heated to 150 °C, and the vapour was examined by UV photoelectron spectroscopy. After the removal of the traces of water and one unidentified further volatile impurity during the heating up process (this took about 10–15 min) the spectrum remained unchanged for several hours. Variation of the sample temperature between 130 °C (lower limit to get a signal with an acceptable signal to noise ratio) and 150 °C (upper limit set by the detector) the ionization energies and the band intensities remained constant, excluding the formation of volatile decomposition products. The observed spectrum can be seen in Fig. 3. Also the measured ionization energies are compiled together with the OVGF calculated ones (this method usually provides an accuracy of a few tenth of eV)[22] for the same compounds and the adduct **8a** in Table 3. It is clear that the measured spectrum cannot be assigned to **6a**, since not only do the observed band positions show the best agreement with the simulated spectrum of **7a**, but this is the only compound, where the measured intensity ratio (2 : 2 : 1 for the first three bands) is in agreement with the calculations. It is also clear that the measured spectrum cannot correspond to the carbene **5**, since no band is seen at about 8 eV, where the first ionization should appear (*cf.* also with the 7.68 eV first ionization energy value of 1,3-di-*tert*butyl-imidazol-2-ylidene).[31]

Table 3 Observed and calculated ionization energies (in eV)

	Calculated				
Observed	**7a**	**6a**	**5**	**8a**	Acetic acid
				6.98	
8.6(5)	8.78	8.14	8.09	9.34	
	8.90	8.27	8.44		
		8.41			
9.7(6)	9.79	10.10	9.53		
	9.95			10.32	
11.1(6)	10.50	11.07		10.95	11.05
		11.41		11.49	

To investigate the evaporation products from EMIM acetate, mass spectroscopic investigation was also carried out. One characteristic feature of the spectrum (Fig. 4) is the intense peak at 110 amu corresponding to 1-ethyl-3-methyl-imidazole-2-ylidene[32] **5**. The 60 amu peak is attributable to acetic acid, this assignment is further supported by the presence of peaks at 15, 29, 43, 45, exhibiting the characteristic fragmentation pattern for acetic acid.[33] The base peak at 82 amu can be attributed to an ethylene loss from the 110 amu molecule (**5**), likewise the base peak of the mass spectrum (obtained at 70 eV electron bombardment) of 1,3-di-*tert*butyl-imidazol-2-ylidene is the one derivable by double isobutylene loss from the molecular ion.[34] The appearence of the peaks corresponding to carbene and the acid in the MS of EMIM based ionic liquids is unprecedented. The hitherto reported mass spectra (all with anions derived from strong acids, such as Tf_2N^-,[17,35,36] $EtSO_4$,[17] BF_4,[17] PF_6,[17] OTf[17]) are dominated by the peak corresponding to the stable imidazolium cation using both electron ionization[17,35] and the softer electrospray ionization methods.[36] Also no intense peak corresponding to the anionic part of the ion pair was observed.[35] To examine if

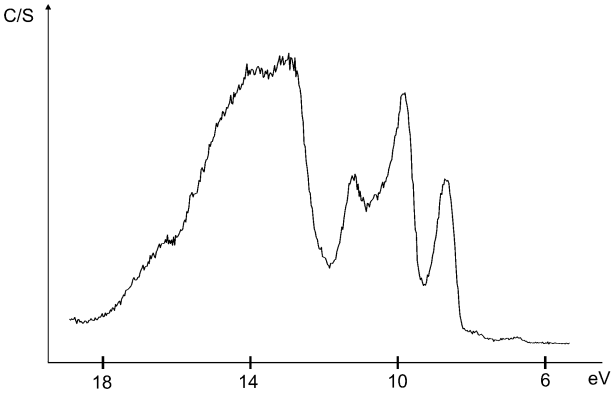


Fig. 3 Photoelectron spectrum of the vaporized 1-ethyl-3-methyl-imidazolium-acetate.

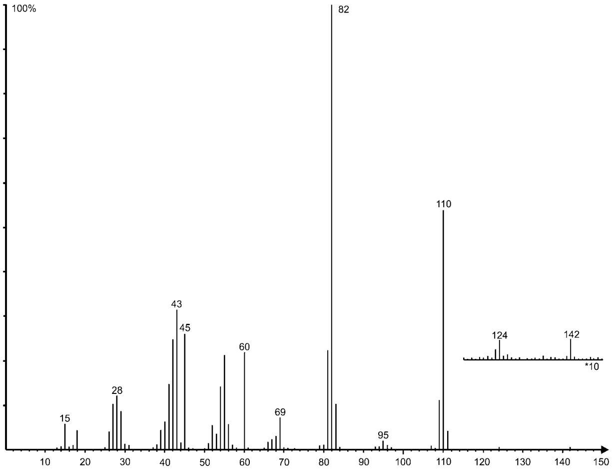


Fig. 4 Mass spectrum of the vaporized 1-ethyl-3-methylimidazolium-acetate.

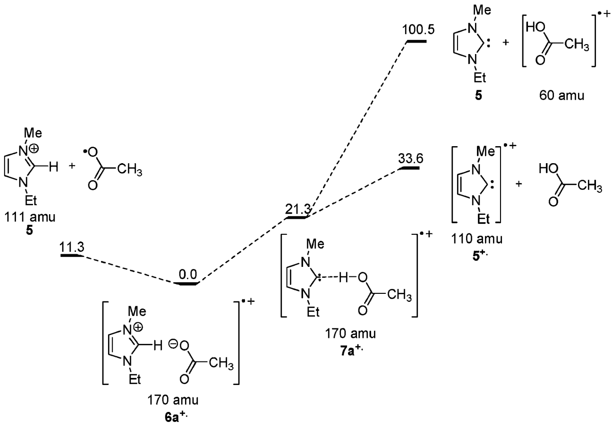


Fig. 5 Possible decomposition routes of decomposition for **6a**$^+$, and their energies in kcal mol^{-1} at the B3LYP/6-31+G* level.

both the 110 and the 60 amu peaks could be formed by different fragmentation channels from the radical cations of either **6a** or **7a** (**6a**$^+$ or **7a**$^+$), first we investigated computationally the two radical cations. The radical cation **6a**$^+$ is more stable than **7a**$^+$ by 21.3 kcal mol^{-1} at the B3LYP/6-31+G* level. The least endothermic dissociation process is the formation of the acetate radical and imidazolium cation (ΔE_{diss} = 11.3 kcal mol^{-1} at the B3LYP/6-31+G* level), while the energy demand for the dissociation to the carbene radical cation and acetic acid, or carbene and acetic acid radical cation is significantly bigger than that (by 22.3 (22.5) kcal mol^{-1}; and 89.2 (95.1) kcal mol^{-1} at the B3LYP/6-31+G* (MP2/6-31+G* in parenthesis) level, respectively, see Fig. 5). Thus, from the ion pair the formation of the imidazolium cation would be favoured, furthermore, the energy demand for the formation of the carbene radical cation and the acetic acid radical cation differs by more than 60 kcal mol^{-1}, thus the simultaneous presence of the two intense peaks in the mass spectrum is difficult to explain from the dissociation of **6a**$^+$ (or **7a**$^+$). Since in the mass spectrometer the pressure (*ca.* 10^{-6} mbar) is much lower than that in the photoelectron spectrometer, the dissociation of the carbene–acetic acid complex is favored under MS conditions, explaining the presence of the observed two intense peaks (acetic acid *and* NHC). Nevertheless, some **7a** (or **6a**) should be present during the MS experiment, since the small peak at 142 amu can easily be assigned to a process leading to an ethylene loss from **7a**$^+$ (or **6a**$^+$).

Conclusion

We have shown that anions with high basicity (*e.g.* acetate) enable a proton transfer in imidazolium-based ionic liquids providing an imidazole-2-ylidene derivative and an acid (*e.g.* acetic acid). Depending on the pressure and temperature, these two neutral species are either attached to each other by a hydrogen bond (as in photoelectron spectroscopic measurements), or are dissociated (as in mass spectroscopic measurements, under lower pressure). The results of the quantum chemical calculations indicate that the fine tuning of the carbene concentration in the imidazolium based ionic liquids is possible by using counteranions with different basicity. The selective tuning of the NHC concentration in ionic liquids allows for a tailored combination of the rapidly developing carbene chemistry in the field of organo or organometallic catalysis, with the beneficial use of the environmentally benign ILs.

Acknowledgements

Financial support from the Hungarian Scientific Research Fund (OTKA T049258) is gratefully acknowledged.

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