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Gas-phase Reactions of the 4-Dehydroanilinium Ion and its Isomers

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Collisional activation of protonated 2-, 3- and 4-iodoanilines in a dual-cell Fourier transform ion cyclotron resonance spectrometer results in the loss of an iodine atom to yield product ions of *m/z* 93. Ion–molecule reactions and energy-resolved collision-activated dissociation experiments demonstrate that these three ions are structurally distinct, and that they are distonic ions. The ions were identified as the 2-, 3- and 4-dehydroanilinium ions, the high-energy distonic isomers of ionized aniline. The reactivity of these charged phenyl radicals is largely analogous to that of the phenyl radical. For example, the 4-dehydroanilinium ion abstracts an iodine atom from isopropyl iodide, a thiomethyl group from dimethyl disulfide, and adds to cyclohexene. Comparison of the collision-activated dissociation product abundances of the ion formed upon CH_3S abstraction to that of a reference ion suggests that bond formation occurs at the formal radical site upon CH_3S abstraction. Hence, the reaction probably occurs via a simple radical abstraction mechanism similar to that of the phenyl radical. However, some neutral reagents react with the charge site of the 4-dehydroanilinium ion, and yet others undergo a two-step reaction sequence involving the charge site in addition to the radical site. For example, certain basic molecules induce isomerization of the 4-dehydroanilinium ion to the significantly more stable ionized aniline by deprotonating the charge site and then donating a hydrogen atom to the radical site.

INTRODUCTION

The direct observation of free radicals is possible by two well established techniques, electron paramagnetic resonance (EPR) spectroscopy[1] and chemically induced dynamic nuclear polarization (CIDNP) spectroscopy.[2] Although suitable for the structural characterization of free radicals, these techniques lack the versatility of some other spectroscopic methods. For example, laser flash photolysis techniques[3] are capable of generating relatively high concentrations of free radicals and therefore enable the examination of the reaction kinetics of these radicals. However, these latter studies are limited to radicals that either contain a chromophore or that form a chromophore-containing product.[4] Frequently, none of the techniques mentioned above is suitable for the examination of a free-radical reaction, and indirect methods such as competition experiments must be employed.[5,6]

In contrast to the difficulties encountered when directly monitoring reactions of free radicals, the reactions of ionic species are easily studied using mass spectrometry. As a result, the field of gas-phase ion chemistry has made tremendous contributions to our understanding of the properties and reactivity of ionic species.[7] Recent research has revealed that certain radical cations react with neutral reagents in a manner that resembles the reactions of free radicals rather than ions. Specifically, the spatially separate charge and radical sites that are present in distonic ions[8] provide these ions with the capability of reacting at either of the two reactive sites.[9] These species might provide a tool to study radical reactions by using the powerful method of mass spectrometry.

Ideally, a distonic ion suitable for modeling free-radical reactions will contain a completely inert charge site, which would serve as a 'handle' for the manipulation and detection of the species in the mass spectrometer. Recently, we have identified a few distonic ions, which, for the most part, undergo reactions at the odd-spin site. For example, all of the ion–molecule reactions of the α-distonic ion $(CH_3)_2S^+{-}CH_2^{\cdot}$ seem to be initiated by the odd-spin site.[10] However, although the charge site of this distonic ion is relatively inert, it does influence the radical reactions by a strong electron-withdrawing effect.

In order to minimize the role that the charge site plays in the radical-type reactions of distonic ions, it is desirable to study the reactivity of distonic ions that have an inert charge site far removed from the radical site. We recently reported the synthesis of such a distonic ion, the 4-dehydroanilinium ion formed by collision-activated dissociation of protonated 4-iodaniline (Scheme 1).[11] We describe here in detail the synthesis, characterization and reactivity of this ion together with its isomers, the 2- and 3-dehydroanilinium ions.

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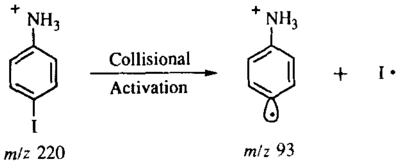


Scheme 1

EXPERIMENTAL

Ketene and ketene-d_2 were prepared by the pyrolysis of acetone and acetone-d_6, respectively. All other reagents were purchased from commercial suppliers and used as received or purified by standard methods. The iodoanilines were recrystallized twice from dichloromethane–pentane prior to use.

All experiments were performed in a dual-cell Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (FTMS Model 2001, Extrel-FTMS, Waters) that has been described in detail.[12] Briefly, the instrument consists of a rectangular cell that is partitioned into two 4.7 cm cubic regions by a common wall, the conductance limit plate. Each side of the dual cell is differentially pumped by a turbomolecular pump. The cell is housed within a 3 T superconducting magnet that was operated at 2.2 T for the experiments performed here.

The primary ions were generated by electron impact ionization and trapped in either side of the dual cell by applying a 2.0 V trapping potential to the plates perpendicular to the magnetic field lines, including the conductance limit plate. Aniline and other neutral reagents, with the exception of the iodoanilines, were introduced into the desired side of the dual cell at a nominal pressure of *ca.* 1×10^{-7} Torr (1 Torr = 133.3 Pa) through Extrel-manufactured batch inlet systems equipped with a variable leak valve. The neutral molecules were subjected to electron impact ionization or isobutane chemical ionization (70 eV electron energy, 4–10 μA filament current, 30 ms beam time).

A solids probe maintained at room temperature was used to introduce the iodoanilines into one side of the dual cell at a nominal pressure of 2×10^{-7} Torr. For these experiments, an approximately equal pressure of isobutane was introduced into the same side of the cell by means of a Varian Model 951-5106 leak valve. The mixture of iodoaniline and isobutane was subjected to electron impact ionization (70 eV beam energy, 4 μA filament current, 30 ms beam time). The molecular ion of the iodoaniline (*m/z* 219) was always the most abundant ion under these conditions. The amount of this ion was minimized by continuously ejecting it out of the cell during the ionization event through the application of a radio-frequency pulse at a frequency corresponding to *m/z* 219. Protonation of neutral iodoaniline was accomplished by allowing the remaining ions to react with iodoaniline for 700 ms.

The product ions formed as described above were transferred into the other side of the dual cell by grounding the conductance limit plate for 100–140 μs; this allowed the ions to pass through a 2 mm hole in the center of this plate. The transferred ions were cooled by collisions with argon that was either pulsed into the instrument at a maximum pressure of about 1.5×10^{-5} Torr or that was present at a stationary pressure of 3×10^{-7}–5×10^{-7} Torr. The ion of interest was isolated by ejecting all other ions from the cell by using a series of single-frequency pulses and stored waveform inverse Fourier transform (SWIFT) waveforms generated by using an Extrel SWIFT module.[13] After isolation, the ion was either allowed to react with neutral reagents pulsed into the instrument or present at a stationary pressure of 1×10^{-7}–3×10^{-7} Torr or they were subjected to collision-activated dissociation, as described below. Ions were excited for detection by using a radiofrequency sweep (124 V_{p-p} amplitude, 2.7 MHz bandwidth and 3.0 kHz μs^{-1} sweep rate), or by using a SWIFT waveform.

Collision-activated dissociation of protonated iodoanilines was performed by translationally exciting the ions by either of two methods in the presence of a static pressure of 3×10^{-7}–5×10^{-7} Torr of argon. The first method of excitation made use of a 3.5 V_{p-p} radiofrequency pulse for a duration of 450–600 μs at the cyclotron frequency of the ion. After the excitation, a delay time of 1–1.5 s was used to provide ample time for collisions to occur and to facilitate cooling of the dissociation products. The yield of the product ion (*m/z* 93) arising by loss of iodine was optimized by varying the strength and duration of the radiofrequency pulse and the pressure of the collision gas. Maximum amounts of the product were obtained when the protonated iodoanilines were excited to a translational energy of 50 eV in the presence of 3×10^{-7} Torr of argon. Typically, 30% of protonated 4-iodoaniline could be converted into the product ion of *m/z* 93 under these conditions. Slightly higher yields of the product ion of *m/z* 93 were obtained when the protonated iodoanilines were collisionally activated by the sustained off-resonance irradiation (SORI) technique.[14] This excitation method has been developed by Jacobson and co-workers.[14] For this method, the protonated iodoanilines were irradiated for 1.5–2 s at a frequency 0.5–1.0 kHz higher than the cyclotron frequency of the ion. Again, a delay time of 1–1.5 s was used after the excitation. Typically, the intensity of the product ion of *m/z* 93 was greater than 40% of the measured abundance of the protonated iodoanilines before irradiation. The product ion of *m/z* 93 was isolated by ejecting all other ions from the cell as described above. The isolated ions were allowed to undergo reactions with neutral reagents by adding the reagents into the cell by means of a pulsed valve assembly. A variable reaction time of 3–5 s was used prior to detection of the ions.

Energy-resolved collision-activated dissociation experiments were performed by on-resonance excitation of the ions followed by a 100 ms delay time. The translational energy of the ion was calculated according to an equation that takes into account the electric field produced within a cubic cell.[15] For these experiments, the ions of *m/z* 93 were synthesized from the iodoanilines by the SORI technique with an argon collision gas pressure of 1×10^{-7} Torr. This lower gas pressure was necessary to minimize the effects due to multiple collisions of the ion during the energy-resolved collision-activated dissociation experiment.

RESULTS AND DISCUSSION

Synthesis and structural characterization of the 4-dehydroanilinium ion

Protonated 4-iodoaniline was selected as a possible precursor for a distonic ion with the charge site separated from the radical site by three heavy atoms. This molecule is almost certainly nitrogen-protonated under the conditions employed since aniline has been shown to be nitrogen-protonated under the same conditions,[16] and earlier studies[17] demonstrate that only electron-donating substituents at the *meta* position tend to favor ring protonation of substituted anilines. The C—I bond in iodobenzene is relatively weak.[18] Therefore, protonated 4-iodoaniline can be expected to lose an iodine atom readily when energized.

Protonated 4-iodoaniline was generated by isobutane chemical ionization in one side of the dual cell, transferred into the other side, collisionally cooled with argon [Fig. 1(a)] and isolated by ejecting all other ions from the cell [Fig. 1(b)]. Upon the following collisional excitation the protonated 4-iodoaniline dissociates by the expected iodine atom loss to produce an abunda ion of *m*/*z* 93 [Fig. 1(c)]. This ion was isolated [Fi 1(d)] and allowed to react with a variety of neutr reagents added to the cell with a pulsed valve assembl (Table 1, Fig. 2).

The ion of *m*/*z* 93 reacts with dimethyl disulfide b abstraction of a thiomethyl radical [Fig. 2(a), Table 1] Only distonic radical cations are known to undergo thi reaction.[11] Hence, the ion of *m*/*z* 93 is concluded tc have spatially separated radical and charge sites. The

Table 1. Reactions of the distonic ion of *m*/*z* 93 with neutral reagents

Reagent	Products (abundance)	Reaction
Dimethyl disulfide	*m*/*z* 140 (100%)	$CH_3S^{\bullet}$ abstraction
2-Iodopropane	*m*/*z* 220 (100%)	$I^{\bullet}$ abstraction
Pyridine	*m*/*z* 80 (100%)	Proton transfer
Cyclohexene	*m*/*z* 94 (18%)	$H^{\bullet}$ transfer
	m/*z* 174 (25%)	Adduct − $H^{\bullet}$
	m/*z* 175 (57%)	Adduct
Ketene	*m*/*z* 107 (7%)	H_2C: abstraction
	m/*z* 120 (93%)	Adduct − $H_3C^{\bullet}$

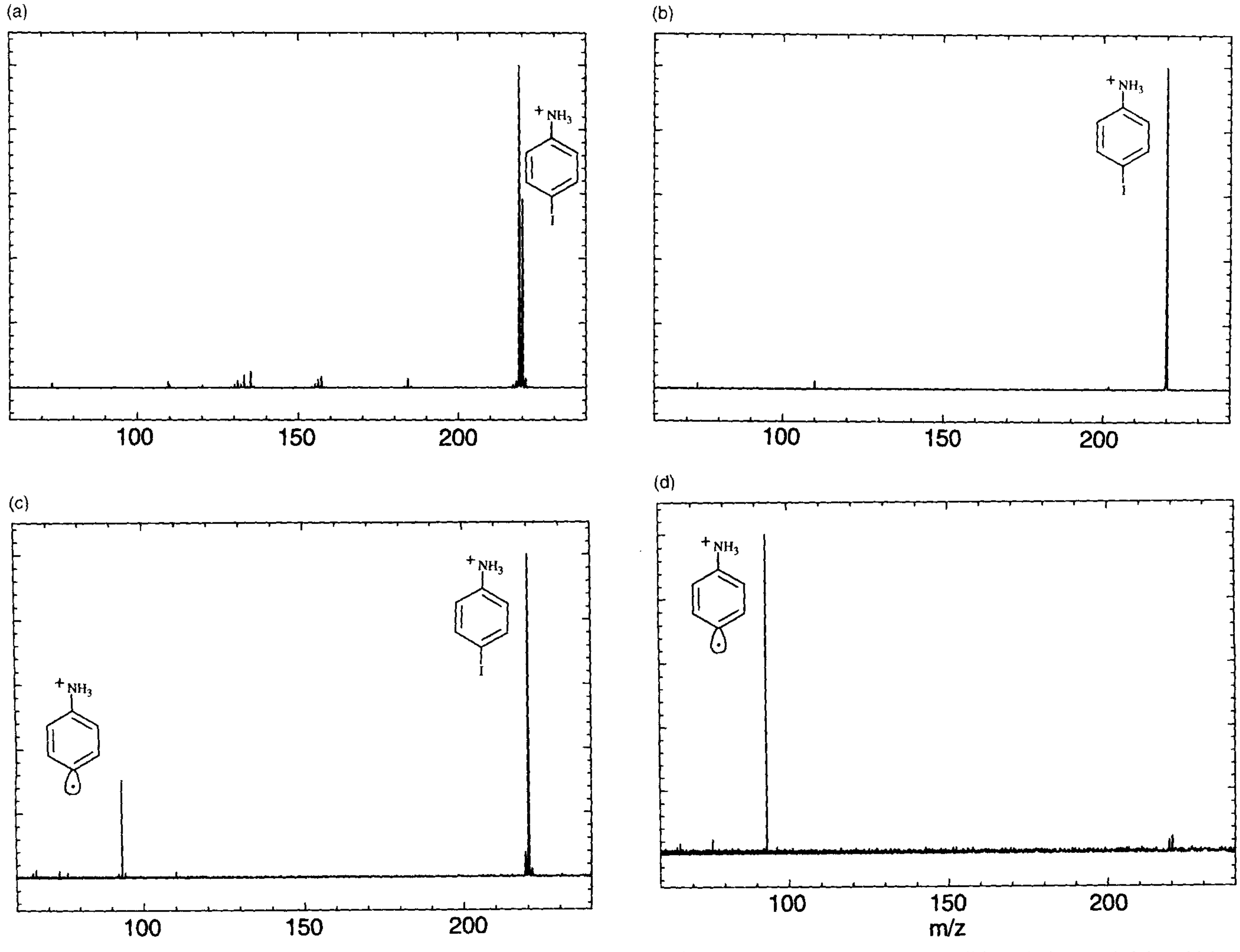


Figure 1. (a) Chemical ionization mass spectrum of 4-iodoaniline with isobutane as the reagent gas. (b) Isolation and (c) collision-activated dissociation of protonated 4-iodoaniline. (d) Isolation of the 4-dehydroanilinium ion.

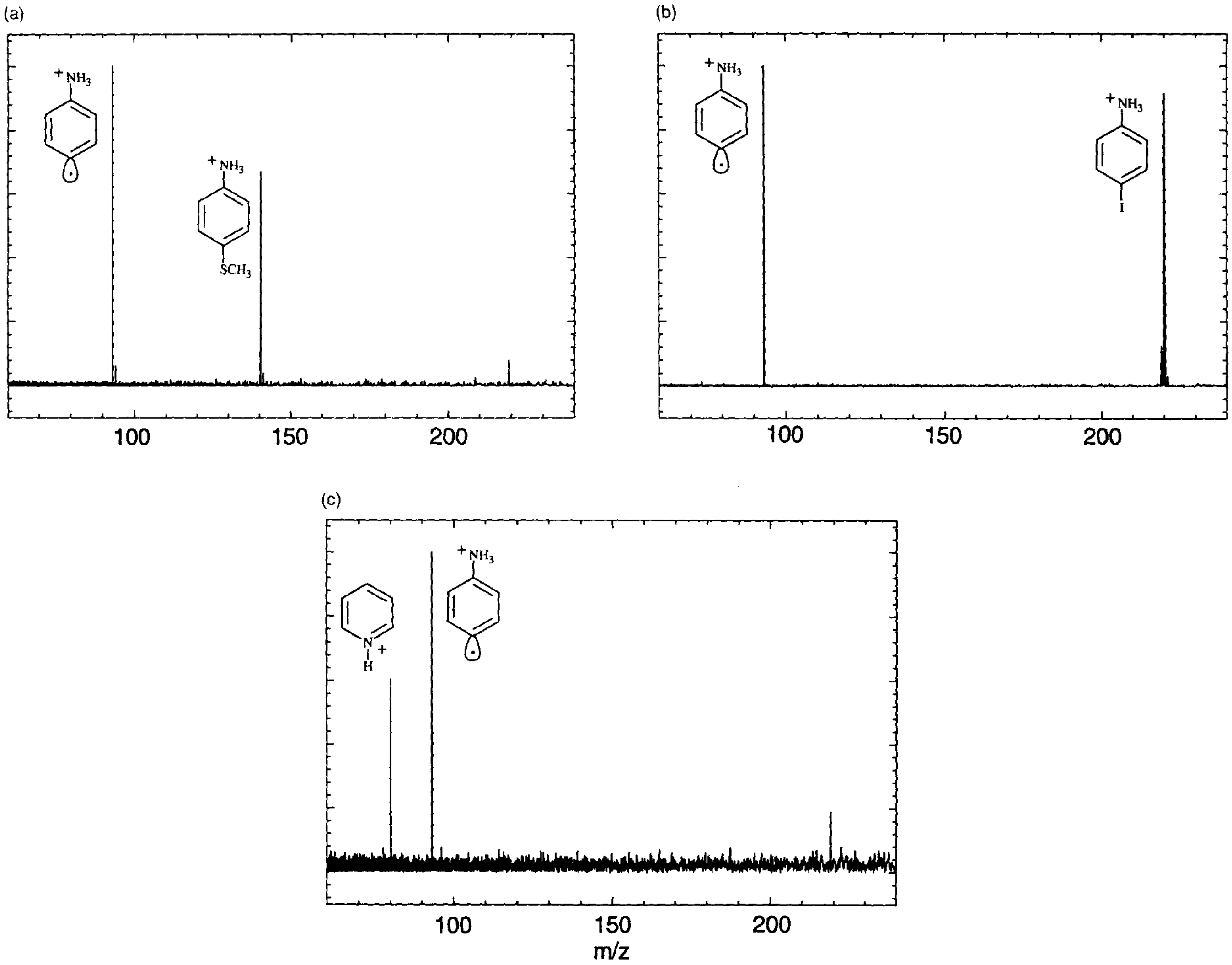


Figure 2. Reaction of the 4-dehydroanilinium ion with (a) dimethyl disulfide, (b) 2-iodopropane and (c) pyridine.

observation of iodine atom abstraction from 2-iodopropane [Fig. 2(b), Table 1] provides further evidence in support of a distonic structure since iodine abstraction is common for distonic ions with a carbon radical center, e.g. $(CH_3)_2S^+—CH_2^{\cdot}$ and $^{\cdot}CH_2CH_2CH_2CO^+$.[10,20] Finally, the ion of *m/z* 93 readily protonates pyridine, a finding that demonstrates the presence of acidic protons in the ion [Fig. 2(c), Table 1). In sharp contrast, ionized aniline does not protonate pyridine. In fact, ionized aniline is unreactive toward all the reagents mentioned above. Hence, the results presented here conclusively demonstrate that the fragment ion of *m/z* 93 of protonated 4-iodoaniline is a distonic isomer of ionized aniline.

Synthesis and structural characterization of the 2- and 3-dehydroanilinium ions

The data described above are consistent with the 4-dehydroanilinium structure for the ion of *m/z* 93 formed from protonated 4-iodoaniline. However, these experiments alone do not unambiguously rule out the possibility that the 4-dehydroanilinium ion exists in equilibrium with the two other distonic forms of ionized aniline, the 2- and 3-dehydroanilinium ions. In order to address this issue, ions expected to be the distonic ring isomers of the 4-dehydroanilinium ion were prepared by collision-activated dissociation of protonated 2-iodoaniline and protonated 3-iodoaniline, respectively. Both of these product ions abstract a thiomethyl group from dimethyl disulfide, which demonstrates that the ions have distonic structures. Both ions also abstract an iodine atom from 2-iodopropane, as was observed for the 4-dehydroanilinium ion.

The three distonic ions derived from the *ortho*, *meta* and *para* isomers of protonated iodoaniline cannot be distinguished based on the ion–molecule reactions discussed above. Hence, the ions were subjected to energy-resolved collision-activated dissociation. As seen in Fig. 3, the three ions display different dissociation product distributions over the energy range studied. The most striking feature of these data is that the distonic ion believed to be the 2-dehydroanilinium ion dissociates to produce an ion of *m/z* 66 as the exclusive product at low energies. This product ion was verified to have the elemental composition C_5H_6; hence it is likely to have

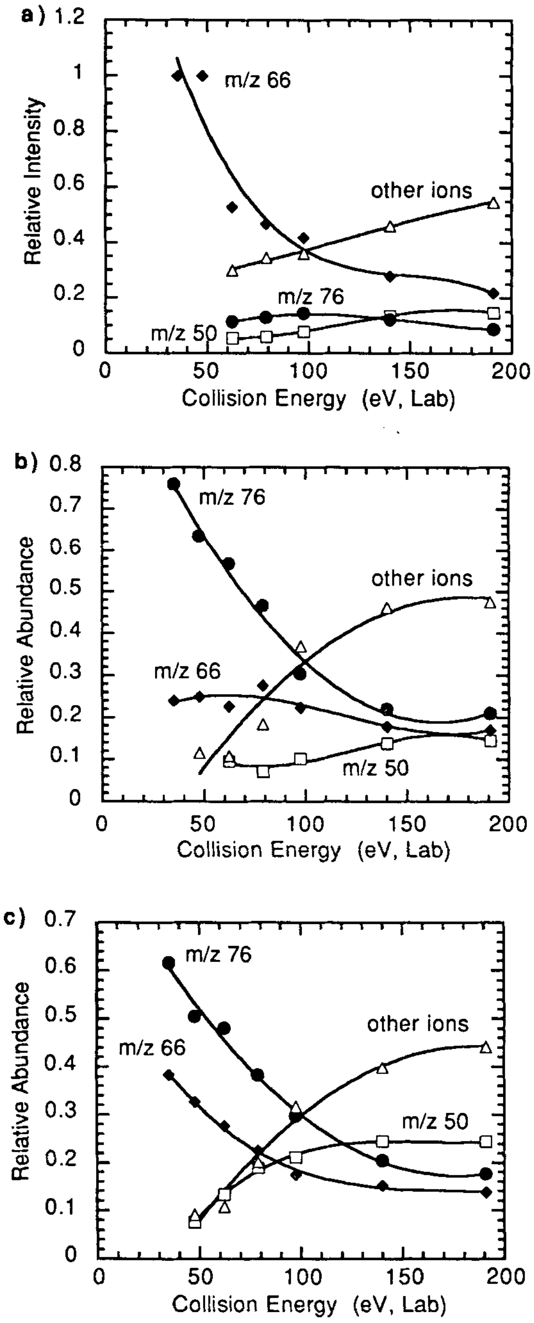


Figure 3. Energy-resolved collision-activated dissociation products for (a) the 2-dehydroanilinium ion, (b) the 3-dehydroanilinium ion and (c) the 4-dehydroanilinium ions as a function of laboratory collision energy. (□) *m/z* 50; (◆) *m/z* 66; (●) *m/z* 76; (△) all other ions.

the structure of ionized cyclopentadiene. This fragment ion is probably formed[21] by loss of HNC, in analogy to the dissociation of ionized aniline.[21] In sharp contrast to the 2-dehydroanilinium ion, the ions presumed to be the 3- and 4-dehydroanilinium ions lose NH_3 at low collision energies (to yield an ion of *m/z* 76 with the verified elemental composition C_6H_4). The latter two ions can be distinguished from each other on the basis of the relative abundances of several product ions [Fig. 3(b) and (c)]. These results demonstrate that the three ions of *m/z* 93 have different structures and that equilibration does not occur between the isomers. This conclusion is not without precedence since 1,2-hydrogen atom transfers in neutral hydrocarbon radicals are known to be associated with high barriers.[22]

Collision-activated dissociation of ionized aniline (Fig. 4) produces several ions with the same *m/z* values as those obtained from the distonic isomers. In particular, the ion of *m/z* 66 is the most abundant product at low collision energies. In contrast to the distonic isomers, however, ionized aniline does not dissociate by loss of NH_3. This observation provides an independent demonstration that the ions generated by collisional activation of the protonated iodoanilines are structurally different from ionized aniline.

Comparison of the reactivity of the 4-dehydroanilinium ion and the phenyl radical

Neutral phenyl radicals are known to abstract a thiomethyl group from dimethyl disulfide.[23] The mechanism of this reaction is believed to involve an intermediate in which the radical adopts a collinear arrangement with the sulfur atom and the leaving group.[23c,24] A similar mechanism is likely to be operative in the reaction between the 4-dehydroanilinium ion and dimethyl disulfide. Direct involvement of the charge site during the abstraction is not possible because the ammonium cation is located at the opposite end of the phenyl ring. Hence, the occurrence of thiomethyl abstraction demonstrates that this charged radical is capable of reacting at the radical site without the direct involvement of the charge site. Collision-activated dissocation of the isolated thiomethyl abstraction product suggests that this product has the expected 4-(methylmercapto)-anilinium skeleton. The dissociation is dominated by the loss of $CH_3S^\bullet$ (*m/z* 93), accompanied by a less favored loss of $CH_3^\bullet$ (*m/z* 125; *m/z* 93 corresponds to about 70% and *m/z* 125 to about 30% of the product ion distribution at 65 and 125 eV laboratory collision energies). A reference ion, protonated 4-(methylmercapto)aniline, yields an identical dissociation product distribution. These findings provide support for the proposal that CH_3S abstraction by the 4-dehydroanilinium ion occurs via a simple radical abstraction mechanism.

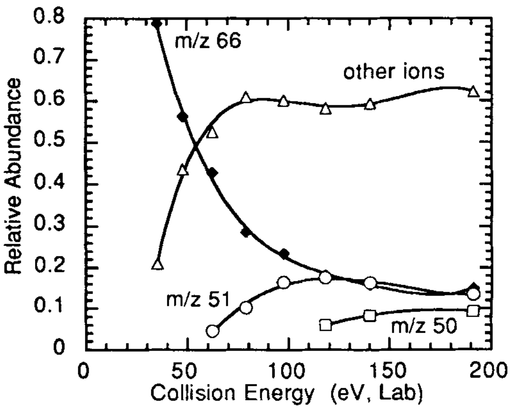


Figure 4. Energy-resolved collision-activated dissociation products of ionized aniline as a function of laboratory collision energy. (□) *m/z* 50; (○) *m/z* 51; (◆) *m/z* 66; (●) *m/z* 76; (△) all other ions.

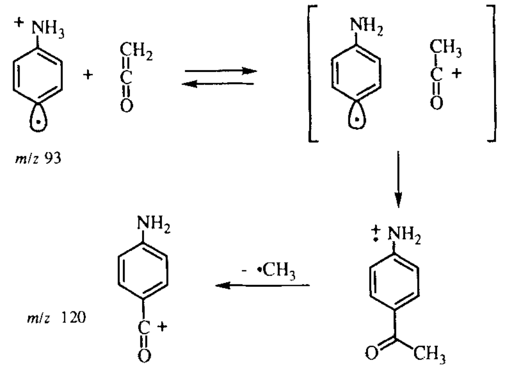
Alkyl iodides are known to trap free radicals through a mechanism that is similar to the mechanism for dimethyl disulfide.[25] The relatively weak carbon–iodine bond in these reagents is responsible for the high reactivity toward free radicals. In particular, it is well known that phenyl radicals abstract iodine atoms from alkyl iodides.[25a,26] Hence, the abstraction of an iodine atom from 2-iodopropane by the 4-dehydroanilinium ion provides another example of reactivity resembling that of the phenyl radical. Again, the reaction must proceed without direct involvement of the charge site. It is noteworthy that some aliphatic distonic ions, such as $^{\bullet}CH_2CH_2CH_2CO^+$,[20] react with alkyl iodides via pathways that are unusual for neutral alkyl radicals, e.g. alkyl radical abstraction. These reactions have been rationalized on the basis of a charge-catalyzed mechanism wherein the alkyl iodide initially bonds to the charge site, and this is followed by radical reaction via a cyclic transition state.[9c,20] This sort of mechanism is not accessible for the rigid 4-dehydroanilinium ion. Indeed, no unusual products were observed for this species.

The reaction of the 4-dehydroanilinium ion with cyclohexene (Table 1) is also a typical radical-type process. The two major product ions correspond to adduct formation and loss of a hydrogen atom from the adduct, respectively. A minor product from hydrogen atom abstraction is also observed (Table 1). The addition products are probably formed by attack of the radical site of the ion at the double bond. Similar reactivity has been reported for the distonic ion $(CH_3)_2S^+—CH_2^{\bullet}$ toward alkenes.[27]

Reactions involving the charge and the radical site of the 4-dehydroanilinium ion

The reaction of the 4-dehydroanilinium ion with ketene is of special interest since many distonic ions with a carbon radical center are known to abstract the terminal methylene group from ketene.[28] Indeed, methylene abstraction was observed also for the 4-dehydoanilinium ion. However, the most abundant product ion does not correspond to methylene abstraction but to loss of a methyl radical from the collision complex. This interesting reaction has not been observed for other distonic ions.[28] Isomerization of the 4-dehydroanilinium ion to ionized aniline within the collision complex does not explain the observed reactivity, since ionized aniline is unreactive toward ketene.

A conceivable mechanism for the dominant reaction channel with ketene involves initial deprotonation of the 4-dehydroanilinium ion (the proton binding energy is probably close to the proton affinity of aniline,[18] 209.5 kcal mol^{-1} (1 kcal = 4.184 kJ) by ketene (proton affinity[18] 198 kcal mol^{-1}), followed by radical addition to the carbonyl carbon of protonated ketene and subsequent loss of $CH_3^{\bullet}$ (Scheme 2). Examination of the reaction with $CD_2{=}C{=}O$ supports the proposal that the initial encounter of the 4-dehydroanilinium ion and ketene involves reversible deprotonation. This reaction leads to CD_2 abstraction and to the loss of a methyl radical in about the same ratio as for ketene. The latter reaction is associated with slow hydrogen–deuterium exchange between deuterated ketene and the 4-dehydroanilinium ion, as indicated by the production of ions from loss of CH_2D (10%) and from loss of CHD_2 (90%).

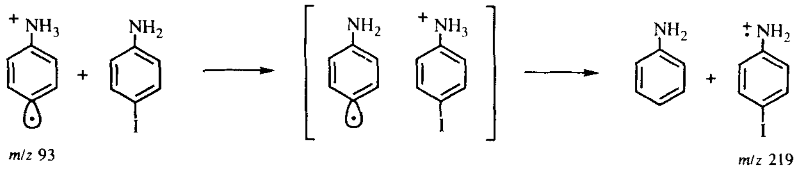


Scheme 2

The ketene reaction discussed above suggests that certain neutral reagents are able to undergo a two-step reaction sequence involving both the charge and the radical sites of the 4-dehydroanilinium ion. Further evidence in support of the occurrence of such processes is provided by the finding that certain bases induce isomerization of the 4-dehydroanilinium ion to ionized aniline.

Many of the reactions of the 4-dehydroanilinium ion do not go to completion, i.e. a proportion of the reactant ions appears unreactive in many experiments (the same is true for the 2- and 3-dehydroanilinium ions). This finding suggests that although the 4-dehydroanilinium ion is structurally distinct from ionized aniline prior to collisions with a neutral reagent, the collisions induce a partial isomerization of the ion to ionized aniline which is unreactive toward the reagents studied. Further, the 4-dehydroanilinium ion was observed to abstract an electron from neutral 4-iodoaniline. However, the energy released on addition of an electron to a phenyl radical is too low (about 1 eV[18]) to account for this reaction as a simple electron transfer. Isomerization of the 4-dehydroanilinium ion to ionized aniline prior to the reaction is a more likely alternative since ionized aniline was found to readily abstract an electron from 4-iodoaniline. It is also conceivable that the 4-dehydroanilinium ion initially reacts with 4-iodoaniline by proton transfer as shown in Scheme 3. Hydrogen atom transfer then occurs from protonated iodoaniline to the phenyl radical within the collision complex. Dissociation of the collision complex yields neutral aniline and ionized 4-iodoaniline as the final products (Scheme 3). A similar mechanism is believed to be operative in the base-catalyzed isomerization of the sulfur-containing distonic ion, $H_2S^+—CH_2^{\bullet}$, to ionized methanethiol.[29]

Assuming that the C—H bond enthalpy at the *para* position in protonated aniline is similar to the C—H bond enthalpy in benzene (113.5 ± 0.5 kcal mol^{-1}),[30] and using the known heat of formation of 177 kcal mol^{-1} for protonated aniline,[18] a heat of formation of 238 kcal mol^{-1} is estimated for the 4-dehydroanilinium ion. The heat of formation of ionized aniline is 198 kcal mol^{-1}.[18] Hence, the distonic ion is about 40 kcal mol^{-1} higher in energy than the conventional ion, and



Scheme 3

the rearrangement to ionized aniline has a significant driving force.

CONCLUSIONS

The radical-type atom and group abstraction reactions observed for the 4-dehydroanilinium ion demonstrate that reactions can take place at the odd-spin sites of distonic ions with minimal direct involvement of the charge site. Therefore, distonic ions derived from substituted benzene are promising candidates for the study of radical reactions in the gas phase through the use of mass spectrometry. However, the 4-dehydroanilinium ion itself is a Brønsted acid, and some reactions take place at the charge site rather than the radical site of this species. Furthermore, some neutral molecules react with the charge site in addition to the radical site within the same collision complex. In some instances, this results in isomerization of the 4-dehydroanilinium ion to the significantly more stable ionized aniline.

Acknowledgements

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