CH₂⁺· Transfer to Pyridine Nucleophiles: A Means of Producing α-Distonic Ions

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The distonic radical cation C₅H₅N⁺·CH₂ can be generated by the reactions of neutral pyridine with the radical cations of cyclopropane, ethylene oxide, and ketene, as well as with the [C₃H₆]⁺· ion from fragmentation of tetrahydrofuran. The distonic product ion can be distinguished from isomeric methylpyridine radical cations because the former gives characteristic [M - CH₂]⁺, [M - CH₂NCH]⁺, and a doubly charged ion, all of which are produced on collisional activation. Furthermore, the distonic species completely transfers CH₂⁺ to more nucleophilic, substituted pyridines. These properties are all consistent with the assigned distonic structure. Another distonic isomer, the (3-methylene)pyridinium ion, can be distinguished from the (1-methylene)pyridinium ion on the basis of their different fragmentation behaviors. The latter ion exhibits higher stability (lower reactivity) than the prototypal [·CH₂NH₃]⁺, making available a distonic species whose bimolecular reactivity can be readily investigated. (*J Am Soc Mass Spectrom* 1993, 4, 117-124)

Positively charged distonic ions are radical cations that have charge and radical sites located on different atoms. For α-distonic ions, also termed *ylidions*, the charge and radical are found on adjacent atoms. The existence and stability of many distonic ions have been confirmed by laboratory experiments and supported by extensive theoretical studies. Molecular orbital calculations have shown that small heteroatom-containing distonic ions (e.g., ·CH₂NH₃⁺, ·CH₂OH₂⁺, ·CH₂FH⁺, ·CH₂OHCH₃⁺) have lower energies than their corresponding conventional isomers [1]. The interested reader is referred to an important review of the subject by Hammerum [2].

Because distonic ions usually have no stable neutral counterparts, they are often generated by isomerization [3,4] or by unimolecular fragmentations [5,6]. Ion-molecule reactions are another method for preparing distonic ions. For example, the gas-phase cycloaddition of the vinyl methyl ether radical cation and neutral 1,3-butadiene proceeds in two steps; the first step involves the addition of the radical cation to the neutral molecule to yield a distonic intermediate [7]. The resulting distonic ion undergoes ring closure to complete the cycloaddition. Another example is the reaction of the benzene radical cation with neutral

cyclopropane or cyclobutane. A distonic intermediate is first formed [8], but it undergoes competitive radical- and cation-based isomerizations to give stable, nondistonic products.

The first experimental demonstration that distonic ions are formed in ion-molecule reactions was by Gross and McLafferty [9]. Cyclopropane radical cations react with neutral ammonia in the cells of ion cyclotron resonance (ICR) or Fourier transform (FT) mass spectrometers to generate a putative γ-distonic species (I, eq 1) that rapidly decomposes to give an observable α-distonic ion (II, eq 1):

The structure of I was later verified by preparing it at higher pressures than those typically used in ICR spectrometry and studying it by tandem sector mass spectrometry [10].

Ring opening of many small cyclic ether radical cations leads to distonic ions that transfer the [(CH₂)_n]⁺ group (where n = 1, 2, 3, ...) to appropriate nucleophiles [11, 12, 13]. Ethylene oxide and tetrahydrofuran are known to carry out such reactions. The

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distonic structure of the ring-opened form of ethylene oxide $[\text{CH}_2=\text{O}-\text{CH}_2]^+$ is well characterized and observed to transfer the CH_2^+ group to nucleophiles such as CH_3CN [14,15]. Tetrahydrofuran radical cations fragment to give a cyclic C_3H_6^+ species [16], and the resulting radical cation reacts with neutral ammonia in the same fashion as does ionized cyclopropane. Another CH_2^+ transfer reagent, the ketene radical cation [15,16], also reacts with neutral ammonia to give the distonic $[\text{CH}_2\text{NH}_3^+]$ ion, as was determined by Drewello et al. [17].

Some distonic ions generated by ion-molecule reactions, such as those described above, are susceptible to fragmentation with or without rearrangement to form a closed-shell species [4,17,18]. Generally, as a distonic ion increases in size and the radical and charge sites become farther apart, low-energy isomerization reactions become more prominent. Yates and Radom [19] found that the isomerization energies for converting $(\text{CH}_2)_n\text{NH}_3^+$ ions to the corresponding conventional alkyl amine molecular ions decrease monotonically from 46 kcal/mol, for $n = 1$, to 18 kcal/mol, for $n = 4$. This isomerization restricts the opportunities to investigate further the properties of distonic ions. Another limiting property is the capacity for proton transfer. For example, $\text{CH}_2-\text{NH}_3^+$ rapidly reacts with its reactant precursor NH_3 to give NH_4^+ , thus making a study of its biomolecular reactivity difficult.

One purpose of the research reported here is to design, prepare, and characterize distonic ions that do not isomerize or react by proton transfer. In that way, copious quantities of these ions can be generated in the gas phase for studies aimed at probing their biomolecular chemical properties. Neutral pyridine was selected as the nucleophile to react with likely distonic ion precursors, such as cyclopropane, ethylene oxide, and ketene radical cations, as well as with C_3H_6^+ from the fragmentation of tetrahydrofuran (THF). Because the radical cations of all the precursors are known to transfer CH_2^+ to other nucleophiles, the formation of the distonic ion $\text{C}_5\text{H}_5\text{N}-\dot{\text{C}}\text{H}_2$ is expected. The aromatic functionality should stabilize the ion and reduce its propensity to isomerize or to undergo proton-transfer reactions. The structure and chemical reactivities of the product ions were determined by using both Fourier transform (FT) and tandem sector mass spectrometry.

While this research was underway, de Koster et al. [14(b)] published results showing that the (1-methylene)pyridinium ion that we seek here can indeed be prepared by the reaction of ethylene oxide radical cation and neutral pyridine. They determined the structure by using collisional-activated decompositions and isotopic labeling and supported their conclusions with molecular orbital calculations. Our work extends that of de Koster et al. [14] by using FT mass spectrometry, charge stripping, and methylene-transfer reactions to characterize further this interesting α -distonic ion.

Experimental

Materials

Cyclopropane and ethylene oxide were obtained from Matheson Gas Products (East Rutherford, NJ). Acetone was reagent grade from EM Science (Gibbstown, NJ), and 3-(hydroxymethyl)pyridine was from Sigma Chemical Co. (St. Louis, MO). Pyridine, high-performance liquid chromatography grade; pyridine- d_5 , 99 atom %D; THF, reagent grade; acetic anhydride, reagent grade; hexafluorobenzene, 99%; propionyl chloride, 97%; 2-bromopropene, 99%; allyl bromide, reagent grade; 2-methylpyridine, 98%; 3-methylpyridine, 99.5%; 4-methylpyridine, 99%; and 3,5-dimethylpyridine, 98%, were purchased from Aldrich Chemical Co. (Milwaukee, WI).

Ketene was prepared by the thermal decomposition of acetone or acetic anhydride. A custom-built glass tube with a metal coil centered inside was used. The coil was heated by an appropriate power supply (Powerstat 3PN116B) to dull red. Acetone or acetic anhydride vapors in nitrogen gas were admitted to the tube and allowed to contact the hot coil. The resulting product, ketene, and unreacted acetone (or acetic anhydride) vapor were collected in two consecutive U-shaped glass tubes immersed in acetone/dry ice. Ketene was then distilled into a gas tube immersed in liquid nitrogen by slowly warming the U-shaped glass tubes one by one to room temperature. Gaseous impurities were removed by several freeze-pump-thaw cycles.

The (3-methylene)pyridine propionylate was prepared by adding a stoichiometric amount of propionyl chloride slowly to stirred 3-(hydroxymethyl)pyridine in a round-bottomed reaction flask. Some of the HCl by-product was released as a gas, and the ester product remained as a pale yellow solid. No purification was done before use.

Apparatus and Procedure

Low-pressure ion-molecule reactions were studied in a custom-built FT mass spectrometer interfaced to a Nicolet Analytical Instruments (now Extrel ANS, Madison, WI) FTMS-2000 computer system [20]. A 2.54-cm stainless steel cubic ion trap cell was used in a magnetic field strength of 1.2 T, and the trap plate voltage was 1 V. Typical instrument parameters were 20- μA emission current, 10-15-eV ionization energy, and 20-40-ms beam duration. For all kinetics studies, the pyridine was maintained at a constant pressure, whereas the partial pressure of the other reagent was adjusted so that the initial signal of the reacting radical cation had about the same magnitude as that of the pyridine radical cation. The total pressure was typically 2×10^{-7} torr, as was measured on an Bayard/Alpert ionization gauge located between the turbomolecular pump and the ion trap. All data acqui-

sition and processing utilized the computer software provided by Nicolet Analytical Instruments.

Collision-activated decomposition (CAD) spectra were acquired by using a triple-sector Kratos MS-50 TA mass spectrometer (Kratos Analytical, Ramsey, NJ) of EBE geometry [21]. Ion beams were accelerated to 8 keV, selected at a mass resolution of greater than 2500 (10% valley definition) by using the first electrostatic analyzer (ESA) and the magnet sector. The selected ions were activated by collisions with He in the third field-free region. The collision pressure was adjusted to give 50% main beam attenuation, and the β -slit width after the second ESA was maintained at 0.50 mm. A CAD spectrum was obtained by scanning the second ESA; each spectrum is an average of at least ten 20-s scans.

The ion–molecule reactions were also carried out in a Mark II Kratos chemical ionization (CI) source. The ionization voltage was set at 280 V. Hexafluorobenzene [ionization energy (IE) = 9.9 eV] or CS₂ (IE = 10.1 eV) were used as both charge-transfer and collisional stabilization reagents. The total pressure was approximately 0.5 torr inside the reaction chamber, and the ratio of neutral pyridine, the radical cation precursor, and hexafluorobenzene (or CS₂) was 1:1:10. The metastable ion spectra were obtained under the same conditions as for CAD spectra, except that the collision gas was excluded.

The rate-constant measurements were performed in the FT mass spectrometer. The reaction rates were obtained by monitoring the decay curve of the reactive radical cation species. Because the ionization gauge (Veeco model RG-840) used in the experiments does not measure the absolute pressure of the reactive neutral species, the pressure was determined by using the rate constant and ion abundances as a function of time for a standard reaction, namely that of dimethylamine cation and neutral pyridine [22].

AM1 Molecular Orbital

The computation of heats of formation of radical cations was performed by using MOPAC 5 (Stewart's MOPAC QCMP024), which was ported to a UNIX-based CCG 5000 coprocessor (The Computational Chemistry Group, Inc., Denver, CO [23]). The coprocessor, installed in a generic personal computer system, used a

standard 80,286-chip motherboard and a 380-Mbyte hard disk. PCMODEL (Serena Software, Bloomington, IN) was ported to the same board and was used to construct the MOPAC input files after molecular mechanics minimization with the MMX force field. The output .arc files were converted to .mop files that could be read by PCMODEL and from which the geometry of each molecule was examined for reasonableness. Each ion-output geometry was subjected to a force calculation wherein the Hessian matrix was diagonalized to ensure that a stationary point was reached on the potential energy surface [24].

Results and Discussion

Cyclopropane⁺ + Pyridine

The reactions occurring in an ionized mixture of cyclopropane and pyridine at low pressure were investigated with an FT mass spectrometer. The abundance of a product ion corresponding to CH₂⁺ transfer to pyridine (i.e., of m/z 93) increases with time. The cyclopropane radical cation at m/z 42 was determined to be the reactive species by using a double-resonance experiment in which pyridine radical cations were ejected continuously. The nitrogen atom is the likely nucleophilic site on the basis of previous results [14b]. Other major products are the ions at m/z 120 that result from the reaction of [C₃H₆]⁺ and neutral pyridine with the concomitant loss of a hydrogen atom and at m/z 80, which is protonated pyridine.

The reaction of pyridine with the cyclopropane radical cation is facile (the rate constant is shown in Table 1). The ion signal intensities as a function of reaction time for the cyclopropane radical cation and the two major products are shown in Figure 1. The product ion of m/z 93, when isolated from the rest of the ions by triple-resonance experiments, is stable (undergoes no observable decomposition or biomolecular reactions) over a period of 20 s in the FT mass spectrometer cell at a pressure of 2×10^{-7} torr for a 1:5 ratio of pyridine and cyclopropane. The reaction that produces the m/z 93 and 120 ions presumably proceeds via an energetic adduct (III, eq 2) that rapidly eliminates neutral ethylene and forms the C₅H₅N–CH₂ ion of m/z 93. This species is unlikely to undergo proton transfer to its neutral pyridine precursor, a reaction that quickly de-

Table 1. Rate constants for the reactions of various radical cations and neutral pyridine as determined by FT mass spectrometry and average dipole orientation calculations

Radical cations	Experiment (10 ⁻⁹ cm ³ molecule ⁻¹ s)	ADO (10 ⁻⁹ cm ³ molecule ⁻¹ s)
Cyclopropane	1.9 ± 0.2	2.47
Ketene	3.9 ± 0.2	2.47
Ethylene oxide	1.2 ± 0.1	2.43
Tetrahydrofuran	2.6 ± 0.2	2.47

Figure 1. Temporal dependence of product abundances for the reaction of cyclopropane radical cations and neutral pyridine in the FT mass spectrometer (partial pressure of pyridine, 5×10^{-8} torr; partial pressure of cyclopropane, 2.0×10^{-7} torr).

pletes the abundance of other α -distonic ions such as $[\text{CH}_2\text{NH}_3^+]$ [17, 25]:

There is evidence that α -distonic ions transfer CH_2^+ to appropriate nucleophiles [11-15]. If the m/z 93 ion is indeed distonic, it should transfer CH_2^+ to a nucleophile better than pyridine. When methylpyridine or dimethylpyridine was introduced into the FT mass spectrometer cell through a pulsed valve to react with the isolated product ion of m/z 93, a slow CH_2^+ exchange reaction (eq 3) did take place:

Thirty seconds after the introduction of neutral 3,5-dimethylpyridine, 15% of the ion of m/z 93 still remained. The depletion of the neutral dimethylpyridine (as measured by monitoring the molecular ion signal) caused by continuous pumping of the reaction chamber had diminished the rate of reaction. The concentration of dimethylpyridine was reduced to approximately 50% of the peak concentration 5 s after it was introduced into the reaction chamber, and approximately 15% remained after 20 s. When neutral dimethylpyridine was introduced into the cell in two consecutive pulses separated by a time of 2.5 s, the precursor ion became undetectable within 5 s because the partial pressure was kept higher. This result indicates a homogeneous population of ions, all of which are reactive in CH_2^+ transfer. The reverse reaction (i.e., transfer back to pyridine) does not occur to any measurable extent.

A proton from amine α -distonic ions that have hydrogen atoms bonded to the nitrogen can be transferred to other potential nucleophiles such as neutral amines [17, 26]. This reaction channel, however, is shut down for the product ion of m/z 93 because there are no acidic hydrogens attached to the nitrogen atom.

Collision-Activated Decomposition Spectra of $\text{C}_6\text{H}_7\text{N}^{+}$ Species

Although the FT mass spectrometer results point to formation of an α -distonic ion, more conclusive evidence permitting the assignment of the structure of $\text{C}_5\text{H}_5\text{N}-\dot{\text{C}}\text{H}_2$ comes from the high-energy CAD spectra obtained with the tandem mass spectrometer. High-energy CAD has been the classic tool for the distonic ion chemist. There are two distinct features about the CAD of the product ion of m/z 93. First, the ion is able to lose CH_2 to give a fragment ion at m/z 79 (Figure 2), whereas this process is not detectable on CAD of the isomeric methylpyridine radical cations (Figure 3). The reaction of pyridine- d_5 with the cyclopropane radical cation gives a product that principally loses the CH_2 group that was transferred from the cyclopropane radical cation (Figure 4). The peaks in the relevant region of the CAD spectrum, when submitted to a Gaussian peak-fitting procedure, indicate a small amount of signal intensity at m/z 83 for loss of CHD . The loss of CH_2 (giving rise to a fragment at m/z 84), however, accounts for more than 91% of the total loss of CHD and CD_2 .

These spectra agree well with those reported by de Koster et al. [14(b)] for the ion produced by CH_2^+ transfer from the ethylene oxide radical cation, except that we see that the loss of CH_2 from the pyridine- d_5 adduct (Figure 4) is greater than that of CH_2D , whereas CH_3 loss is preferred for the unlabeled distonic ion. Our data suggest an isotope effect for the hydrogen transfer that is involved in methyl loss. We do not understand the reason for the difference in the spectrum in Figure 4 and the corresponding spectrum in the report of de Koster et al. [14(b)].

Figure 2. CAD spectrum of the product ion of m/z 93 from the reaction of cyclopropane radical cations and neutral pyridine in the CI source (hexafluorobenzene was used as an ionization and collisional stabilization gas).

Figure 3. CAD spectra of the radical cations of (a) 2-methylpyridine; (b) 3-methylpyridine; (c) 4-methylpyridine.

The second revealing feature of the CAD of the m/z 93 ion is the unmistakable appearance of a doubly charged ion at m/z 46.5 (m/z 49 for the deuterium-labeled ion) that is produced by a second ionization or charge stripping. Although methylpyridine radical cations also undergo charge stripping, the abundances of the resulting doubly charged ions are lower by at least an order of magnitude. Because distonic ions are known to be susceptible to charge stripping [2], the observed propensity for it and the favorable loss of the CH₂ neutral fragment are convincing evidence for a distonic ion structure. We cannot rule out, however, a

Figure 4. CAD spectrum of the product ion of m/z 98 formed in the reaction of cyclopropane radical cations and neutral pyridine- d_5 in the CI source.

small contribution by either the 3-methyl or the 4-methyl pyridine (< 10%) to the ion population examined in the CAD experiment.

The product ions of m/z 93 undergo another characteristic reaction to give m/z 41 ions. The spectrum of the $C_5D_5\dot{N}-CH_2$ ion (Figure 4) indicates there are at least three hydrogen atoms in the m/z 41 fragment; that is, the mass shifts to m/z 44. The structure $[CH_2=N=CH]^+$ is suggested, which is consistent with a shift to m/z 42 for the ^{15}N -labeled adduct [14(b)].

Extensive H/D exchange does not occur in the product of the cyclopropane radical cation/neutral pyridine- d_5 reaction. Four major ions in the region of m/z 68–71 appear in the CAD spectrum of the distonic ion from reaction with pyridine- d_5 instead of the three ions in the spectrum of the unlabeled species, pointing to some H/D exchange. It was suggested that the distonic ion $C_5H_5\dot{N}-CH_2$ loses $[H_2CN\cdot]$ to give $C_5H_5^+$ on CAD [14(b)] (Scheme I). This proposal finds support in the dominant shift of the product ion to m/z 70. There is, however, some exchange in competition with fragmentation (Scheme I). The resulting loss of $[HDCN\cdot]$ yields the ion at m/z 69 and $[D_2CN\cdot]$ at m/z 68. The ratio of the abundances of the resulting ions does not equal the theoretical ratio for complete H/D exchange ($D_2CN:HDCN:H_2CN = 10:10:1$), verifying that the exchange reaction is incomplete. The ions of m/z 71 and some of those of m/z 70 are formed by losses of HCN and DCN, respectively.

To add evidence that the distonic ion $C_5N_5\dot{N}-CH_2$ is substituted on the nitrogen rather than on a ring carbon, another structural isomer, (3-methylene)pyridinium distonic ion (V, eq 4) was also investigated. This distonic ion was obtained from the fragmentation of the (3-methylene)pyridinium propionate (IV, eq 4) that was ionized by proton transfer (CH_4 CI) in the CI source:

The distonic structure of the (3-methylene)pyridinium radical cation is consistent with the CAD formation of an $[M-CH_2]^+$ ion and with the charge stripping to give the ion at m/z 46.5 (Figure 5). The CAD spectrum of this distonic ion, however, shows a pattern different

Scheme I

Figure 5. CAD spectra of the product ions of m/z 93 generated from the dissociation of (3-methylene)pyridinium propionate.

than that of the α -dystonic ion $C_5H_5\dot{N}-\dot{C}H_2$ (Figure 2), indicating a different structure.

Another isomeric dystonic ion, the (4-methylene)pyridinium radical cation, was recently investigated [26] for another purpose. The authors were able to distinguish the dystonic ion from the 4-methylpyridine radical cation. The CAD spectra at low (5 eV) and higher (50 eV) collision energy are quite different from each other and from the high collision energy (8 keV) spectra reported here. The lower collision energy spectra cannot give evidence for the distinctive charge-stripping process, and loss of CH_2 was seen only at 50-eV collision energy.

Molecular Orbital Calculations of the $C_5H_5\dot{N}-\dot{C}H_2$ α -Dystonic Ion

The modified neglect of differential overlap (MNDO) molecular orbital calculations of de Koster et al. [14(b)] also point to the stability of the dystonic ion $C_5H_5\dot{N}-\dot{C}H_2$. They find that the formation of a (1-methylene)pyridinium radical cation/formaldehyde complex is favored by 20 kcal/mol over a 3-methylpyridine radical cation/formaldehyde complex. We obtain a similar result by using AM1, MOPAC 5; the 1-methylene pyridinium radical cation is 18 kcal/mol more stable than the radical cation of 3-methylpyridine (Table 2). The heat of formation of the dystonic ion, although lower than those of all the other corresponding conventional isomers, is approximately 12 kcal/mol higher than that of another dystonic ion, the

(3-methylene)pyridinium radical cation. Both dystonic ions have enhanced stability with respect to the conventional isomers, a rather general property of simple α -dystonic ions such as $[\cdot CH_2NH_3^+]$.

We addressed also the stabilities of the dystonic ions but used AM1 methods because MNDO is known to be less quantitative, especially for calculating heats of formation [14(b)]. To calibrate the AM1 method, we compared the theoretical heats of formation for the methylpyridine isomers with the calculated values (Table 2). The largest unsigned error is 2%. Furthermore, the calculated heats of formation of various hydrocarbon ions, discussed recently by us [8] were compared with experimental values (in parentheses): benzene [235 (233) kcal/mol], toluene [219 (215) kcal/mol], propylbenzene [206 (203) kcal/mol], and dihydroindan [197 (196) kcal/mol]. Again, the largest unsigned error in ΔH_f° is 2%.

Structure of the Product Ion of m/z 120

The structure of the other major product ion at m/z 120, formed in the reaction of the cyclopropane radical cation and neutral pyridine was also determined by using tandem mass spectrometry. Allyl bromide and 2-bromopropene were reacted separately with pyridine in the CI source of the tandem sector instrument to produce two possible isomers. The two bromo compounds are known to generate distinctive $[M-Br]$ carbocations on electron ionization [27]. We expected the two carbocations to react with pyridine according to eqs 5 and 6:

The CAD spectra of the resulting product ions of m/z 120 from the allyl bromide/pyridine and the 2-

Table 2. Calculated heats of formation of the C_6H_7N dystonic ions and the corresponding methylpyridine radical cations

Radical cation	Calculated heat of formation (kcal/mol)	Experimental heat of formation (kcal/mol) ^a
(1-Methylene)pyridinium	213	
2-Methylpyridine	234	232
3-Methylpyridine	231	234
4-Methylpyridine	238	233
(3-Methylene)pyridinium	202	

^aFrom H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data* 1977, 6, 235.

bromopropene/pyridine reaction were compared with that formed in the cyclopropane/pyridine reaction (Figure 6). Because the latter spectrum closely resembles the CAD spectrum of the product formed from the allyl bromide/pyridine reaction but not that formed in the 2-bromopropene/pyridine reaction, the structure of the ion at m/z 120 is principally C₅H₅N—CH₂—CH=CH₂ (eq 5), a product that would be expected if both the m/z 120 and m/z 93 ions have the same precursor.

Reactions of Cyclopropane Radical Cations and Other Pyridine Nucleophiles

Cyclopropane radical cations also react with other substituted pyridines, such as methylpyridines, dimethylpyridines, 4-propylpyridine, 4-chloropyridine, pyridazine, pyrimidine, pyrazine, and quinoline, as shown by experiments in the FT mass spectrometer. All nucleophiles react to give [M + CH₂]⁺⁺ and [M + 41]⁺. As the basicity of the neutral pyridine increases, the C—N bond of the distonic ion becomes stronger because no CH₂ exchange reaction was observed to occur from a more basic to a less basic pyridine. The complete transfer of CH₂⁺ from pyridine to 3,5-dimethylpyridine, as was discussed earlier, is but one

example. The general reactivity of pyridine nucleophiles with the various radical cations studied here is contrary to the predictions of Shaik and Pross [28].

CH₂⁺ Transfer from Other Radical Cations

Ethylene oxide and ketene radical cations, as well as the [C₃H₆]⁺⁺ fragment from THF, are also potential CH₂⁺ transfer reagents. Low-pressure reactions of these distonic ion precursors with neutral pyridine were carried out separately in the FT mass spectrometer. A product ion of m/z 93 was generated in each experiment. No adduct from attack of the radical cations on pyridine could be observed, however.

The reactive form of the ethylene oxide radical cation is the acyclic species [CH₂—O=CH₂]⁺⁺, the heat of formation of which was calculated to be approximately 20 kcal/mol less than that of its cyclic form [14(b)]. There are two major products from the reaction with pyridine: the product ion of m/z 93 from an adduct ion fragmenting by loss of CH₂O and protonated ethylene oxide at m/z 45. The rate constant for disappearance of [C₂H₄O]⁺⁺ is 1.2×10^{-9} cm³/molecule · s (Table 1). The CAD spectrum of the m/z 93 product ion is identical to that of C₅H₅N—CH₂ (Figure 2) within experimental error. de Koster et al. [14] recently published their results on the ethylene oxide/pyridine system. Although the CAD spectra reported for this system by de Koster et al. [14] resemble closely those reported here, no doubly charged ion was seen as a result of charge stripping, and no FT mass spectrometry experiments were conducted. Pyridine labeled with ¹⁵N was used [14] in the reactions to elucidate the structure of the m/z 65 ion, which was suggested to be [M — CH₂N].

Tetrahydrofuran radical cations fragment to yield [C₃H₆]⁺⁺, which also transfers a CH₂⁺ to pyridine; the rate of disappearance of C₃H₆⁺⁺ is 2.5×10^{-9} cm³/molecule · s (Table 1). We do not understand why the rate constant is slightly greater than that for the reaction of the *c*-C₃H₆⁺⁺ and pyridine. The CH₂⁺ transfer chemistry supports conclusions from previous investigations in which the [C₃H₆]⁺⁺ fragment from THF was shown to have the same structure as that of ionized cyclopropane [16]. The CAD spectrum of the product ion C₅H₅N—CH₂ is identical within experimental error to that of the cyclopropane radical cation/pyridine product.

The distonic ion C₅H₅N—CH₂ also forms via the direct attack of the ketene radical cation on neutral pyridine followed by the loss of CO. The reaction occurs with high efficiency; the rate constant is 3.9×10^{-9} cm³/molecule · s. Other products are from the dimerization of the ketene radical cation and neutral ketene. The CAD spectrum of the product ion is also identical within experimental error to that in Figure 2.

The theoretical rate constant calculated from the average dipole orientation (ADO) theory [29(a)], which was recently updated [29(b)], is 2.47×10^{-9}

Figure 6. CAD spectra of the m/z 120 ions formed in the reactions of neutral pyridine and (a) the radical cations of cyclopropane; (b) the [C₃H₅]⁺ ion from allyl bromide; and (c) the [C₃H₅]⁺ ion from 2-bromopropene.

$\text{cm}^3/\text{molecule} \cdot \text{s}$ for the reactions of pyridine and the radical cations of cyclopropane, ketene, and the $[\text{C}_3\text{H}_6]^+\cdot$ ion from THF fragmentation. For the reaction of ethylene oxide radical cation and pyridine, the theoretical value is $2.43 \times 10^{-9} \text{ cm}^3/\text{molecule} \cdot \text{s}$. The experimental rate constants are at least 40% of the ADO value, with the exception of that of the ketene radical cation, for which the rate constant is slightly greater than the theoretical value (see Table 1). These results point to a highly efficient production of the distonic ion from appropriate $\text{CH}_2^+\cdot$ -transfer agents.

Metastable Ion Spectra

The metastable ion spectrum of $\text{C}_5\text{H}_5\text{N}^+-\dot{\text{C}}\text{H}_2$ shows that no fragmentation, other than the loss of hydrogen atoms, occurs; this is also true for **V** in eq 4. The $\text{N}-\text{CH}_2$ bonding is obviously strong. The metastable ion spectra of methylpyridines, in contrast to those of distonic ions, show that the conventional isomers give the fragments $[\text{M}-\text{H}]^+$, $[\text{M}-2\text{H}]^+$, $[\text{M}-\text{C}_2\text{H}_2]^+$, and $[\text{M}-\text{HCN}]^+$, as previously reported [30]. These results establish that the distonic ion products have not interconverted with the methyl pyridine radical cations, even when the internal energy is sufficient to give a metastable species.

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