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The 4-Dehydroanilinium Ion: A Stable Distonic Isomer of Ionized Aniline

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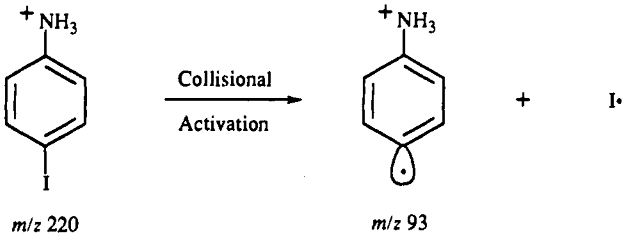
Distonic radical ions are reactive intermediates with a spatially separated radical and charge site.[1] Depending on their structure, these ions may exhibit either ionic or radical-type reactivity.[2] Recently, our research has focused on the chemical properties of distonic ions that react preferentially at the radical center because these ions may provide a tool to study free-radical chemistry in the gas phase by using mass spectrometry.[3] The reactivity of several α-distonic ions, such as $(CH_3)_2S^+{-}CH_2^{\cdot}$,[4] has been studied. These ions, however, have the charge site adjacent to the radical center, which makes it difficult to determine the role of the charge site in the radical-type reactions of these ions.[4] Distonic ions with more than one heavy atom separating the charge and radical sites have also been examined. However, the ions studied to date have flexible structures which do not prohibit a neutral reagent from interacting with the charge and radical centers simultaneously.[5]

As a result of the above considerations, we are in the process of examining the chemical properties of distonic ions which have the reactive centers located at opposite ends of a rigid molecular framework. One possible way to form such a distonic ion involves collisional activation of an even-electron ion that contains a weak bond in a position remote from the charge site. Herein we describe the generation of the 4-dehydroanilinium ion, a stable distonic isomer of ionized aniline, by collision-activated dissociation of protonated 4-iodoaniline. This novel distonic ion presents an opportunity to study the reactivity of aryl radicals in a mass spectrometer, and some of our initial results are outlined here.

The compound 4-iodoaniline was protonated in one side of a dual-cell FT-ICR mass spectrometer[5,6] under chemical ionization conditions with isobutane as the reagent gas (Figure 1a).[7,8] The resulting ion (m/z 220) was transferred into the other cell, and all other ions were ejected (Figure 1b). When the protonated 4-iodoaniline was translationally excited and allowed to undergo multiple low-energy collisions with argon,[9,10] loss of atomic iodine occurred, to yield an ion of m/z 93 (Figure 1c). This product ion reacts with dimethyl disulfide by abstraction of a thiomethyl radical (Figure 1d,e). Since thiomethyl abstraction from dimethyl disulfide occurs for distonic ions and not for conventional radical cations,[4a] the formation of this product ion indicates a distonic reactant ion. This distonic ion undergoes other radical reactions, as well. For example, reaction of the ion with 2-iodopropane results in iodine atom abstraction. On the other hand, deprotonation occurs when the ion is allowed to react with pyridine. This finding demonstrates that the ion contains acidic protons. Ionized aniline is unreactive toward dimethyl disulfide, 2-iodopropane, and pyridine. Therefore, the ion generated by collision-activated dissociation of protonated 4-iodoaniline is structurally different from ionized aniline.

Scheme 1



The above observations are consistent with the formation of the 4-dehydroanilinium ion upon collisional activation of protonated 4-iodoaniline (Scheme 1). However, these experiments alone cannot rule out the possibility that the initially generated 4-dehydroanilinium ion rearranges to *a different distonic ion* during or after generation. Therefore, 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. The product ions abstract a thiomethyl group from dimethyl disulfide and hence are concluded to have distonic structures. These ions can be differentiated from the 4-dehydroanilinium ion by energy-resolved collision-activated dissociation. At low excitation energies, loss of HNC yields the major product ion for the 2-dehydroanilinium ion while loss of NH_3 is the predominant fragmentation pathway for the 3- and 4-dehydroanilinium ions. The latter two ions can be distinguished from each other on the basis of the production of different abundances of a fragment ion of m/z 50 ($C_4H_2^{\cdot+}$) at high collision energies. These results demonstrate that the 4-dehydroanilinium ion is stable toward intramolecular hydrogen shifts, in agreement with literature results on neutral hydrocarbon radicals. 1,2-Hydrogen atom transfer in these radicals is generally associated with a high barrier.[11] Nevertheless, the stability of the 4-dehydroanilinium ion toward rearrangement to ionized aniline is quite remarkable as the heat of formation of the distonic ion is predicted to be 39 kcal/mol higher than the heat of formation of ionized aniline.[12,13]

In summary, we have shown that collision-activated dissociation of the protonated 2-, 3-, and 4-iodoanilines yields the three distonic isomers of ionized aniline and that these ions are stable toward isomerization. The 4-dehydroanilinium ion, another rare example of a stable δ-distonic ion,[3,14] is of special interest since reactions occurring at the odd-spin site of this ion must take place with minimal direct involvement of the charge site. Indeed, the observed radical-type reactivity of this distonic ion parallels that of the phenyl radical, providing further support for the expectation

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(7) The nominal pressure of the iodoanilines (introduced using a solids probe) as well as isobutane (leak valve) was 2×10^{-7} Torr.

(8) Protonation of 4-iodoaniline is believed to occur at nitrogen under these conditions: (a) Pollack, S. K.; Devlin, J. L., III; Summerhays, K. D.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4583–4584. (b) Summerhays, K. D.; Pollack, S. K.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4585–4586. (c) Lau, Y. K.; Nishizawa, K.; Tse, A.; Brown, R. S.; Kebarle, P. *J. Am. Chem. Soc.* **1981**, *103*, 6291–6295. (d) Karpas, Z.; Berant, Z.; Stimac, R. M. *Struct. Chem.* **1990**, *1*, 201–204.

(9) Either on-resonance excitation or sustained off-resonance excitation was used (ref 10).

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(12) Using D(C–H) of benzene as an approximate bond enthalpy for protonated aniline, ΔH_f of the distonic ion is about 237 kcal/mol.

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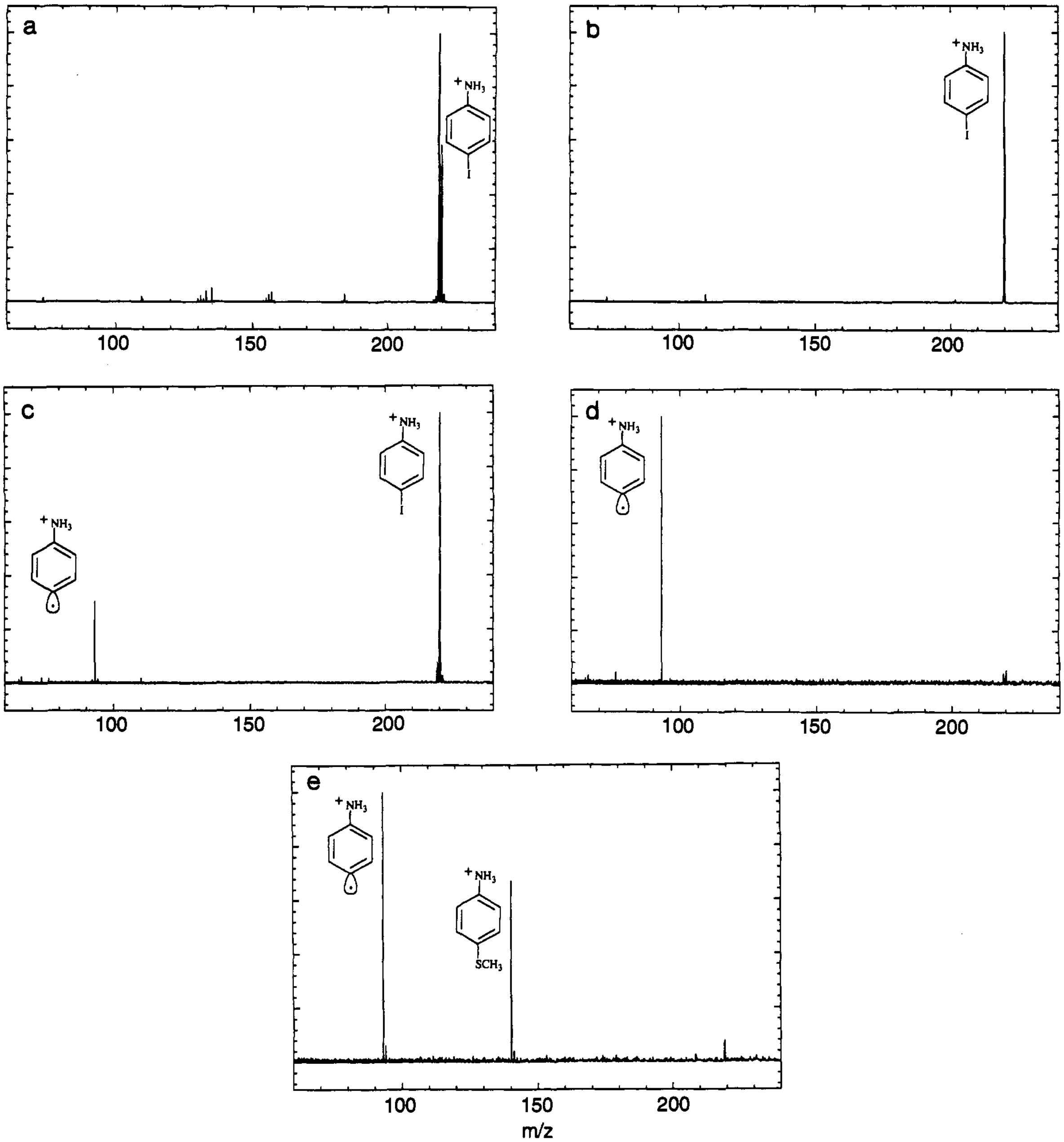

Figure 1. (a) Chemical ionization mass spectrum of 4-iodoaniline. (b) Isolation and (c) collision-activated dissociation of protonated 4-iodoaniline. (d) Isolation and (e) reaction of the fragment ion of *m/z* 93 with dimethyl disulfide.

that distonic ions may allow the mass spectrometric study of gaseous polyatomic free radicals.

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