

The β -Distonic Ion from the Reaction of Pyridine Radical Cation and Ethene: A Demonstration of High-Pressure Trapping in Fourier Transform Mass Spectrometry

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Abstract: The adduct ion formed in the reaction of pyridine radical cation and ethene exhibits different chemical reactivities and fragmentation behavior than the isomeric ethylpyridine radical cations. The most characteristic features of the adduct ion are the collisionally activated loss of C_2H_4 to give back the pyridine radical cation and the second ionization to produce a doubly charged ion. A characteristic reaction is with dioxygen to form a new adduct, which may have the structure of a distonic peroxy radical cation. The reactive site for attachment of C_2H_4 is the nitrogen atom of the pyridine, giving rise to the β -distonic ion adduct, $C_5H_5N^+-CH_2C^*H_2$, which can be differentiated from the isomeric α -distonic ion, $C_5H_5N^+-C^*HCH_3$. Formation of the β -distonic ion requires collisional stabilization, and this species cannot be directly observed under conventional Fourier transform mass spectrometry (FTMS) conditions. Incorporation of a new radiofrequency (RF)-only-mode event in FTMS allows the adduct to be formed and then to be characterized under the high-pressure conditions of two of these RF-only-mode events.

Introduction

Distonic ions are radical ions whose charge and radical sites are localized on different atoms. For example, a β -distonic ion is one in which the charged and radical sites are on atoms separated by one intervening atom. The current interest in distonic ions follows from their role as key intermediates in many gas-phase chemical transformations and from their unique existence as ions; that is, their corresponding neutrals are not stable. They are especially interesting because the localization of the charge and radical site gives them a unique "duality" and imparts the potential to participate in reactions as an ion, a radical, or both. Distonic ions have been identified and characterized by using an interplay of techniques. *Ab initio* calculations are used to predict and confirm the existence of distonic ions that owing to a susceptibility to rearrangement may be difficult to identify experimentally.¹ Structural techniques such as collisionally activated dissociation or metastable scans identify distonic ions by revealing fragmentation processes that differ from those of the corresponding radical cation isomers.² Ion-molecule reactions are used to determine the location of the charge and radical sites that distinguish these ions from conventional radical cations.³

To study systematically the reactivity of distonic ions, it is desirable to generate them in relatively large quantities. As a means to this end, the production of distonic ions by ion-molecule reactions is attractive because, when a suitable reaction is designed, the yield can be increased by extending the reactant pressure or the reaction time.

One approach for the study of ion-molecule reactions has involved tandem mass spectrometry equipped with a chemical ionization (CI) or high-pressure (0.1–0.5 Torr) ion source.⁴ The high pressure assures an adequate number of collisions between

reactants, thereby increasing the product yield. Furthermore, sequel collisions of an adduct with neutrals provide for collisional stabilization, removing energy from the adduct before it undergoes fragmentation or reversion to its precursors. Tandem mass spectrometry contributes established structural-determination techniques such as collisionally activated dissociation (CAD) and metastable ion characteristics and, as a result, has been an excellent means for the structural characterization of adducts.⁵

Unfortunately studies employing CI/tandem mass spectrometry are subject to ambiguities. For example, the two reagents that are necessary to give an adduct will exist in the CI source as both ion and neutral. Often tandem mass spectrometry techniques are not sufficient to determine if the adduct is the product of an ion-neutral or neutral-ion combination. An additional complication is that residence times of ions in CI sources or in collision cells of tandem instruments are in the microsecond time frame, making difficult the study of consecutive reactions. Thus, a complementary technique is sought to facilitate the study of production and subsequent reactions of novel ionic species. Ion-trapping techniques are an answer because they provide a means both to isolate ions and to study their bimolecular reactivity.

Currently there are two approaches for the trapping and analysis of ions. One, the quadrupole ion trap or QUISTOR, employs a Paul trap that confines ions through the use of oscillating or dynamic electric fields.⁶ The second, Fourier transform mass spectrometry (FTMS), employs a Penning trap that confines ions by static magnetic and electric fields.⁷ Of the two, FTMS has the established advantages of multichannel detection, routine high resolving power at low mass, exact mass measurement capability, and nondestructive detection. The detection scheme of FTMS is ion trajectory dependent. Because collisions with neutrals alter ion trajectories, there is a degradation of performance at pressures greater than 1×10^{-7} Torr. Although FTMS has historically been an important tool for the study of ion bimolecular reactivity, the low-pressure requirement stifles flexibility in ion-chemistry investigations.

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We recently showed⁸ that the incorporation of a RF-only-mode event into the FTMS sequence allows the transition from the low-pressure, static-field-trapping mechanism used in conventional FTMS to the high-pressure ($\sim 3 \times 10^{-3}$ Torr), dynamic-trapping mechanism used in QUISTORS, without a significant loss of the ion population. The utility of this new event for ion chemistry was demonstrated by collisionally stabilizing in an FTMS cell an ion-molecule adduct that cannot be observed under the usual low-pressure conditions of FTMS.⁸ The RF-only-mode provides a new capability for FTMS that should bridge the gap between the high-pressure CI and low-pressure FTMS.

The approach used for this study builds significantly on the new features of FTMS with an RF-only-mode or high-pressure event. The goal is to prepare a stable β -distonic radical cation by a condensation reaction so that sufficient quantities are available for studying its bimolecular reactivity and, ultimately, for lending insight into the radical/cation duality of these ions. The ion's fragmentation and metastable ion decay will also be investigated by a tandem mass spectrometer equipped with a CI source.

A major subset of distonic ions may be viewed as radicals in which constituent heteroatoms are protonated. The ions have been formed by several routes such as fragmentation, rearrangement-fragmentation, ion-molecule reactions, isomerization, or ring opening; for details, see the reviews by Hammerum⁹ and Kenttämäa.¹⁰ Fragmentations, for example, have been used to prepare β -distonic ammonium,^{11,12} oxonium,¹³ and phosphonium¹⁴ ions of the general structure $C^+H_2CH_2X^+H$. Although these ions are readily characterized in terms of structure, little insight has been gained into their bimolecular reactivity beyond proton transfer involving acidic hydrogens on the heteroatom.

The formation of a β -distonic ion without hydrogens on the heteroatom removes the opportunity for proton donation and permits the investigation of other bimolecular chemistry. This strategy has been successfully demonstrated for the β -distonic ion $CH_2=O^+CH_2C^+H_2$, which has a lifetime of at least 1 ms and transfers ionized ethene to neutral acetonitrile.^{15,16} Wittneben and Grützmacher¹⁷ proposed the transfer of ionized ethene to acetonitrile occurs by either a radical or ionic process, but unfortunately a collisional activation study using deuterated isotopomers failed to distinguish the mechanisms. In an attempt to gain further insight into the transfer mechanism, the authors reacted the distonic ion with neutral pyridine but did not observe ethene transfer to give the β -distonic $C_5H_5N^+CH_2C^+H_2$ ion, which we seek in this study. Instead the formyl group is transferred to yield $C_5H_5N^+CH=O$. The authors surmise that, because a radical addition to pyridine would result in the loss of aromaticity, the mechanism of the formyl transfer must be nucleophilic attack of the pyridine N. The β -distonic ion, in both instances, is reacting as an electrophile. The authors conclude that "further investigations are needed for a better understanding of the electrophile-radical 'dualism' in the reactivity of distonic ions".

More evidence that distonic $CH_2=O^+CH_2C^+H_2$ ions transfer ionized ethene via an ionic mechanism comes from studies by

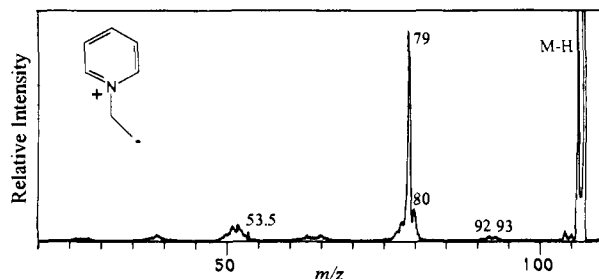
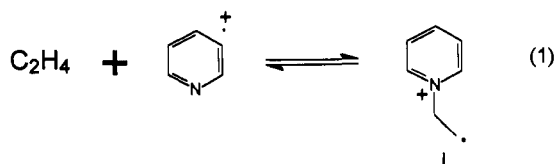


Figure 1. CAD of the adduct of m/z 107 formed by the pyridine radical cation and ethene neutral. The spectrum is magnified by a factor of 325. The ratio of m/z 106/79 is 1.4.

Kenttämäa and co-workers.¹⁸ Transfer of ionized ethene to NH_3 was found to take place, but it cannot occur by a radical mechanism because the nitrogen would become hypervalent. The original ion also transfers ionized ethene to trimethyl phosphate to form a new β -distonic $(CH_3O)_3P^+OCH_2C^+H_2$ ion. Because there are no acidic hydrogens, the ion undergoes no rapid bimolecular reactions but transfers ethene slowly to strong nucleophiles such as trimethyl or triethyl phosphite.

Although it is becoming established that $CH_2=O^+CH_2C^+H_2$ and other β -distonic ions react predominantly at the charge site, radical reactivity of other distonic ions is known.¹⁰ In two studies relevant to this work, de Koster,¹⁹ using oxirane, and we,²⁰ using cyclopropane, prepared the α -distonic 1-methylpyridinium ion $C_5H_5N^+-C^+H_2$ by electrophilic attack of the radical cation on neutral pyridine. Respective losses of neutral formaldehyde or ethene result in methylene transfer and no loss of aromaticity. The attenuated acidity of the $C_5H_5N^+-C^+H_2$ ion allowed us to demonstrate other bimolecular reactivity.

The homologous β -distonic ion, $C_5H_5N^+CH_2C^+H_2$, would also be expected to show reactivity at the radical site because the charge site has no protons. To generate the β -distonic homolog, however, a more appropriate ethene transfer agent than $CH_2=O^+CH_2C^+H_2$ must be found or a different strategy for ethene addition realized. Therefore, we developed, as reported here, an appropriate means whereby the *electrophilic* pyridine radical cation reacts with neutral ethene under high-pressure conditions of both FTMS and tandem MS to give the desired β -distonic ion.



Results and Discussion

Collisionally Activated Dissociation (CAD) Spectra of $[C_7H_9N]^+$ Isomers. The ion-molecule reactions of an ionized mixture of pyridine and ethene were first studied under high-pressure conditions in the chemical ionization source of a three-sector tandem mass spectrometer. The adduct ion of m/z 107 was selected by using the first stage of the instrument and collisionally activated (the mass spectrum is shown in Figure 1). After the H loss, the dominant fragmentation is loss of neutral C_2H_4 to give back the ion at m/z 79, apparently the pyridine radical cation. This reversion to form the charged electrophile appears to be a typical reaction of β -distonic ions.¹² Losses of H, C_2H_3 , and C_2H_5 suggest that the bonding is more than that of a loosely bound complex.

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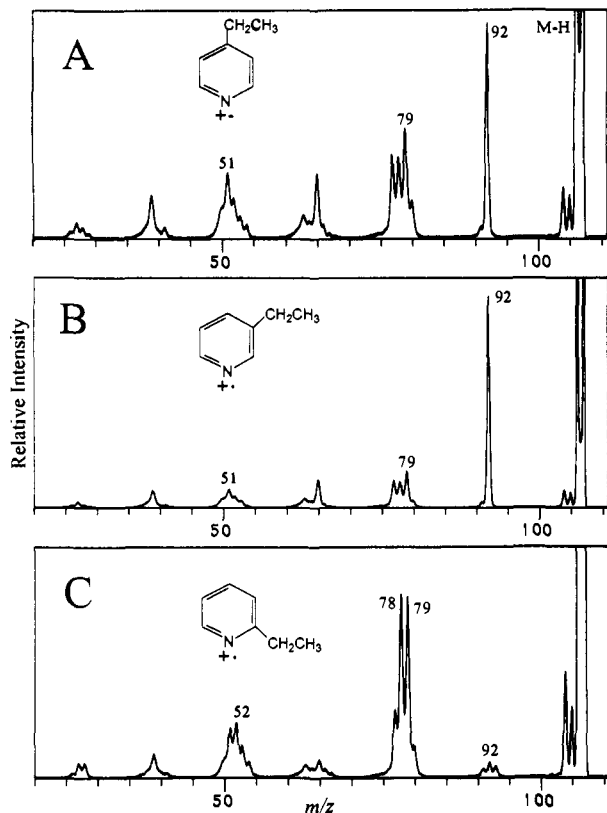


Figure 2. CAD of the ethylpyridine radical cations: (A) 4-ethylpyridine; (B) 3-ethylpyridine; (C) 2-ethylpyridine. Spectra are magnified by factors of 890, 97, and 325, respectively. The ratios of m/z 106/79 are 16.0, 15.8, and 17.9, respectively.

Although the ethylpyridine isomers also produce fragment ions at m/z 79, the magnitudes are quite different, as seen in their CAD spectra (Figure 2). The characteristic loss of CH_3 as well as other reactions of the isomeric 3- and 4-ethylpyridines distinguishes these ions from that of the pyridine/ethene adduct (see Figure 2). The 2-ethylpyridine isomer undergoes a facile loss of C_2H_5 , which is also a property of the adduct. It is possible, therefore, that a small amount (<8%) of this isomer can coexist with the adduct (Figure 2).

The CAD spectrum of the adduct ion (Figure 1) reveals a relatively low-intensity but sharp peak at m/z 53.5; this indicates the formation of a doubly charged species via a second ionization (charge stripping). Because molecules such as O_2 and N_2 are more efficient charge-stripping reagents than helium,²¹ air was used as the collision gas in these experiments. The CAD of the adduct from the reaction of [pyridine- d_5 + ethene]⁺ (Figure 4a) also produces the doubly charged ion. This observation provides evidence that the adduct ion has a distonic nature; distonic ions are susceptible to second ionization upon collisional activation.^{9,22,23} The doubly charged ion is not detected in the narrow-scan CAD spectra of the 3- and 4-ethylpyridine radical cations under the same experimental conditions whereas that of the 2-ethylpyridine radical cation does show formation of a doubly charged ion at m/z 53.5.

The adduct ion of m/z 107 also produces low-abundance ions of m/z 93 and 92. The former is produced via the loss of CH_2 , a process that is characteristic of some distonic ions but does not pertain to the 3- and 4-ethylpyridine radical cations. Although 2-ethylpyridine radical cation also fragments to product ions at m/z 92 and 93, their relative abundances are different.

To distinguish the putative β -distonic ion (I) from its α -isomer (II) we prepared the latter by a reaction of pyridine and ionized

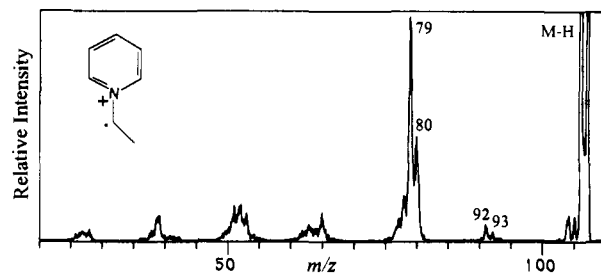


Figure 3. CAD of the product ion of m/z 107 from the reaction of methylcyclopropane radical cation and pyridine neutral. The spectrum is magnified by a factor of 292. The ratio of m/z 106/79 is 6.6.

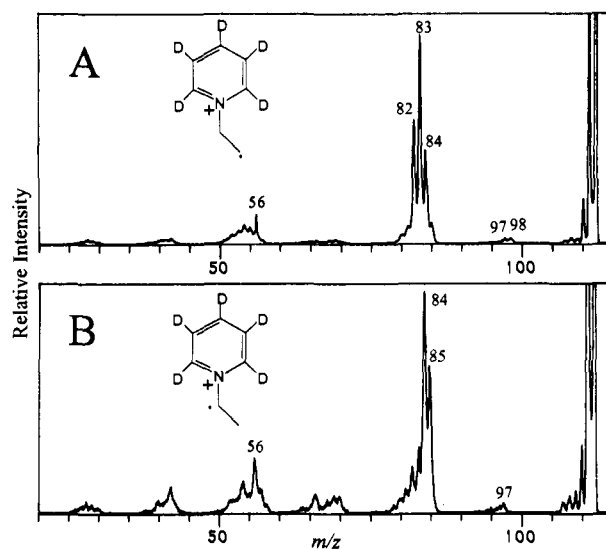
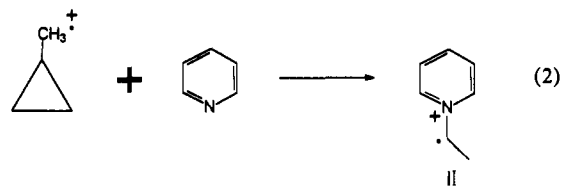


Figure 4. CAD of the (A) β -distonic ion (I) and (B) α -distonic ion (II), formed with pyridine- d_5 . The spectra are magnified by factors of 165 and 480, respectively. The ratios of m/z 111/84 are 3.0 and 8.4, respectively.

methylcyclopropane²³ (eq 2). The CAD spectrum (Figure 3) of



the product generated from this reaction clearly shows the product is different from the ethylpyridine radical cations and the pyridine/ethene adduct (I). The most distinctive feature is the abundant loss of C_2H_3 to give the pyridinium ion at m/z 80. On the basis of the CAD spectra, we conclude that both radical cations I and II are distonic but structurally different ions.

Additional structural information comes from the CAD spectrum of the adduct ion resulting from the reaction of ionized pyridine- d_5 and ethene (Figure 4A). In addition to formation of the doubly charged ion at m/z 56, the loss of CH_2CH_2 from the unlabeled species now occurs as losses of C_2H_4 , $\text{C}_2\text{H}_3\text{D}$, and $\text{C}_2\text{H}_2\text{D}_2$ to give ions of m/z 84, 83, and 82, respectively, indicating H/D exchange prior to fragmentation. This exchange takes place principally with the hydrogens on one carbon of the ethene species, and the transition structure is likely to involve a five-membered ring, as is illustrated in Scheme 1.

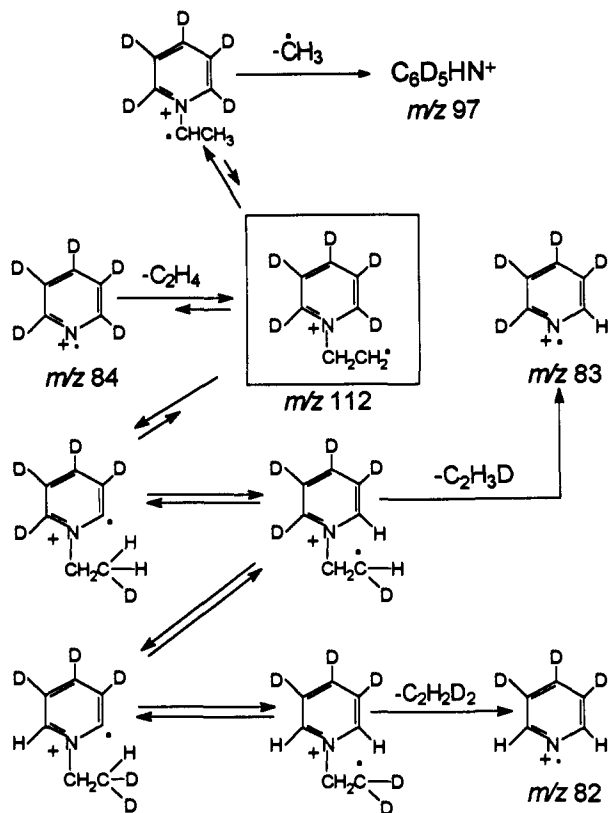
The low-abundance ions of m/z 92 and 93 from the unlabeled species shift to m/z 97 and 98, indicating that the losses of methylene and methyl involve only the ethylene group of the adduct. When the reaction of ionized pyridine and ethene was conducted at reduced pressures, the relative abundance of m/z

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Scheme I



98 decreased and that of m/z 97 increased. There may be another structural isomer for the adduct ion. At high pressure, the adduct ions are "cooled" by sequential collisions with bath gas (CS_2) and exist mainly in their initial form. As the pressure of the collision gas is decreased, the ions retain higher internal energy and some isomerize. The new isomer undergoes loss of CH_3 and some loss of CH_4 , which are characteristic of the isomeric distonic ion II (see Figure 4B). It is possible that I isomerizes to II in the absence of sufficient stabilization. Using low-abundance ions such as those of m/z 65, 80, or 92 and assuming they originate from the α -isomer, we can estimate the fraction of α -distonic ion in the population of pyridine/ethene adduct is less than 23–30%.

When the methylcyclopropane radical cation reacts with neutral pyridine- d_5 , H/D exchange occurs to a much lesser extent than that for the adduct ion from the pyridine- d_5 /ethene reaction (Figure 4B). The formation of m/z 84 via the elimination of C_2H_4 dominates over loss of labeled ethene, indicating the rate of H/D exchange of this radical cation is slower than that of the pyridine/ethene adduct ion (Figure 4A). Nevertheless, the enhanced abundance of the m/z 85 ion and the additional low-abundance ions of m/z 78 to 83 indicate that some H/D exchange has occurred.

Both the α - and putative β -distonic ions fragment to give product ions of m/z 80, which shift to m/z 85 when deuterated pyridine is used. Both radical cations, therefore, undergo a one-hydrogen rearrangement from the side chain to the aromatic ring to give what is likely to be the pyridinium ion.

The principal fragmentation of the β -distonic ion is the loss of a hydrogen atom, the majority of which is from the ethene group (see Figure 1). Subsequent activation of the $[M - H]^+$ ion via an MS/MS/MS experiment gives a CAD spectrum that is nearly identical to that of the m/z 106 ion formed by the reaction of vinyl cation and neutral pyridine. Both ions have the same structure, $C_5H_5N^+ - CH=CH_2$, offering support for the hypothesis that the pyridine radical reacts with ethene at the nitrogen atom of pyridine and not at one of the aromatic carbons.

Postma et al.^{24b} provide *ab initio* evidence for a hydrogen-bridged water/ethene radical cation complex. There is little support for the formation of the proton-bound species $[C_5H_5N \cdots H \cdots CH=CH_2]$. The proton affinity of pyridine is 921 kJ/mol,²⁵ and that of $CH_2=CH^+$ is 732 kJ/mol.^{24a} If the proton-bound species were formed, protonated pyridine is expected to be more abundant than that seen in the CAD spectrum of the adduct ion (Figure 1). Furthermore, the adduct ion undergoes charge stripping to give an intact doubly charged ion, a species that is unlikely to form a loosely associated, proton-bound ion. Finally, the adduct undergoes considerable H/D exchange when labeled reagents are used; exchange is not a property of proton-bound radical cations.²⁶

Metastable Ion Spectra. The metastable ion spectrum of the adduct [ethene + pyridine] $^{++}$ is different from those of the ethylpyridine isomers (Table I). The elimination of a hydrogen atom occurs readily for the conventionally bound isomers whereas loss of neutral C_2H_4 to give the ion at m/z 79 is facile only for the adduct. The adduct with ethene also shows different decomposition chemistry than that of the α -distonic isomer (Table I).

The kinetic energy release associated with the ion of m/z 79 was measured by the half-height method²⁷ to be 0.01 eV. A small release of kinetic energy is consistent with a simple bond cleavage, which is all that is required for the β -distonic ion to fragment to the m/z 79 ion.

Ethene is lost as C_2H_4 , C_2H_3D , and $C_2H_2D_2$ in the ratio of 1:6:4.3 when pyridine- d_5 is reacted, providing strong support for the covalently bound distonic ion rather than a loosely bound complex. Ethene is lost more readily from the apparent β -isomer, whereas the α -isomer undergoes less H/D exchange prior to expelling ethene.²⁸

Low-Pressure FTMS Experiments. The adduct ion from $[C_5H_5N + C_2H_4]^{++}$ is too unstable to be detected at a pressure of 10^{-7} Torr. Evidence that the adduct is indeed formed in conventional FTMS must be obtained indirectly. For example, when pyridine- d_5 was used in the reaction, ions at m/z 84, 83, and 82 (partially deuterated pyridines) were observed to increase in abundance with time. Moreover, when ethene was replaced with C_2D_4 in the reaction with nondeuterated pyridine, the masses shifted in an opposite direction from m/z 79 to 80 and 81. A bimolecular reaction must be occurring to give an adduct that lives for a sufficiently long time for H/D exchange to occur. At the pressures of conventional FTMS, however, no intact adduct can be detected.

High-Pressure FTMS Experiments. The ability to trap ions at pressures greater than 10^{-7} Torr is a characteristic of the QUISTOR. Thus, incorporation of a QUISTOR-type mode into the FTMS sequence should allow us not only to stabilize the β -distonic ion under investigation here but also to open FTMS to a whole new set of experiments at high pressure. Unlike the static fields employed in FTMS, the oscillating fields of the QUISTOR focus ions to the center of the trap as they lose kinetic energy by collisions with neutrals.⁶ The number of collisions the ion undergoes is increased by the introduction of a bath gas, such as helium, so that a QUISTOR cell is operated at a total pressure in the range 10^{-3} to 10^{-2} Torr.

The isolated pyridine radical cation reacts with ethene neutrals during a 3.6-s, RF-only-mode event (a QUISTOR-type mode

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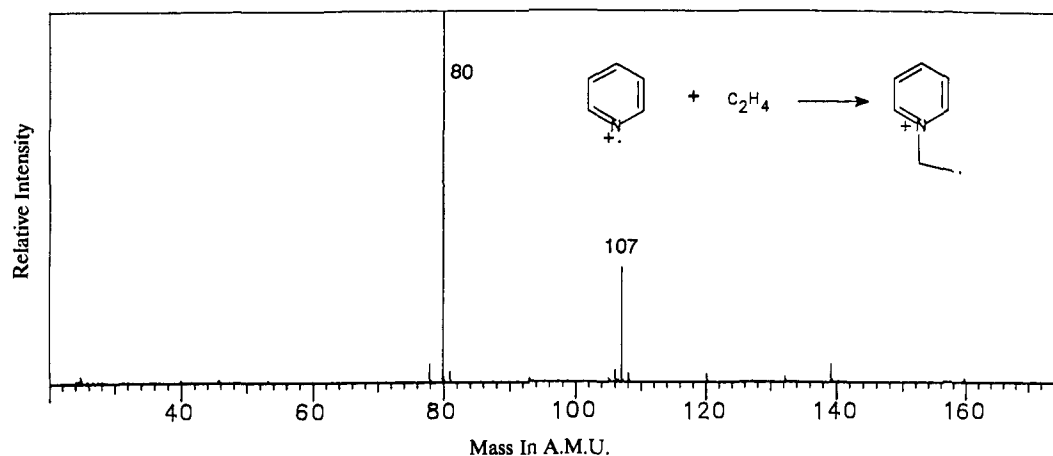
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Table I. Normalized Ion Intensities from the Metastable Decomposition of the Various Radical Cations of m/z 107

	adduct ion I β -dystonic	product ion II α -dystonic	2-ethylpyridine	3-ethylpyridine	4-ethylpyridine
m/z 107	100 000	100 000	100 000	100 000	100 000
m/z 106	206	115	750	330	250
m/z 92				5	3
m/z 80	6.4	1.4	1.9	1.3	2.3
m/z 79	79	14	3.3	3.7	2.4
m/z 78			1.2		

**Figure 5.** Formation of the β -dystonic ion of m/z 107 in the FTMS cell via collisional stabilization with the RF-only-mode event. The adduct is formed but not detected without the event.

event) to give readily observed adduct. This event consists of the imposition of a 1000-V_{o-p}, 1.25-MHz supplementary potential onto the static-trapping potential. Concurrently, a modified leak valve is opened for the first 1.3 s of the event to pressurize the cell to $\sim 3 \times 10^{-3}$ Torr with helium bath gas. The duration of the event is determined by the desired reaction time, the rate of turning off and on the radio frequency voltage, and the rate of bath gas removal to return to normal FTMS operating pressures following the event. Analysis of the reaction products (Figure 5) reveals that two abundant ions form, one at m/z 80, which corresponds to protonated pyridine, and the other at m/z 107, which corresponds to the mass of the β -dystonic ion, a species that is not observed without the RF-only-mode event. Other ions observed at higher mass-to-charge ratios indicate the RF-only-mode is collisionally stabilizing the products of other yet-to-be-established reactions.

One means of characterizing the adduct ion of m/z 107 is collisionally activated dissociation as is customarily done in tandem mass spectrometers. The low-energy CAD of the adduct ion at m/z 107 shows that the only significant decompositions are the loss of hydrogen to give the m/z 106 ion and the reversion to the pyridine radical cation at m/z 79. The same processes were observed as preferred routes for dissociation upon high-energy CAD of the β -dystonic ion.²⁹ The adduct that can be collisionally stabilized in FTMS as a result of the RF-only-mode event is the same as that formed in the chemical ionization source of the sector instrument. Double resonance isolation of the pyridine radical cation before the RF-only-mode event, moreover, provides unambiguous evidence that the reaction occurs via the radical cation of pyridine and not via that of ethene. Establishing this important fact is very difficult and at best indirect in tandem-sector MS.

When substituted pyridine compounds, such as methylpyridines and dimethylpyridines, react with ethene, the adduct ions can be detected without the collisional stabilization provided by the RF-only-mode event, although the relative abundances of the adduct ions are low. Either the additional degrees of freedom provided

by the methyl groups allow for better accommodation of the energy released in the reaction or they cause the exothermicity to be reduced, or a combination of both.

The adduct of m/z 112 from the reaction of pyridine- d_5 radical cation and ethene can also be observed if collisionally stabilized during the RF-only-mode event. Low-energy CA causes loss of C_2H_4 , C_2H_3D , and $C_2H_2D_2$ to give ions of m/z 84, 83, and 82, respectively, in the ratio 1:3:2:2.7. Ions at m/z 85 and 86 are also formed and are most likely protonated and deuterated pyridine- d_5 . These are not observed to a great extent in the corresponding sector experiment because activation of the adduct at m/z 112 occurs in a region of the instrument that contains little neutral pyridine. Thus, there is no opportunity for the dystonic ion to react with neutral pyridine during activation. FTMS is a tandem-in-time technique, meaning collisional excitation of the adduct involves some collisions with neutral pyridine, leading to increased production of $C_5D_5NH^+$ and $C_5D_5ND^+$. Indeed, as the background pressure of neutral pyridine- d_5 was increased, so were the relative amounts of the m/z 85 and 86 ions.

On the basis of tandem MS results (see Figure 4A and B), hydrogen/deuterium exchange occurs principally at the 2- and 6-positions of the aromatic ring. In a series of conventional FTMS experiments, a maximum of two hydrogens were exchanged with deuterium when ethene- d_4 was reacted with 3,5-dimethylpyridine, as is expected. In the reactions of 2-methylpyridine or 2,6-dimethylpyridine with ethene- d_4 , H/D exchange involves not only the hydrogen on the 6-position of the aromatic ring but also the hydrogens on the methyl groups. As a result, a maximum of four and six hydrogens are exchanged with deuterium for the 2-methylpyridine and 2,6-dimethylpyridine adducts, respectively. The source for H/D exchange of 2,6-dimethylpyridine must be more than one ethene molecule. This is accommodated if pyridine is the radical cation and neutral ethene adds reversibly.

The methylcyclopropane radical cation reacts with neutral pyridine without a RF-only-mode event in the FT mass spectrometer to give an m/z 107 ion, which is less than 10% relative abundance. When the product ion incorporates pyridine- d_5 very little H/D exchange occurs. This is additional evidence that the product ion generated from the reaction of methylcyclopropane

(29) The ratio of abundances of m/z 79 to 80 was 6.2:1 for the sector-acquired CAD spectra and 10.9:1 for the FTMS-acquired CAD spectra.

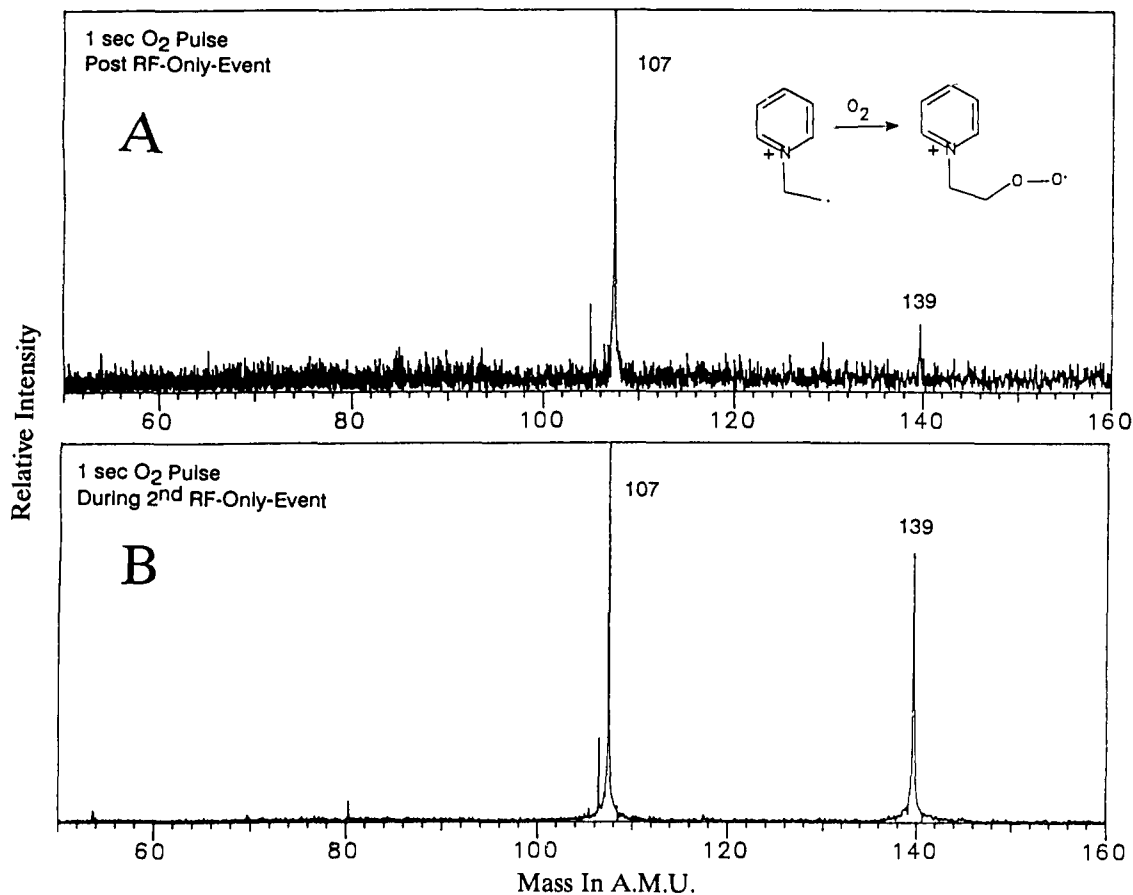


Figure 6. Reaction of the β -distonic ion with dioxygen to form an adduct of m/z 139 (A) without and (B) during a second RF-only-mode event.

radical cation and pyridine is indeed different from the adduct ion formed by pyridine radical cation and ethene.

Bimolecular Reactivity of the β -Distonic Ion. The ability to form a stable β -distonic ion in the Fourier transform mass spectrometer presents the opportunity for systematic study. Reactions with neutrals probe a distonic ion's reactivity as well as its structure, as discussed in a recent review.¹⁰ In an extensive study of reactivity, Rusli and Schwartz³⁰ investigated the reactions of acetonitrile, propyne, acetylene, trimethylsilylacetylene, and tetramethylsilane with the distonic ions $C^+H_2CH_2C^+H_2$ and $CH_2=O^+C^+H_2$. In an early example of how such reactions can be used diagnostically, Bursey and co-workers³¹ showed the β -distonic ion $CH_3O^+HCH_2C^+H_2$, produced from ionized 1,2-dimethoxyethane, transfers ethene specifically to nitriles but not to other functionalities. In a study of oxygen-containing radical cations, Kenttämäa and co-workers³² showed that distonic isomers abstract CH_3S^+ from CH_3SSCH_3 whereas nondistonic isomers undergo fast charge exchange, providing a diagnostic reaction for distonic ions with the oxygen functionality. It is interesting to note that, in Kenttämäa's study, the ions were collisionally cooled by a high-pressure argon pulse prior to reaction, offering another example of why cooling strategies are needed for FTMS.

As a first step to probe the structure and reactivity, the β -distonic ion was formed by the condensation of the pyridine radical cation with ethene, and the adduct was reacted with dioxygen to form a new adduct at m/z 139 (this adduct may be a δ -distonic ion). Dioxygen was chosen because it is a diradical, and the β -distonic species is expected to be reactive at its radical site. Although this reaction occurs without a RF-only-mode event (Figure 6A), the formation of the adduct is significantly increased if the reaction

takes place during a *second* RF-only-mode event (Figure 6B). Here is a single experimental sequence in which the instrument performs as (1) an FT mass spectrometer to isolate the reacting radical cation, (2) a QUISTOR to stabilize collisionally the adduct, (3) an FT mass spectrometer to isolate the adduct, (4) a QUISTOR to stabilize collisionally the product of the reaction of the adduct with dioxygen, and (5) an FT mass spectrometer to detect the O₂-adduct. The ability to use higher reagent pressures during the RF-only-mode event dramatically increases the number of ion-molecule collisions and provides collisional stabilization. Furthermore, the dynamic-trapping field focuses ions to the center of the cell to give and maintain an ion cloud shape suitable for detection³³ and to reduce ion loss, permitting longer reaction times at higher neutral pressures.

Although we have little structural information for the O₂-adduct, we did establish that ethylpyridine radical cations and the isomeric α -distonic ion do not produce oxygen adducts. A possible explanation is the radical site is delocalized in these systems whereas the site is isolated from the ring in the β -isomer.

Summary

The reaction of the pyridine radical cation with neutral ethene yields a new aromatic β -distonic ion $C_5H_5N^+-CH_2C^+H_2$. The CAD spectrum of this radical cation is distinctively different from those of the conventional isomers, the ethylpyridine radical cations, and from another distonic structural isomer $C_5H_5N^+-C^+HCH_3$ generated in the reaction of methylcyclopropane radical cation and neutral pyridine.

The adduct, which cannot be seen under conventional FTMS conditions, can be collisionally stabilized under the high-pressure conditions of a new event in the FTMS sequence, an event we call the RF-only-mode event. Subsequent collisional activation in

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the FT mass spectrometer leads to elimination of neutral ethene and, when pyridine-*d*₅ was used, to H/D exchange at only two positions of the adduct, indicating it is the same ion that is produced in a high-pressure CI source.

The RF-only-mode event presents new opportunities for the systematic study of adducts whose formation requires collisional stabilization or of ions that require thermalization. During the RF-only-mode event, the number of ion-molecule collisions per unit time is significantly increased over what is possible with conventional FTMS, and the ions are focused to the center of the cell before detection. Moreover, a series of RF-only-mode events can be concatenated to allow, as we demonstrated here, sequential reaction such as that of the β -distonic ion with molecular oxygen.

Experimental Section

Materials. Ethene was purchased from Matheson Gas Products. Methylcyclopropane was from Columbia Organic Chemicals Co., Inc. Pyridine, HPLC grade; pyridine-*d*₅, 99 atom % D; 2-ethylpyridine, 97%; 3-ethylpyridine, 98%; 4-ethylpyridine, 98%; 3,5-dimethylpyridine, 98+%; and vinyl bromide, 98%, were purchased from Aldrich. In all cases, the purities were specified by the suppliers, and the chemicals were used without further purification.

Apparatus and Procedure. For the tandem-sector mass spectrometer, the ion-molecule reactions were carried out in a Mark II Kratos chemical ionization (CI) source. The ionization voltage was 280 V. Hexafluorobenzene (IP = 9.20 eV) or CS₂ (IP = 10.07 eV)³⁴ was used as charge transfer and collisional stabilization reagents. The total pressure of the reaction chamber was approximately 0.5 Torr. The ratio of pyridine, ethene, and hexafluorobenzene (or CS₂) was 1:1:10. The partial pressure of each ethylpyridine isomer was approximately 0.05 Torr, and the CI source pressure was brought to a total pressure of 0.5 Torr with hexafluorobenzene (or CS₂).

The CAD spectra were acquired by using a triple-sector Kratos MS-50 mass spectrometer of EBE geometry.³⁵ In an MS/MS experiment, the ion beam was accelerated to 8 kV and mass/selected by the first electrostatic analyzer and the magnet of the first stage (MS1) at a resolving power of greater than 2500 (10% valley definition). The selected ion beam was activated by collisions with neutral helium in the collision cell located in the third field-free region at the focal point of MS1. Air was used as the collision gas to enhance the charge-stripping process for selected experiments. The collision gas pressure was adjusted to give 50% main beam attenuation. A CAD spectrum was obtained by scanning the second electrostatic analyzer from 0 V to the main beam voltage. In narrow scan experiments, MS2 was set up to scan only a small region of a spectrum so as to obtain sufficient data points for defining better the narrow charge-stripping peaks. The β -slit width after the second ESA was maintained at 0.50 mm.

In the sequential activation or MS/MS/MS experiment,³⁶ the parent ion was collisionally activated by admitting the collision gas (helium) into a cell in the first field-free region. The pressure was adjusted to obtain the optimal signal from the fragment ion of interest. This fragment ion was mass selected by reducing the fields of ESA1 and the magnet to the values of $(m_2/m_1)E_1$ and $(m_2/m_1)B_1$, respectively, where m_2 and m_1 are the masses of the fragment and parent ions and E_1 and B_1 are the

electric field of ESA1 and the magnetic field strength. The selected ion was then activated in the third field-free region by collisions with helium. A CAD spectrum was obtained in the same manner as in the MS/MS experiments.

The metastable ion spectra were acquired under similar conditions and by using the same experimental parameters as those used in acquiring the CAD spectra, with the exception that the collision gas was excluded. All spectra were the average of at least ten 20-s scans.

Low-pressure ion-molecule reactions were studied in a custom-built FT mass spectrometer interfaced to a Nicolet Analytical Instruments FTMS-2000 computer system.³⁷ A 5.08-cm stainless steel cubic ion trap mounted between the poles of a Varian V-7300 electromagnet at a magnetic field strength of 1.2 T and a trap plate voltage of 1 V was used. Typical instrument parameters were 10- μ A filament current and 40-ms beam duration. The ionization voltage used in single-resonance experiments was 10 V, and 10 or 15 V was used in double-resonance experiments (the IP values for pyridine and ethene are 9.25 and 10.50 eV). The typical total pressure was 2×10^{-7} Torr as measured on a Bayard/Alpert ionization gauge located between a turbo molecular pump and the ion trap. All data acquisition and processing were with computer software provided by Nicolet Analytical Instruments (now Extrel).

The FTMS system for all RF-only-mode event experiments was a 2.54-cm molybdenum cubic trap mounted between the poles of a Varian V-3400 iron magnet and interfaced to a Nicolet Analytical Instruments FTMS-1000 computer system. The FTMS sequence to form the adduct was performed at 1.2 T with a 1-V trapping potential. The cell was pressurized to approximately 5.3×10^{-7} T (uncorrected from a Bayard/Alpert gauge) with pyridine and ethene at roughly a 3:1 ratio. Ionization was at 12 eV employing 400 nA of emission current for 200 ms. The RF-only-mode event was implemented by superimposing a 1000-V_{o-p}, 1.25-MHz potential onto the trapping potential by employing a custom-made radio frequency-power supply and a Rockland 5100 programmable frequency generator. Simultaneously the cell was pressurized to approximately 3×10^{-3} Torr with He by opening a modified Varian Model 451-5100 leak valve with a solenoid for 1.3 s. The duration of the RF-only-mode event was 3.6 s unless otherwise specified and was determined as described in the FTMS discussion section. Once the transition to the static mode of trapping was complete, normal FTMS excitation and detection events were employed.

In the low-energy CAD experiments, the time of the RF-only-mode event was shortened by 0.68 s so that static trapping resumed before the He bath gas had been completely removed ($\sim 3 \times 10^{-6}$ Torr total cell pressure). The adduct at m/z 107 was selected by double resonance followed by excitation to approximately 20% of the cell's radius to increase the ion's kinetic energy. A delay of 300 ms before excitation and detection allowed for activation by collision dissociation with residual bath gas and neutrals, and rerandomization of the ion phases.

The reaction of the adduct with molecular oxygen was by a second RF-only-mode event of 6 s that followed the first RF-only-mode event and isolation of the adduct. The dioxygen inlet system consisted of a gas tube, a conductance limit made from 15 m of 25 μ m o.d. capillary tubing, and a General Valve Series 9 two-way pulse valve connected to a mechanical pump. The flow of the dioxygen raised the pump pressure to 32 mTorr. When the pulse valve has held open, the dioxygen flow was divided into the high-vacuum system, raising the cell total pressure, including the partial pressures of pyridine and ethene, to $\sim 2 \times 10^{-5}$ Torr. During the second RF-only-mode event, the oxygen pulse valve was opened for the first 1 s of the event.

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