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Gas-Phase Chemistry

Multiply Charged (Di-)Radicals**

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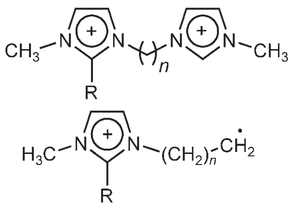
Charged radicals[1,2] are, in many ways, very unique species. These distonic cations or anions, with the charged and radical sites formally placed apart in the molecular framework, are employed as convenient probes for mass spectrometric studies on the intrinsic reactivity of gaseous radicals. Although reactions may take place at either the charge or the radical sites, or even at both of these sites,[3–9] the correct choice of reactants or chemically saturated charged sites prevent the charge site from directly participating in the reactions; hence, the charged site just functions as a convenient "handle" for the mass spectrometric manipulation of such isolated gaseous species.

So far, however, only singly charged radicals (cations or anions) have been formed and characterized in the gas phase. The effect of multicationic "handles" on the reactivity of the radical site has therefore not yet been investigated. In addition, only a few charged diradicals (and a single charged triradical[10]) of the pyridyl cation class have been formed and used to study the intrinsic reactivity of gaseous multiradicals.[11–14] The "singly charged restriction" that limits the diversity of charged radicals arises from the ways in which these ions are normally formed. Gaseous charged radicals have been formed mostly by direct electron or chemical ionization of monocations followed by their dissociation or rearrangement. Therefore, these methods produce singly charged radicals.[1,2] Charged radicals have been formed in solution by electrochemical processes that also favor formation of the monoradical monocations.[1]

The continued search for new types of ionic liquids (ILs) that would broaden their vast range of applications,[15–17] has recently led to the synthesis of ILs with several imidazolium ion sites.[18,19] We have therefore prepared the IL **1a–f**(X_n), with the anticipation that the interesting multiply charged cations **1a–f** (Scheme 1 and Figure 2) would function as gaseous precursors of suitable probes for the intrinsic reactivity of multiply charged (di-)radicals.



1a: R= H, *n*= 1, *m/z* 89.07
1b: R= H, *n*= 2, *m/z* 96.07
1c: R= Me, *n*= 2, *m/z* 103.09
1d: R= H, *n*= 3, *m/z* 103.09
1e: R= H, *n*= 4, *m/z* 110.09

2a: R= H, *n*=0, *m/z* 96.07
2b: R= Me, *n*=0, *m/z* 110.09
2c: R= H, *n*=1, *m/z* 110.09

Scheme 1. Structures of the diimidazolium ions **1a–e** and radical imidazolium ions **2a–c**.

In the condensed phase, the relatively small dications **1a–e** and the trication **1f** are known to be stabilized by intramolecular interactions with solvents and counteranions to form extensive supramolecular networks[20,21] that are preserved to some extent in the gas phase.[22–27] However, the transfer of the isolated ions **1a–f** from the solution directly to the gas-phase environment by electrospray ionization (ESI)[28–31] would remove the intermolecular stabilization and these ions with high charge density may therefore be fragile gaseous species. The alkyl bridges (the longer the better) would however be expected to electronically isolate the two or three positively charged imidazolium rings. Some highly dense multiply charged cations have also been shown by mass spectrometry (MS) to constitute stable, long-lived species.[5,32–35]

Herein we report, by using **1a–f** as proof-of-principle cases, the use of $(CH_2)_n$-bridged ($n=1$–4) multiply charged imidazolium ions as convenient precursors of novel multiply charged (di-)radicals. We also show that these gaseous species function as unique probes for the intrinsic (solvent- and counterion-free) reactivity of isolated (di-)radicals. Furthermore, the gas-phase unimolecular chemistry of these multiply charged imidazolium ions has been investigated for the first time. We selected the di- and triimidazolium species **1a–f** (details for their preparation[36] are provided in the Supporting Information) because they bear *N*-methyl substituents and are expected to dissociate mainly at the internal alkyl $(CH_2)_n$ bridges.

The ESI mass spectra (not shown) obtained in the positive-ion mode of solutions of **1a–f**(X_n) in acetonitrile show prominent gaseous cations arising from the gentle ionization of **1a–f**; for example, the mass spectrum of **1a** shows an ion of *m/z* 89.07 together with its ^{13}C isotopologue of *m/z* 89.56, in normal relative abundances and with both of

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these doubly charged ions separated, as expected, by 0.5 *m/z* units. The ion of *m/z* 89.07 was isolated by quadrupole selection and dissociated further in a hexapole collision cell by 20-eV collisions with argon. The resulting ESI tandem mass spectrum (Figure S1 in the Supporting Information) shows that this gaseous diimidazolium ion dissociates mainly at the methylene bridge (Scheme 1 and Figure S1 in the Supporting Information) to form two singly charged ions: the α-distonic monoradical ion **2a** of *m/z* 96.07 and ionized *N*-methylimidazole of *m/z* 82.06. Both of these primary fragment ions dissociate further by H loss to form the ions of *m/z* 95.06 and 81.06, respectively.

The ethylene-bridged diimidazolium ion **1b** of *m/z* 96.07 appeared, at first sight, to dissociate mainly by the loss of H_2 to form one doubly charged fragment ion of *m/z* 95.06 (Figure S1 in the Supporting Information). However, the ESI tandem mass spectrum of ^{13}C isotopologue ions (Figure S2 in the Supporting Information) reveals the correct (but not so evident) process, that is, the homolytic cleavage of the CH_2-CH_2 bridge that forms two units of the α-distonic singly charged monoradical ion **2a** of exactly the same *m/z* 96.07 as its doubly charged precursor ion **1b** (Scheme 1). Although this dissociation contravenes the even-electron rule,[37] it requires just a moderate amount of energy (+24.2 kcal mol^{-1}) according to B3LYP/6-31G(d,p) calculations. Homolytic cleavage of the ethylene bridge is probably favored since it preserves the aromatic rings of the imidazolium ion while forming the relatively stable distonic ion **2a** with charge–spin separation.[1] The occurrence of the unique "in-half" dissociation[5] for ion **1b** was corroborated when ion **1c** was isolated and dissociated (Figure 1). This asymmetric diimidazolium ion with a methyl group at one of the 2-positions (*m/z* 103.09) dissociates to form two singly charged α-distonic ions: **2a** of *m/z* 96.08 and **2b** of *m/z* 110.08 in almost the same abundances. Both ions **2a** and **2c** dissociate further by H loss to form the ions of *m/z* 95.08 and 109.09.

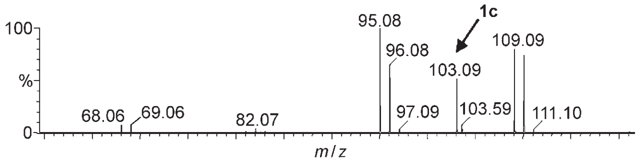

Figure 1. ESI tandem mass spectrum for CID of the diimidazolium ion **1c**.

Dissociation of the asymmetric $(CH_2)_3$-bridged diimidazolium ion **1d** of *m/z* 103.09 (Figure S1 in the Supporting Information) forms, as by now expected, two α-distonic monocations: **2a** of *m/z* 96.08 and **2c** of *m/z* 110.08 (Scheme 1 and Figure S1 in the Supporting Information) as the primary fragments. Both ions **2a** and **2c** dissociate further by H loss to form the ions of *m/z* 95.08 and 109.09 (Figure S3 in the Supporting Information). As for ion **1b**, a similar "in-half" dissociation pathway is also observed for the $(CH_2)_4$-bridged homologue ion **1e** of *m/z* 110.09 (Figure S1 in the Supporting Information); it forms two units of the β-distonic singly charged monoradical ion **2c** with the same *m/z* 110.09 as its precursor dication (Scheme 1). The primary fragment ion **2c** undergoes further dissociation by H loss to form the fragment ion of *m/z* 109.09 as well as by the loss of ethylene to form ionized *N*-methylimidazole of *m/z* 82 (Figure S3 in the Supporting Information). Other competitive homolytic cleavages along the 1,4-butylene bridge of ion **1e** forms, as nascent ions, the γ-distonic and δ-distonic ions **3** and **4** (Figure S2 in the Supporting Information) concomitantly with ion **2a** of *m/z* 96.07 and ionized *N*-methylimidazole of *m/z* 82, respectively. Both the nascent ions **3** and **4** dissociate promptly by H loss to form ions of *m/z* 123.10 and 137.12, respectively (Figure S2 in the Supporting Information).

Even more striking dissociation chemistry was observed for the trication **1f**. The ESI tandem mass spectrum obtained after isolation and dissociation of this CH_2-CH_2-bridged triimidazolium ion of *m/z* 95.73 (Figure 2) shows that the precursor ion **1f** and three of its fragment ions are all detected within an *m/z* window as narrow as one unit. As observed for ions **1a–e**, and to preserve its three aromatic imidazolium ion rings, **1f** dissociates (Figure S3 in the Supporting Information) by the cleavage of its CH_2-CH_2 bridge (a process that is exothermic by −10.9 kcal mol^{-1}) to form a unique pair of two distonic ions: the α-distonic monoradical monocation **2a** of *m/z* 96.07 (also formed from ions **1a–d**) and an unprecedented type of ion: the α-distonic monoradical diimidazolium ion **5** of *m/z* 95.56 (Figure 2).

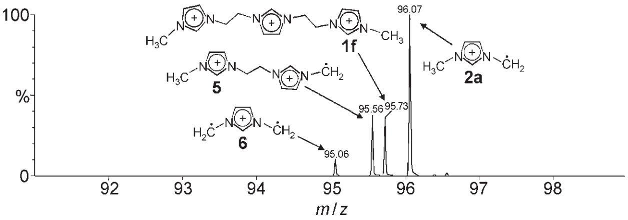

Figure 2. ESI tandem mass spectrum for CID of the triimiazolium ion **1f**.

The structural assignments of the three charged radicals **2**, **5**, and **6** of different types formed from the trication **1f** were corroborated when they were isolated and dissociated (Figure S3 in the Supporting Information). To form these fragment ions in the ESI source, the energy (cone potential) used for sampling ion **1f** into the mass spectrometer was increased so as to cause dissociation (in-source CID). As can be easily rationalized from their structures, the singly charged radical **2a** loses mainly an H atom, the doubly charged radical **5** of *m/z* 95.56 dissociates to ions **2a** and **6**, whereas the singly charged diradical **6** dissociates mainly by CH_3 loss.

Figure 3 shows the B3LYP/6-31G(d,p)[38–40] optimized structures and spin densities calculated for **2a**, **5**, and **6**. Note that the spin densities are highly concentrated on the α-methylene groups, which indicates a pronounced charged radical nature. The calculations on the precursor ions **1a–f** and product ion **5** also show that intramolecular repulsion of the two (or three) positively charged imidazolium ion rings causes negligible stretching of the $(CH_2)_n$ chains (for more details see the Supporting Information).

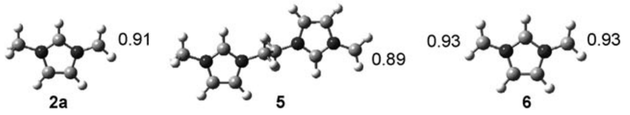

Figure 3. B3LYP/6-31G(d,p) optimized structures and spin densities at the α-methylene groups of the charged (di-)radicals **2a**, **5**, and **6**.

The group of three charged radicals of different types **2a**, **5**, and **6** formed from the triimidazolium ion **1f** is unique in several ways; it not only provides access to different and new types of gaseous charged (di-)radicals but also allows, from the same precursor and the same experimental conditions, the formation, isolation, and comparison of the intrinsic reactivity in gas-phase reactions typical of radicals of three correlated species. These studies involving this and similar groups of ions would allow the evaluation of the influence of the charged state of the "MS handle" on the kinetics and outcome of gas-phase reactions of multiply charged[41,42] (di-)radicals. Figure 4 illustrates such studies.

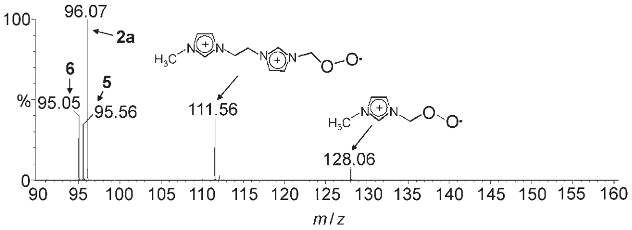

Figure 4. ESI tandem mass spectrum for simultaneous ion/molecule reactions of ions **2a** of *m/z* 96.07, **5** of *m/z* 95.56, and **6** of *m/z* 95.05 with O_2 (32 Da).

To collect this product-ion mass spectrum, the three ions **2a**, **5**, and **6** where isolated concomitantly by Q1 selection (one *m/z*-wide selection window) and allowed to react with the diradical oxygen molecule. O_2 was selected because it has been shown to add readily to several charged radicals.[43,44] The singly charged monoradical **2a** of *m/z* 96.07 is found to react to a modest extent to form the O_2 addition product of *m/z* 128.06 (about 10% conversion into product) whereas the doubly charged monoradical **5** of *m/z* 95.56 reacts with O_2 much more readily (about 55% conversion into product) to form the O_2 adduct of *m/z* 111.56 (Figure 4 and Scheme S5 in the Supporting Information). This finding indicates that polar effects play an even greater role in the reactivity of doubly charged radicals, than in singly charged (di-)radicals.[2] The singly charged diradical **6** of *m/z* 95.05 is found, in contrast, to be practically inert towards single (*m/z* 127.05) or double (*m/z* 159.05) addition of O_2. The reduced reactivity of **6** as a diradical is likely to result from its closed-shell singlet ground state,[45] similar to what was observed for singly charged (pyridinium ion) diradicals.[12] Note that the addition of O_2 to **5** is a rare example of a bond-forming reaction involving a molecular dication with maintenance of the twofold charge.[41,42]

We have shown, therefore, that α-distonic monoradical diimidazolium ions (**5**), α,α-distonic diradical monoimidazolium ions (**6**), and α-distonic monoradical monoimidazolium ions (**2a–c**), as well as homologous but nascent β-(**3**) and γ-distonic (**4**) ions, can be formed by dissociation of gaseous $(CH_2)_n$-bridged di- and triimidazolium ions (**1a–f**). Groups of "packed" (*m/z* values within a narrow window of one unit) multiply charged (di-)radicals (**2a**, **5**, and **6**) can also be formed and selected concomitantly from the dissociation of triply charged imidazolium ions (**1f**) and their analogues. These ions function as unique probes for the investigation of the intrinsic (solvent- and counterion-free) reactivity of gaseous multiply charged (di-)radicals. We are currently applying this novel strategy to form a variety of gaseous multiply charged (di-)radicals, from multiply charged imidazolium ions and their analogues with a wide range of charge states (tetracations and higher) and short and long $(CH_2)_n$ bridges.

Experimental Section

ESI mass and tandem mass spectra in the positive ion mode were acquired using a Waters Micromass (Manchester, UK) QTOF instrument with ESI-QTOF configuration having 5000 mass resolution and less than 50 ppm mass accuracy in the TOF mass analyzer. The following typical operating conditions were used: 3 kV capillary voltage, 40 V cone voltage, and desolvation gas temperature of 100°C. ESI-MS/MS analyses were performed using 15–30 eV collision-induced dissociation (CID) of mass-selected ions with argon. Selection was generally performed by Q1 using a unitary *m/z* window, and collisions were performed in the rf-only hexapole collision cell, followed by mass analysis of product ions by the high-resolution orthogonal-reflectron TOF analyzer. Reactions were performed by mass selection of the ion of *m/z* 95.73 and through low-energy (about 3 eV) collisions in the rf-only hexapole collision cell with oxygen.

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