

Ion-Molecule Reactions of Distonic Radical Cations

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I. Introduction

An extensive amount of research has been devoted to radical cations that arise by loss of an electron from a stable neutral molecule. These radical cations are often assumed to have a similar bonding arrangement as their neutral precursors. However, recent theoretical and experimental results¹⁻³ indicate that conventional radical cations with the same connectivity as in their neutral precursors can be thermodynamically as well as kinetically less stable than isomeric structures with *spatially separated charge and odd spin sites*. Moreover, isomerization to these more stable structures has now been demonstrated for several conventional radical cations.³⁻⁵

The term "distonic ion" was introduced in 1984 by Yates, Bouma, and Radom^{1,2} for ions with separated charge and radical sites that formally arise from the ionization of a zwitterion or a diradical. Greek letters were proposed to indicate the relative location of the charge and radical sites. When using conventional

valence bond description, α -distonic ions have the charge and radical sites on adjacent atoms while one and two atoms separate the charge and radical sites in β - and γ -distonic ions, respectively. This method of identification is now widely accepted.³

Distonic radical cations are of wide current interest for a number of reasons. These ions play an important role as the central intermediates and products in the dissociation reactions of many ionized organic molecules, the best-known example being the McLafferty rearrangement of the molecular ions of carbonyl compounds. Further, it now seems likely that the gaseous, long-lived molecular ions of many organic compounds may *exist* as their distonic forms.^{4,5} This is also true for the condensed phases: ESR studies indicate that stable distonic ions are generated from many organic molecular ions in low-temperature freon matrices.^{3,6} Furthermore, certain X- or γ -ray-irradiated amino acids produce distonic ions in frozen matrices.⁷ Thus, studies of distonic ions may lead to a better understanding of the biological consequences of ionizing irradiation.

Although distonic radical cations are now accepted as stable and common gas-phase species, the current knowledge of their chemical properties is almost entirely based on the unimolecular reactions of internally excited ions. Bimolecular reactions of several distonic ions have been investigated, but most of the published work has been carried out to structurally characterize the ions rather than to investigate their chemical properties. This paper reviews the present understanding of the reactivity of gaseous distonic radical cations toward neutral molecules and the mechanisms of these reactions. Comparison of the reactivity of distonic ions to that of conventional radical cations and related even-electron ions is carried out where possible. Special attention has been paid to ion structure verification because, by definition, the study of distonic ions is limited to radical cations with certain structural characteristics.

II. Ion Structure Determination

Several methods have been employed to identify distonic ions, including (1) determination of the heat of formation of the ions, (2) examination of metastable ion dissociation characteristics, such as the kinetic energy release, (3) measurement of collision-activated dissociation spectra, (4) investigation of neutralization and reionization reactions as well as the associated fragmentation, (5) study of ion-molecule reactions, and (6) *ab initio* molecular orbital calculations.^{3,9,10} When considering the results obtained using these approaches, one should be aware of the fact that ions with different lifetimes and/or different amounts of internal energy,



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and hence possibly dissimilar structures, may be studied in some of these experiments.⁸

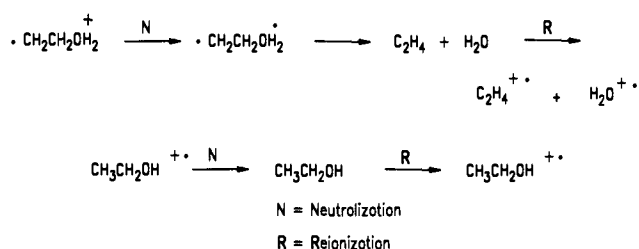
Heat of formation data are used frequently in ion structure determination. If the ΔH_f measured for an ion is the same as that measured or calculated for a particular reference ion, the ions may have similar structures.^{8,9} ΔH_f has been experimentally determined for several distonic ions by appearance energy measurements (the minimum energy necessary to produce a fragment ion from a neutral molecule). This method has its limitations. For example, the structure of the neutral product is often not known but assumed.^{8,9} Further, the accuracy of the measured appearance energy is limited by the kinetic energy distribution of the electrons used;⁹ however, narrowly defined electron energies are attainable using special instrumentation.⁸

During metastable ion decomposition, excess energy is given off as kinetic energy. This results in peak broadening in the measured mass spectrum if the mass analysis of the fragment ions is carried out with an energy analyzer (electrostatic sector). The kinetic energy release⁸⁻¹⁰ (KER) has two main contributions: a nonfixed amount of energy above the energy barrier for decomposition and the reverse activation energy. A

simple bond cleavage is generally expected to have a small reverse activation energy and to yield a small KER, while rearrangement reactions often have large reverse activation barriers and give large KER's.^{8,9} In this way, valuable information has been obtained regarding the decomposition reactions of distonic ions and the structures of the decomposing ions. A recent survey of KER data, however, showed a wide range of values for even the same fragmentation.⁸ Moreover, it must be realized that although the energy range over which metastable transitions occur is narrow, this energy may be high enough to cause isomerization before fragmentation.⁸

Collision-activated dissociation (CAD)^{11,12} has been frequently used to identify distonic ions. In these experiments, an ion is accelerated to a high translational energy and then allowed to collide with a neutral target gas, often helium, nitrogen, or argon. Part of the translational energy is transferred into internal excitation of the ion and leads to fragmentation.^{8,9} The mass selection of the reactant ion and the mass analysis of the product ions can be carried out, for example, by using quadrupole mass filters or magnetic and/or electrostatic sectors. In addition to these instruments consisting of conventional mass analyzers, CAD experiments for distonic ions have been carried out in electrical (quadrupole) and magnetic (ICR) ion traps. CAD is a powerful ion structural tool because it often produces many ionic fragments, and these are usually more abundant than those obtained upon metastable ion dissociation.⁹ Furthermore, since high internal energies can be deposited in the ions upon collisional activation, direct bond cleavages are often favored over the slower and usually less informative rearrangement reactions.⁸ Indeed, many distonic radical cations predominantly fragment by structurally characteristic direct bond cleavages to yield a radical cation fragment and an even-electron neutral molecule.^{3,13} For example, dissociation of the distonic ion $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ yields an abundant ion of m/z 28 (C_2H_4^+) by the loss of CH_2O .⁶ It should be noted here that the ions examined by CAD may have internal energies up to the dissociation

Scheme 1



threshold prior to activation. Hence, the ions to be examined may isomerize prior to activation if the isomerization barrier is low relative to the dissociation threshold.

Neutralization of an ion can generate valuable structural information.^{3,15} For example, when the β -distonic isomer of ionized ethanol, $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$, is reduced, it yields a diradical which quickly dissociates to ethylene and water. The conventional ethanol radical cation is reduced to a stable neutral molecule. Upon reionization, different product ions are observed for these isomeric ions (see Scheme 1).³

Ion-molecule reactions have been employed to determine the structures of distonic ions. Most of these studies have been carried out in Fourier transform ion cyclotron resonance mass spectrometers. Under these low-pressure conditions (10^{-8} – 10^{-6} Torr), only exothermic reactions will be observed if the ions are generated with only small amounts of internal energy or if they are kinetically and internally relaxed prior to reaction. This is the desired situation since the reactivity of an ion can be strongly affected by its internal energy.

Finally, high-level *ab initio* molecular orbital calculations are invaluable in yielding information about an ion's bond lengths, bond angles, and charge distribution. Calculations using high-order Møller-Plesset perturbation theory and large basis sets can give accurate energy relationships and optimized geometries for isomeric radical cations.^{16,17} For distonic ions, in particular, molecular orbital theory has been used to substantiate proposed structures and to define isomerization barriers.^{3,16,17} *Ab initio* calculations have also been utilized in calculating heats of formation which agree well with experimental data for several distonic ions.^{18,19}

III. Experimental Methods

One of the strengths of sector and quadrupole tandem mass spectrometers lies in their ability to study short-lived, ionic species with low abundances. Ion-molecule reactions occurring in the ion source of these devices have been reported for distonic ions. For example, the ion $\cdot\text{CH}_2\text{OCH}_2^+$ was allowed to react with pyridine in a chemical ionization source, the ionic products were selected one at a time with the first mass analyzer, and CAD was allowed to take place for the ions in order to determine their structures.²⁰ However, it is often difficult to unambiguously identify the reaction leading to a particular ionic product in an ion source, since several different ions and neutral molecules are present at the same time.

Fourier transform ion cyclotron resonance mass spectrometers (FT-ICR) are ideal for the study of ion-molecule reactions. Among other useful capabilities,

such as the ability to carry out accurate mass measurements, these instruments allow the isolation of the reactant ions and variation of the reaction time, hence permitting the determination of reaction rates for mass-selected ions. Almost all of the bimolecular reactions of distonic ions known to date were studied in an ICR, and the majority of these studies were conducted in an FT-ICR.

Mass analysis using ion cyclotron resonance dates back to 1949 with the pioneering work of Sommer, Thomas, and Hipple.^{21,22} Later developments in the 1960s and 1970s by Baldeschwieler, Beauchamp, Comisarow, Marshall, McIver, and a host of others brought the ICR through its childhood.²³ More recently, Marshall and Grosshans have described the progress of the ICR through the "teenage years".²⁴ In the first ICR mass spectrometers, ions were drifted through the cell, having several milliseconds to react with neutral molecules in the cell.^{21,23} In 1970, McIver introduced a trapped ion cell wherein ions could be trapped for several seconds by using a crossed electric and magnetic field.²³ In this device, generation of the ions and detection of the ionic products occur at different times, with a variable time period in between for example for ion-molecule reactions to occur.²¹ Early work on distonic ions, such as $\cdot\text{CH}_2\text{CH}_2\text{CH}_2^+$, $\cdot\text{CH}_2\text{OCH}_2^+$, and $\text{CH}_3\text{O}(\text{H}^+)\text{CH}_2\text{CH}_2^+$, was carried out with the use of a trapped ion cell. In 1974, Comisarow and Marshall²⁵ combined the Fourier transform technique with the ICR; by doing so, they were able to decrease the analysis time, enhance the signal-to-noise ratio, increase the resolution, and obtain accurate mass values for ions.^{22,23}

Operation of the Fourier transform ion cyclotron resonance mass spectrometer is based on the fact that ions with a specific m/z value, when in a static magnetic field (B), can be coherently excited to larger orbits. The inverse relationship between the mass value (m/z) of an ion and its cyclotron frequency ($f = qB/2\pi m$; q is the ionic charge in coulombs) allows the determination of the mass values of the kinetically excited ions on the basis of the image current that they induce on the cell plates. Selective excitation can be used to drive endothermic reactions, such as CAD, and to isolate an ion of interest by ejecting all the unwanted ions out of the cell. MS^n experiments involving multiple consecutive reactions and several ion isolation steps are readily carried out in FT-ICR devices by changing the excitation pulse sequence through computer software.²³ These experiments allow, for example, a detailed examination of the ion-molecule reaction products of distonic ions. Further, these ionic products are often distonic ions themselves, and their reactions with neutral molecules may be of interest. For example, $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ reacts with trimethyl phosphate to produce $(\text{CH}_3\text{O})_3\text{P}^+\text{OCH}_2\text{CH}_2^\cdot$ (see Figure 1) whose ion-molecule reactions have been studied.²⁶

In a single-cell FT-ICR, all the events of an experiment are contained within the same space. In this device, unwanted ion-molecule reactions involving, for example, the neutral precursor of the ions, can interfere with the reaction being studied. An FT-ICR equipped with a differentially pumped dual cell²⁷ or an external ion source^{27,28} overcomes this problem by allowing generation of the ions and examination of their reactions in separated reaction chambers. Ion-molecule reactions

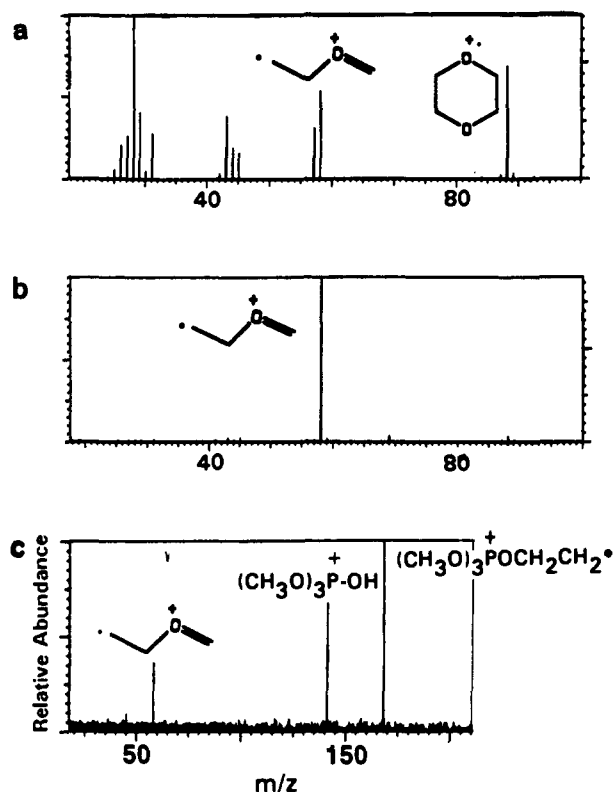


Figure 1. Formation of a new organophosphorus distonic ion by using an ion-molecule reaction:²⁶ (a) 70-eV electron ionization mass spectrum of 1,4-dioxane in a dual-cell FT-ICR; (b) isolation of the distonic fragment ion $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$; (c) reaction of the ion $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ with trimethyl phosphate in the other side of the dual-cell reaction chamber.

of several distonic ions have been investigated in a dual-cell FT-ICR device. In these experiments, transfer of the ions from one cell into the other leads to kinetic excitation. Hence, special attention needs to be paid to relaxation of the ions prior to reactivity studies.

IV. Ion-Molecule Reactions of Distonic Ions

A. Hydrocarbon Ion: $\cdot\text{CH}_2\text{CH}_2\text{CH}_2^+$

The distonic ion $\cdot\text{CH}_2\text{CH}_2\text{CH}_2^+$ is now believed to be formed by ring opening of internally excited, ionized cyclopropane. $\text{C}_3\text{H}_6^{+\bullet}$ ions thought to have the same structure are generated upon loss of formaldehyde from ionized tetrahydrofuran (see Scheme 2), fragmentation of pyrazoline and cyclohexanone (70% of the ions of m/z 42 are $\text{C}_3\text{H}_6^{+\bullet}$) and upon dissociation of ionized hexamethyleneoxide.^{29,30} The structural characterization of this distonic ion, however, has been problematic.^{29,33} Three structures have been considered for the $\text{C}_3\text{H}_6^{+\bullet}$ ions generated from cyclopropane: ionized propene (the lowest energy isomer³¹), the cyclic radical cation (ab initio calculations^{32,33} show that the lowest energy cyclic $\text{C}_3\text{H}_6^{+\bullet}$ species is a scalene triangle with "long bonds"), and the acyclic distonic structure $\cdot\text{CH}_2\text{CH}_2\text{CH}_2^+$. This distonic ion (Figure 2) has been

Scheme 2

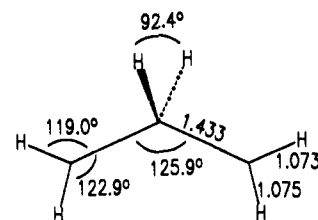
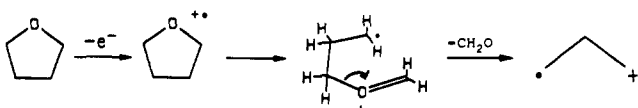
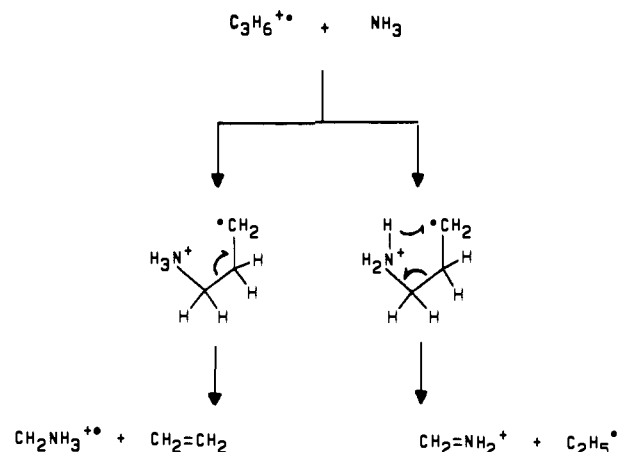


Figure 2.

Scheme 3

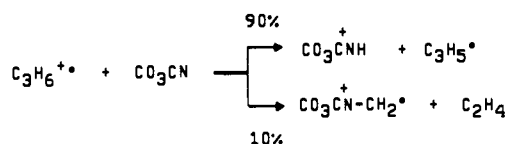


calculated (MP2/6-31G*//UHF/6-31G* level) to be 21.7 kcal mol⁻¹ higher in energy than the cyclic cyclopropane radical cation.³³ An extensive experimental study by Sack, Miller, and Gross²⁹ focusing on dissociation as well as bimolecular reactions of the cyclopropane radical cation showed that the low-energy radical cation is cyclic. Upon excitation, this ion isomerizes to the distonic radical cation, $\cdot\text{CH}_2\text{CH}_2\text{CH}_2^+$,²⁹ and not to ionized propene as suggested earlier.³⁴

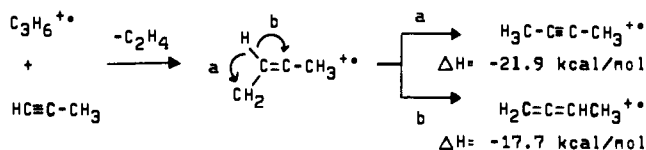
The ion-molecule reactions of $\text{C}_3\text{H}_6^{+\bullet}$ generated from the sources listed above are discussed here since at least in some cases, the reacting ion is likely to be distonic. Proton transfer and transfer of $\text{CH}_2^{+\bullet}$ to neutral reagents are common for these $\text{C}_3\text{H}_6^{+\bullet}$ ions. Most of their reactions can be rationalized on the basis of initial addition of a free electron pair of the neutral reagent to the charged methylene carbon in the distonic structure.

Ionized cyclopropane (as well as the $\text{C}_3\text{H}_6^{+\bullet}$ ion generated from tetrahydrofuran)³⁵ reacts with ammonia to yield two product ions proposed to have the structures shown in Scheme 3.³⁰ Transfer of ionized methylene to yield $\cdot\text{CH}_2\text{NH}_3^+$ and C_2H_4 is 11 kcal mol⁻¹ less exothermic than formation of $\text{CH}_2=\text{NH}_2^+$ and $\text{C}_2\text{H}_5\cdot$.³⁵ In contrast, ionized propene reacts with ammonia by proton transfer.^{29,30} The differences observed in the reactivity of ionized cyclopropane and ionized propene were explained on the basis of the initial formation of a different addition product.^{29,30} Addition of the nitrogen lone pair of ammonia to either the cyclic or the distonic $\text{C}_3\text{H}_6^{+\bullet}$ ion yields an intermediate γ -distonic ion, $[\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+]\cdot$. This intermediate is expected readily to lose ethylene (Scheme 3). On the other hand, addition of ammonia to ionized propene was suggested to yield the distonic ion $\cdot\text{CH}_2\text{CH}(\text{NH}_3)\text{CH}_3^+$ which is not likely to lose ethylene. A number of experimental results have been provided in support of the mechanism shown in Scheme 3.³⁵ For example,

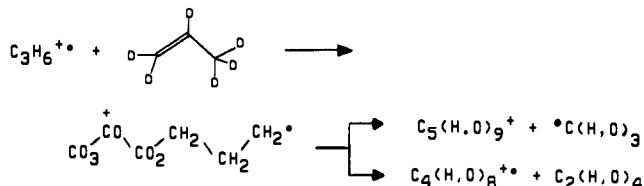
Scheme 4



Scheme 5



Scheme 6



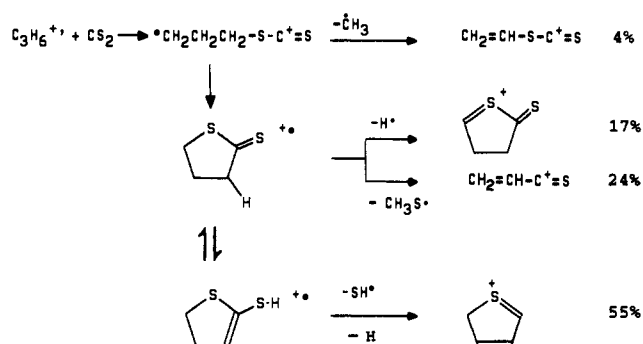
a linear plot of the relative abundance of $\text{CH}_2=\text{NH}_2^+$ as a function of the partial pressure of NH_3 suggests that the $\text{CH}_2=\text{NH}_2^+$ ion is directly produced from the $\text{C}_3\text{H}_6^{+\bullet}/\text{NH}_3$ complex.³⁵ Experiments using differently labeled reagents demonstrated that there is minimal randomization of hydrogen atoms between the three carbons and the nitrogen in the $\text{C}_3\text{H}_6^{+\bullet}/\text{NH}_3$ collision complex.³⁴ For example, only the ions $\bullet\text{CH}_2\text{ND}_3^+$ and $\text{CH}_2=\text{ND}_2^+$ are generated upon reaction of $\text{C}_3\text{H}_6^{+\bullet}$ with ND_3 .

In addition to the products discussed above, ionized cyclopropane yields NH_4^+ when reacted with NH_3 .²⁹ The abundance of NH_4^+ increases with the amount of excess energy imparted in the reactant ion. This led to the suggestion²⁹ that proton transfer occurs for the ring-opened distic structure $\bullet\text{CH}_2\text{CH}_2\text{CH}_2^+$ rather than the cyclic structure.

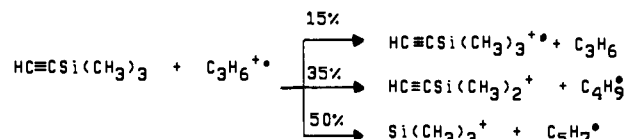
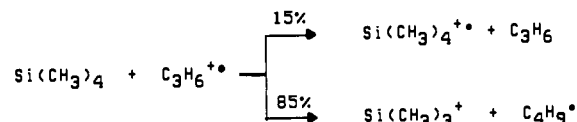
Reactions involving proton or $\text{CH}_2^{\bullet+}$ transfer dominate the reactions of ionized cyclopropane with many neutral molecules, including CD_3CN , propene- d_6 , and alkynes. Rusli and Schwarz³⁶ have reported a branching ratio of 10% for the transfer of $\text{CH}_2^{\bullet+}$ and 90% for the transfer of a proton to CD_3CN (Scheme 4). Two structures were considered for the product from the methylene transfer reaction: $\text{CH}_3\text{CN-CH}_2^{\bullet+}$ and $\text{CH}_3\text{C}(\text{H})\text{NCH}^{\bullet+}$. It was suggested that the former structure is generated first, but that isomerization to the latter structure may occur if enough energy is delivered to the initially formed $\text{CH}_3\text{CN-CH}_2^{\bullet+}$ complex.³⁶

Two possible pathways have been suggested³⁶ for a reaction leading to transfer of $\text{CH}_2^{\bullet+}$ from ionized cyclopropane to neutral alkynes. Both mechanisms involve initial addition of a methylene carbon of the ion to the less hindered terminal alkyne carbon, followed by loss of ethylene. Hydrogen migration in the initially formed product ion yields the final product (Scheme 5). Reaction of the cyclopropane radical cation with propene- d_6 has been proposed²⁹ to be initiated by cationic addition of the distic ion to the carbon-carbon double bond, followed by loss of either a methyl radical or ethylene (the latter reaction results in $\text{CH}_2^{\bullet+}$ transfer to the alkene; Scheme 6).²⁹ Ionized propene

Scheme 7



Scheme 8



reacts with propene- d_6 giving the same products but with different relative abundances.²⁹

The radical cation of cyclopropane does not transfer $\text{CH}_2^{\bullet+}$ to CS_2 or to some silyl substituted compounds. Upon reaction with CS_2 ,²⁹ a covalently bonded intermediate is likely to be initially formed by cationic addition of $\bullet\text{CH}_2\text{CH}_2\text{CH}_2^+$ to the $\text{C}=\text{S}$ double bond.²⁹ Ring closure of the adduct may precede the quite complicated reactions proposed²⁹ to lead to the observed product ions (Scheme 7). The structures of some of the product ions have been verified by comparison of their CAD spectra with those measured for reference ions. Ionized propene reacts with CS_2 in a similar manner but at a slower rate and yields different relative abundances for the product ions.

Ionized cyclopropane undergoes typical charge initiated reactions with $\text{Si}(\text{CH}_3)_4$: methyl anion abstraction (85% of the product distribution) and charge exchange (15%) were observed.³⁶ Similar reactivity was reported for (trimethylsilyl)acetylene: abstraction of an acetylide anion by the distic ion (the reaction yields product ions that correspond to 50% of the product ion distribution) competes efficiently with charge exchange (15%) and methyl anion abstraction (35%) (Scheme 8).³⁶

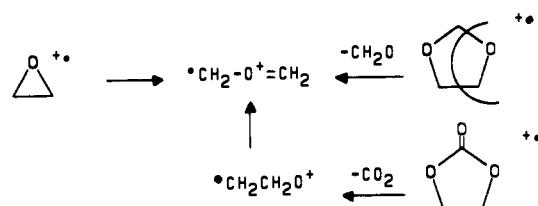
B. Ether Ions

1. $\bullet\text{CH}_2\text{OCH}_2^+$

The acyclic ion $\bullet\text{CH}_2\text{OCH}_2^+$ is formed by electron ionization and subsequent ring opening of ethylene oxide or by loss of CH_2O from ionized 1,3-dioxolane; 1,3-dioxolane-4,4,5,5- d_4 yields $\bullet\text{CD}_2\text{OCH}_2^+$.^{17,37} Ethylene carbonate loses CO_2 to give $\bullet\text{CH}_2\text{CH}_2\text{O}^+$ which quickly isomerizes to $\bullet\text{CH}_2\text{OCH}_2^+$ (see Scheme 9).³⁸

Formation of $\bullet\text{CH}_2\text{OCH}_2^+$ from ionized ethylene oxide was verified by using experiments involving photodis-

Scheme 9



sociation in an ICR,³⁹ ESR spectroscopy,⁴⁰ and electronic absorption spectroscopy.⁴¹ The ion $\cdot\text{CH}_2\text{OCH}_2^+$ was distinguished from an isomer, ionized vinyl alcohol, on the basis of a differing experimental heat of formation (the experimental ΔH_f of the distonic ion is higher than that of ionized vinyl alcohol by 24.5 kcal mol⁻¹).^{37,42,43} Ab initio molecular orbital calculations^{17,44,45} carried out at a high level (MP4/6-311G**) suggest¹⁷ that the cleavage of the C-C bond of ionized ethylene oxide requires only 6.5 kcal mol⁻¹ and yields an ion that is 20 kcal mol⁻¹ lower in energy than the cyclic ethylene oxide radical cation, in agreement with experimental data.¹⁸ The optimized (MP2/6-31G*) structure is given in Figure 3.¹⁷

The reactions of $\cdot\text{CH}_2\text{OCH}_2^+$ reported thus far are summarized in Table 1; all the products reported in the literature are shown. The ion $\cdot\text{CH}_2\text{OCH}_2^+$ shows^{20,36,37,46-51} reactivity similar to that of ionized cyclopropane discussed above. Transfer of $\text{CH}_2^{+\cdot}$ to neutral reagents is common, and it has been observed to be facile for *n*-donor bases. This reaction has not been observed for other $\text{C}_2\text{H}_4\text{O}^{+\cdot}$ isomers.^{37,47} The reactions involving $\text{CH}_2^{+\cdot}$ transfer are likely to be driven by the loss of a stable neutral molecule, CH_2O .^{37,47} Transfer of $\text{CH}_2^{+\cdot}$ is more exothermic for the ion $\cdot\text{CH}_2\text{OCH}_2^+$ than for $\cdot\text{CH}_2\text{CH}_2\text{CH}_2^+$: the former ion eliminates CH_2O ($\Delta H_f = -26.0$ kcal mol⁻¹) while the latter one yields $\text{CH}_2=\text{CH}_2$ ($\Delta H_f = +12.5$ kcal mol⁻¹) as the neutral product. For example, $\Delta H_{\text{rxn}} = +6.3$ kcal mol⁻¹ for $\text{CH}_2^{+\cdot}$ transfer from $\cdot\text{CH}_2\text{CH}_2\text{CH}_2^+$ to $\text{HC}\equiv\text{CH}$, while $\Delta H_{\text{rxn}} = -19.4$ kcal mol⁻¹ for the analogous reaction of $\cdot\text{CH}_2\text{OCH}_2^+$.³⁶ When the $\text{CH}_2^{+\cdot}$ transfer reaction is very exothermic, it is sometimes followed by loss of a hydrogen atom (see Table 1). The partially labeled distonic ion $\cdot\text{CD}_2\text{OCH}_2^+$ transfers either $\text{CH}_2^{+\cdot}$ or $\text{CD}_2^{+\cdot}$ to acrylonitrile at a ratio of 0.7 to 1.0.³⁷ In addition to $\text{CH}_2^{+\cdot}$ transfer, other reactions have been occasionally reported for the ion $\cdot\text{CH}_2\text{OCH}_2^+$. For example, transfer of a proton to the neutral reagent, abstraction of a hydrogen atom by the ion, and $\text{CH}_2^{+\cdot}$ transfer occur upon reaction of $\cdot\text{CH}_2\text{OCH}_2^+$ with ethylene oxide.⁴⁶

The structures of the ionic reaction products have been verified for only a few of the reactions shown in Table 1. These include the reaction of $\cdot\text{CH}_2\text{OCH}_2^+$ with benzene in a chemical ionization source: this reaction yields ionized toluene, as indicated by CAD carried out on the product ion^{20,48} (Scheme 10). The $\text{C}_7\text{H}_7\text{Cl}^+$ ions formed in the reaction of $\cdot\text{CH}_2\text{OCH}_2^+$ with chlorobenzene are mostly (>80%) benzyl chloride radical cations and *m*-chlorotoluene radical cations (15%), with a trace of ionized *o*- and *p*-chlorotoluene.⁴⁹ Reaction of $\cdot\text{CH}_2\text{OCH}_2^+$ with pyridine produces a distonic radical cation, the 1-methylenepyridinium ion (Scheme 11), as indicated by a comparison of the CAD spectra measured for selected reference ions and for

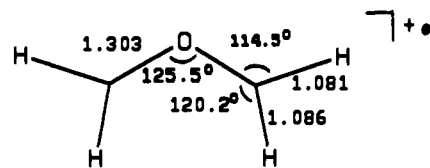


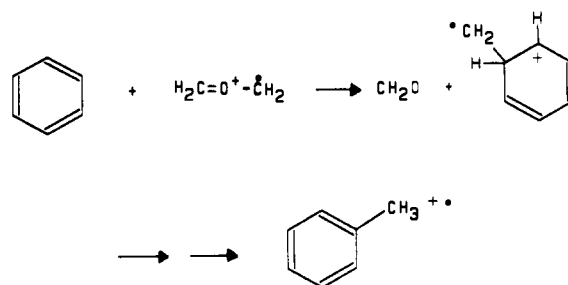
Figure 3.

Table 1. Ion-Molecule Reactions of $\cdot\text{CH}_2\text{OCH}_2^+$

neutral reagent	ionic products	ref(s)
benzene	$\text{C}_6\text{H}_5\text{CH}_3^{+\cdot}$	48
toluene	$\{\text{C}_6\text{H}_5\text{CH}_3 + \text{CH}_2^{+\cdot}\}$	48
acetylene	$\{\text{C}_2\text{H}_2 + \text{CH}_2^{+\cdot} - \text{H}^{\cdot}\}$	36
phenylacetylene	$\{\text{CH}\equiv\text{CC}_6\text{H}_5 + \text{CH}_2^{+\cdot}\}$ $\{\text{CH}\equiv\text{CC}_6\text{H}_5 + \text{CH}_2^{+\cdot} - \text{H}^{\cdot}\}$	37
ethylene oxide	$\text{CH}_2\text{CH}_2\text{OCH}_2^{+\cdot}$ $\{\text{CH}_2\text{CH}_2\text{O} + \text{CH}_2^{+\cdot} - \text{H}^{\cdot}\}$ $\{\text{CH}_2\text{CH}_2\text{O} + \text{H}^{\cdot}\}$ or $\{\text{CH}_2\text{CH}_2\text{O}^{+\cdot} + \text{H}^{\cdot}\}$	37,46
trimethylene oxide	$\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2^{+\cdot}$ $\{\text{CH}_2\text{CH}_2\text{CH}_2\text{O} + \text{CH}_2^{+\cdot} - \text{H}^{\cdot}\}$	37
1,3-dioxolane	$\{\text{CH}_2\text{CH}_2\text{OCH}_2\text{O} + \text{CH}_2^{+\cdot}\}$ $\{\text{CH}_2\text{CH}_2\text{OCH}_2\text{O} + \text{CH}_2^{+\cdot} - \text{H}^{\cdot}\}$	37
1,3,5-trioxane	$\{\text{CH}_2\text{OCH}_2\text{OCH}_2\text{O} + \text{CH}_2^{+\cdot} - \text{CH}_2\text{O} - \text{H}^{\cdot}\}$	47
phenol	$\{\text{C}_6\text{H}_5\text{OH} + \text{CH}_2^{+\cdot}\}$	48
formaldehyde	$\text{CH}_2\text{OCH}_2^{+\cdot}$	37
acetaldehyde	$\text{CH}_3\text{CHOCH}_2^{+\cdot}$	46,49,50
acetone	$(\text{CH}_3)_2\text{COCH}_2^{+\cdot}$	37,47,50
benzophenone	$\{(\text{C}_6\text{H}_5)_2\text{CO} + \text{CH}_2^{+\cdot}\}$	48
acetic acid	$\text{CH}_3\text{C}(\text{OH})\text{OCH}_2^{+\cdot}$	37
methyl benzoate	$\{\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3 + \text{CH}_2^{+\cdot}\}$	48
aniline	$\{\text{C}_6\text{H}_5\text{NH}_2 + \text{CH}_2^{+\cdot}\}$	48
pyridine	$\text{C}_5\text{H}_5\text{NCH}_2^{+\cdot}$	20
nitrobenzene	$\text{C}_6\text{H}_5\text{N}=\text{O}^{+\cdot}$	47
acetonitrile	$\text{CH}_3\text{CNCH}_2^{+\cdot}$	36,37,47
acrylonitrile	$\{\text{CH}_2=\text{CHC}\equiv\text{N} + \text{CH}_2^{+\cdot}\}$	37
benzotrile	$\{\text{C}_6\text{H}_5\text{C}\equiv\text{N} + \text{CH}_2^{+\cdot}\}$	37
3-chloropropene	$\{\text{CH}_2=\text{CHCH}_2\text{Cl} + \text{CH}_2^{+\cdot} - \text{Cl}^{\cdot}\}$	37
3-bromopropene	$\{\text{CH}_2=\text{CHCH}_2\text{Br} + \text{CH}_2^{+\cdot} - \text{Br}^{\cdot}\}$	37
chlorobenzene	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}^{+\cdot}$ $m\text{-ClC}_6\text{H}_4\text{CH}_3^{+\cdot}$ $o\text{- and }p\text{-ClC}_6\text{H}_4\text{CH}_3^{+\cdot}$	48,49
propargyl bromide	$\{\text{CH}\equiv\text{CCH}_2\text{Br} + \text{CH}_2^{+\cdot} - \text{Br}^{\cdot}\}$	37
phosphine	$\text{CH}_2\text{PH}_3^{+\cdot}$	51
tetramethylsilane	$\text{Si}(\text{CH}_3)_4^{+\cdot}$ $\text{Si}(\text{CH}_3)_3^{+\cdot}$	36

^a Based on the data presented in ref 29, this is the most likely structure.

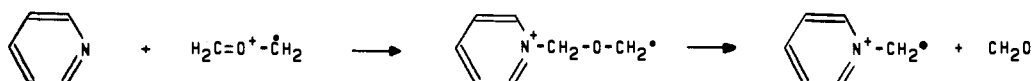
Scheme 10



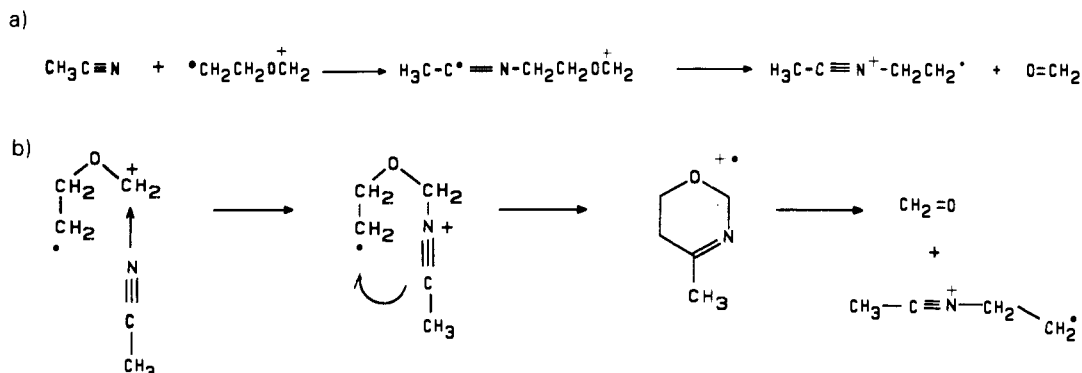
the ionic products obtained upon reaction of $\cdot\text{CH}_2\text{OCH}_2^+$ with pyridine, pyridine-*d*₅ and ¹⁵N-pyridine in a chemical ionization source.²⁰

It is interesting to note that the reaction involving transfer of $\text{CH}_2^{+\cdot}$ from $\cdot\text{CH}_2\text{OCH}_2^+$ to neutral reagents

Scheme 11



Scheme 12



has a close analogy in the chemistry observed for the thoroughly studied methoxy methyl cation, $\text{CH}_3\text{-OCH}_2^+$.⁵² This ion has been shown to readily transfer a methyl cation to various nucleophiles in reactions that lead to elimination of neutral formaldehyde. The reaction has been demonstrated to occur via an $\text{S}_{\text{N}}2$ -type mechanism for example for acetaldehyde and for acetone.^{52c}

2. $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$

The higher homologue of $\cdot\text{CH}_2\text{OCH}_2^+$, the ion $\cdot\text{CH}_2\text{-CH}_2\text{OCH}_2^+$, has also been studied. This ion is formed, for example, by the loss of formaldehyde from ionized 1,4-dioxane.¹⁴ Baumann, MacLeod, and Radom⁵³ have demonstrated by examining the reactions of the partially labeled ions $\cdot\text{CD}_2\text{CD}_2\text{OCH}_2^+$ and $\cdot\text{CH}_2\text{CH}_2\text{OCD}_2^+$ that the ion is stable toward isomerization to the cyclic trimethylene oxide structure. Ab initio molecular orbital calculations (RHF/4-31G//RHF/STO-3G) suggest¹⁶ that $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ is 2.4 kcal mol⁻¹ lower in energy than ionized trimethylene oxide; the energy difference between the experimental heats of formation is 5 kcal mol⁻¹.¹⁸ Figure 4 shows the optimized geometry for $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$.¹⁶

The ion $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ exhibits reactivity similar to that of $\cdot\text{CH}_2\text{OCH}_2^+$. Transfer of ionized ethylene, accompanied by the loss of CH_2O , has been observed upon reaction with several nucleophiles, including $\text{CH}_3\text{-CN}$ ^{14,16,53} (transfer of a proton to acetonitrile also occurs).¹⁴ Examination of the reaction of $\cdot\text{CD}_2\text{CD}_2\text{-OCH}_2^+$ and $\cdot\text{CH}_2\text{CH}_2\text{OCD}_2^+$ with CH_3CN and CD_3CN demonstrated that the reaction occurs without scrambling of the methylene groups within the reacting distonic radical cation.¹⁴ The CAD spectrum of the product ion from transfer of ionized ethylene to $\text{CH}_3\text{-CN}$ is indistinguishable from that of the reference ion $\text{CH}_3\text{CN}^+-\text{CH}_2\text{CH}_2\cdot$ obtained by loss of $\text{CH}_2=\text{O}$ from ionized 5,6-dihydro-4*H*-2-methyl-1,3-oxazine.¹⁴ Two possible mechanisms have been proposed¹⁴ for the exothermic ($\Delta H_{\text{rxn}} = -26$ kcal mol⁻¹) formation of $\text{CH}_3\text{-CN}^+-\text{CH}_2\text{CH}_2\cdot$ in the reaction of $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ with CH_3CN : one is initiated by a "head-on" radical addition of the ion (Scheme 12, route a) to CH_3CN , while the other (Scheme 12, route b) involves an electrophilic addition of the nitrogen lone pair of CH_3CN to the

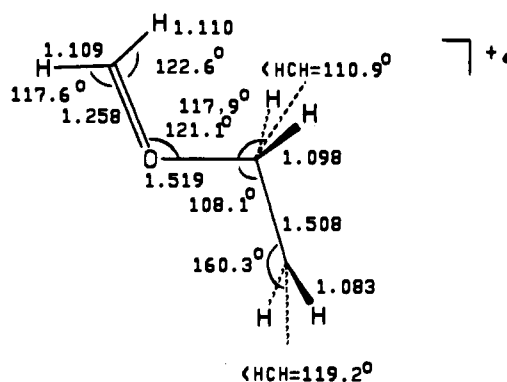


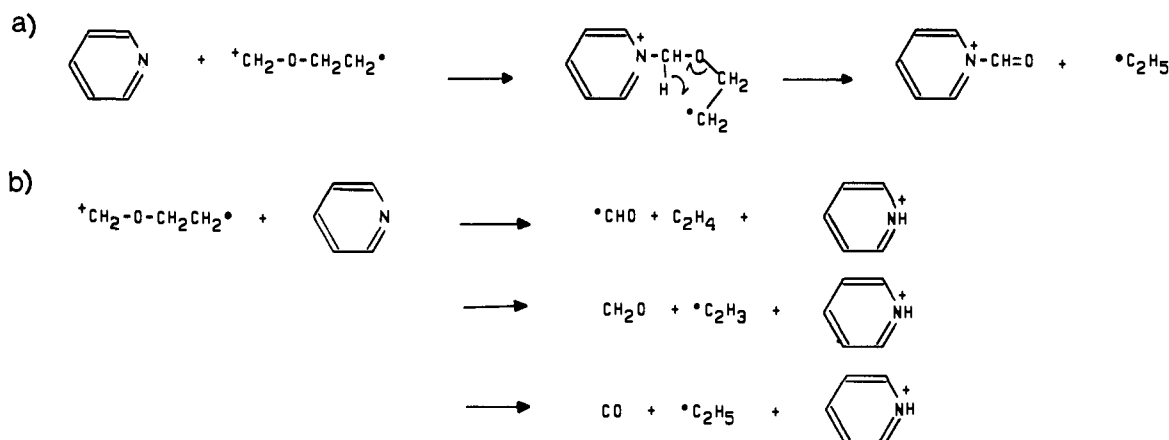
Figure 4.

charge site of the ion, followed by radical cyclization. The authors¹⁴ suggest that the latter one is the more likely possibility. It should be noted here that neither one of these mechanisms explain the facile replacement of CH_2O by NH_3 to generate the ion $\cdot\text{CH}_2\text{CH}_2\text{-NH}_3^+$ reported recently.²⁶

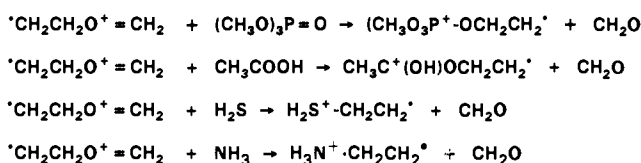
The distonic ion $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ exhibits different reactivity with pyridine than with CH_3CN : transfer of C_2H_4^+ does not occur to pyridine.¹⁴ Instead, a product ion proposed to arise from transfer of CHO^+ from the ion to pyridine ($\Delta H_{\text{rxn}} = -41$ kcal mol⁻¹; Scheme 13) has been reported (the structure of the product ion, however, was not verified). Examination¹⁴ of the partially labeled distonic ions discussed above proved that the H atom in the transferred CHO^+ originates from the terminal OCH_2 group of the reactant ion. In addition to CHO^+ transfer, charge exchange occurs upon reaction of $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ with pyridine.¹⁴

The difference in the reactivity of the distonic ion toward acetonitrile and toward pyridine is puzzling, especially considering the fact that transfer of ionized ethylene to pyridine and transfer of CHO^+ to acetonitrile would each be thermodynamically favored, but are not observed. The following rationalization has been provided for these observations. A mechanism analogous to Scheme 12a, involving radical addition of $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ to pyridine, was thought¹⁴ to be unlikely since it would result in the loss of the aromatic character of the pyridine ring. Therefore, electrophilic addition was proposed¹⁴ to be the more likely initial step for reactions of the distonic ion with pyridine as

Scheme 13



Scheme 14

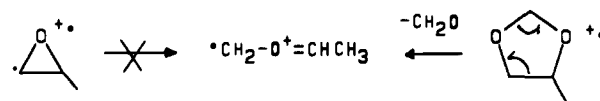


well as with acetonitrile. While the intermediate generated in the reaction with acetonitrile was thought to cyclize (Scheme 12b), this was assumed not to be favorable for the intermediate generated from pyridine because it would result in loss of aromaticity.¹⁴ Instead, electrophilic addition to pyridine was proposed to be followed by intramolecular H-atom abstraction and elimination of $\text{C}_2\text{H}_5\cdot$ (see Scheme 13a). Recent experimental observations²⁶ for reaction of the distonic ion with ammonia, however, are not in accordance with the mechanisms used to rationalize the different outcome of the reactions with acetonitrile and pyridine. An intermediate analogous to that shown in Scheme 12b, generated by the addition of the nitrogen lone pair of ammonia to the charge site of the ion, cannot cyclize; however, predominant $\text{C}_2\text{H}_4^{+\cdot}$ transfer occurs²⁶ to ammonia (see Scheme 14). Furthermore, ammonia does *not* abstract CHO^+ from the distonic ion in spite of the fact that the mechanism shown in Scheme 13a should be equally applicable to ammonia as to pyridine.

A mechanism involving $\text{S}_{\text{N}}2$ substitution by the neutral reagent at the ethylene carbon next to the oxygen would provide a feasible and general explanation for all the $\text{C}_2\text{H}_4^{+\cdot}$ -transfer reactions observed thus far, some of which are shown in Scheme 14.^{26,54} This mechanism is attractive for several reasons, including the fact that the even-electron analogue of the distonic ion, $\text{CH}_3\text{CH}^+\text{OCH}_2$, transfers an ethyl cation to many of the same nucleophiles that abstract ionized ethylene from the distonic ion.⁵⁴

In addition to the reactions discussed above, proton transfer occurs from $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ to acetonitrile and to pyridine.¹⁴ Results obtained from experiments carried out on the reactions of $\cdot\text{CH}_2\text{CH}_2\text{OCD}_2^+$ or $\cdot\text{CD}_2\text{CD}_2\text{OCH}_2^+$ with CH_3CN or CD_3CN imply that all the hydrogen atoms in the distonic ion become equivalent before proton transfer to CH_3CN ; an interfering reaction ($\text{CH}_3\text{CN}^{\cdot+} + \text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CNH}^+ + \cdot\text{CH}_2\text{-CN}$), however, was reported to complicate the interpretation of the results.¹⁴ It was tentatively suggested¹⁴

Scheme 15



that isomerization of $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ to CO and $\text{C}_2\text{H}_6^{+\cdot}$ occurs in the collision complex prior to proton transfer. This would not only explain the observed hydrogen scrambling, but the only exothermic pathway for proton transfer from $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ to CH_3CN involves the elimination of CO and $\cdot\text{C}_2\text{H}_5$ ($\Delta H_{\text{rxn}} = -22 \text{ kcal mol}^{-1}$).¹⁴ In contrast to acetonitrile, three different exothermic pathways are possible for protonation of pyridine (see Scheme 13b).¹⁴

The ion $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ undergoes bimolecular reactions that are quite distinct from those of its conventional isomer, ionized trimethylene oxide, or its even-electron analogue, $\text{CH}_3\text{CH}_2\text{OCH}_2^+$.⁵⁵ For example, the distonic ion has been reported to abstract a thiomethyl group from dimethyl disulfide, while trimethylene oxide radical cation reacts by fast charge exchange.⁵⁵ $\text{CH}_3\text{CH}_2\text{OCH}_2^+$ is unreactive toward this reagent.⁵⁵ These observations led to the conclusion that abstraction of $\text{CH}_3\cdot$ by the distonic ion results in bond formation at the radical site.⁵⁵

3. $\text{CH}_3\text{CH}^+\text{OCH}_2\cdot$

The distonic ion $\text{CH}_3\text{CH}^+\text{OCH}_2\cdot$ is obtained from fragmentation of ionized 4-methyl-1,3-dioxolane as shown in Scheme 15 (60% of the ions of this mass value have the distonic structure; the remaining 40% correspond to ionized methyl vinyl ether). Ionized 2-methyl-1,3-dioxolane fragments to yield a small amount of the distonic ion (20%), together with the isomeric methyl vinyl ether radical cation (80%).^{56,57} The distonic ion $\text{CH}_3\text{CH}^+\text{OCH}_2\cdot$ is not generated upon ring opening of ionized propylene oxide,⁵⁶ in spite of the theoretical prediction (RHF/4-31G//RHF/STO-3G) by Bouma, MacLeod, and Radom¹⁶ that the distonic ion $\text{CH}_3\text{CH}^+\text{OCH}_2\cdot$ is lower in energy by 23 kcal mol^{-1} than the propylene oxide radical cation. On the basis of energetic considerations, photodissociation spectra, and ion-molecule reactions, van de Guchte and van der Hart⁵⁶ concluded that ionized propylene oxide spontaneously isomerizes to ionized methyl vinyl ether which is significantly more stable than ionized propylene oxide and $\text{CH}_3\text{CH}^+\text{OCH}_2\cdot$.¹⁶ The optimized geometry for $\text{CH}_3\text{CH}^+\text{OCH}_2\cdot$ is shown in Figure 5.

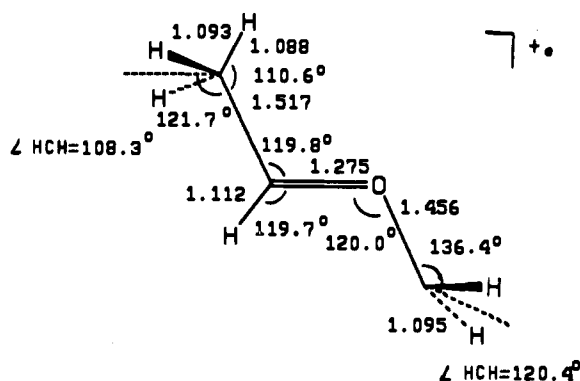


Figure 5.

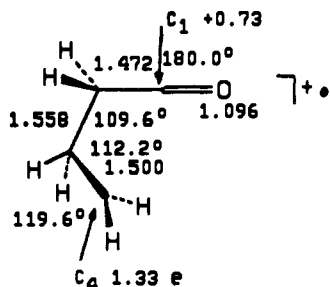


Figure 6.

The ion $\text{CH}_3\text{CH}^+\text{OCH}_2\cdot$ reacts in an analogous manner as the other distonic oxenium ions discussed above. This ion, however, has been observed to transfer either $\text{CH}_2^{\cdot+}$ or $\text{C}_2\text{H}_4^{\cdot+}$ (most likely $\text{CH}_3\text{CH}^{\cdot+}$) to nucleophiles through elimination of CH_3CHO or CH_2O , respectively. Thus, upon collision with acetonitrile, ions with mass values corresponding to $\text{CH}_3\text{CN}^+-\text{CH}_2\cdot$ and $\text{CH}_3\text{CN}^+-\text{CH}^+\text{CH}_3$ are produced (the structures of the product ions have not been verified).

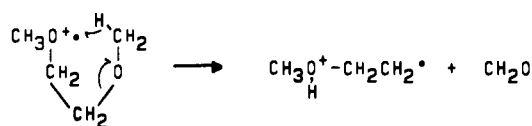
4. $\text{CH}_3\text{O}(\text{H}^+)\text{CH}_2\text{CH}_2\cdot$

An ion likely to have the structure $\text{CH}_3\text{O}(\text{H}^+)\text{CH}_2\text{CH}_2\cdot$ is obtained by loss of CH_2O from 1,2-dimethoxyethane (see Scheme 16).⁵⁸⁻⁶⁰ Support for this distonic structure was obtained from a comparison of the collision-activated dissociation spectra of several isomers.⁵⁹ This distonic ion shows reactivity similar to that of the distonic oxenium ions discussed above. $\text{CH}_3\text{O}(\text{H}^+)\text{CH}_2\text{CH}_2\cdot$ transfers ionized ethylene to various aliphatic ($\text{C}_1\text{-C}_6$) and aromatic nitriles at a rate of about $8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁵⁸ Transfer of $\text{C}_2\text{D}_4^{\cdot+}$ is observed for $\text{CH}_3\text{O}(\text{H}^+)\text{CD}_2\text{CD}_2\cdot$.⁵⁸ Curiously, transfer of $\text{C}_2\text{H}_4^{\cdot+}$ was not observed to a variety of other compounds, including unsaturated and aromatic hydrocarbons, alcohols, ethers, esters, ketones (except for a slow reaction with acetone), aldehydes, and amines. Proton transfer and "other reactions" have been observed but not discussed.⁵⁸ These observations led Busch, Nixon, and Bursey to suggest the mechanism shown in Scheme 17 for the $\text{C}_2\text{H}_4^{\cdot+}$ transfer reaction. No further supporting evidence for this mechanism has been presented.

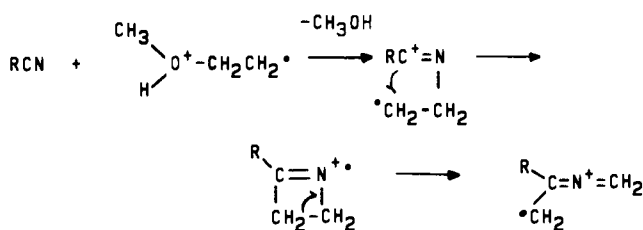
C. Ketone Ions: $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$ and $\cdot\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$

Ionization of cyclobutanone has been suggested to lead to the ring-opened distonic ion $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$

Scheme 16



Scheme 17



on the basis of ab initio molecular orbital calculations (MP2/6-31G**//6-31G**+ZPVE) indicating that the distonic structure is 18 kcal mol⁻¹ lower in energy than the cyclic ion.⁶¹ Differences observed in the CAD spectra and metastable ion dissociation of ionized cyclobutanone and other $\text{C}_4\text{H}_6\text{O}^{\cdot+}$ isomers provided further support for this proposal.⁶² Soon after this, experiments involving gas-phase derivatization of the cyclobutanone radical cation by hydrogen atom transfer, and comparison of the CAD spectrum of the derivatized ion to those of reference ions, conclusively demonstrated that a stable γ -distonic ion is generated upon ionization of cyclobutanone.⁵ The optimized geometry calculated (UHF/6-31G*) for $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$ is given in Figure 6.⁶²

The distonic ion $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$ is the first γ -distonic ion whose ion-molecule reactions have been examined.⁵ While the majority of the bimolecular reactions of distonic ions seem to involve the charged site, the ring-opened cyclobutanone distonic radical cation shows different, radical-type behavior. For example, the ion abstracts a hydrogen atom from acetone in a reaction that involves bond formation at the radical site of $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$ (Scheme 18), as indicated by the CAD spectra measured⁵ for the reaction product and for certain reference ions (see Figure 7; proton transfer from $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$ to acetone is also observed: $k_{\text{total}} = 2.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The distonic ion abstracts a hydrogen atom also from 2-pentanone and from acetaldehyde.⁵⁵ Conventional ketone radical cations (e.g., ionized acetone, ionized cyclopentanone) do not react with acetone.⁵⁴ The same is true for the even-electron analogue of the distonic ion: $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$ (formed by $\text{CH}_3\cdot$ loss from 2-pentanone).⁵⁴

Other radical-type reactions observed for $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$ include the abstraction of $\cdot\text{SCH}_3$ from dimethyl disulfide,^{55,63} (Scheme 19; charge exchange is also observed).⁵⁵ Conventional ketone radical cations do not abstract $\cdot\text{SCH}_3$ from dimethyl disulfide; charge exchange dominates the reactions of these ions.^{55,63} The even-electron ion $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$ is unreactive toward dimethyl disulfide.^{55,63}

The lower homologue of $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$, the ion $\cdot\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$, is produced, for example, by loss of ethylene from ionized γ -butyrolactone.^{55,64} The structure of this ion was deduced on the basis of its dissociation reactions.⁶⁴ The optimized geometry cal-

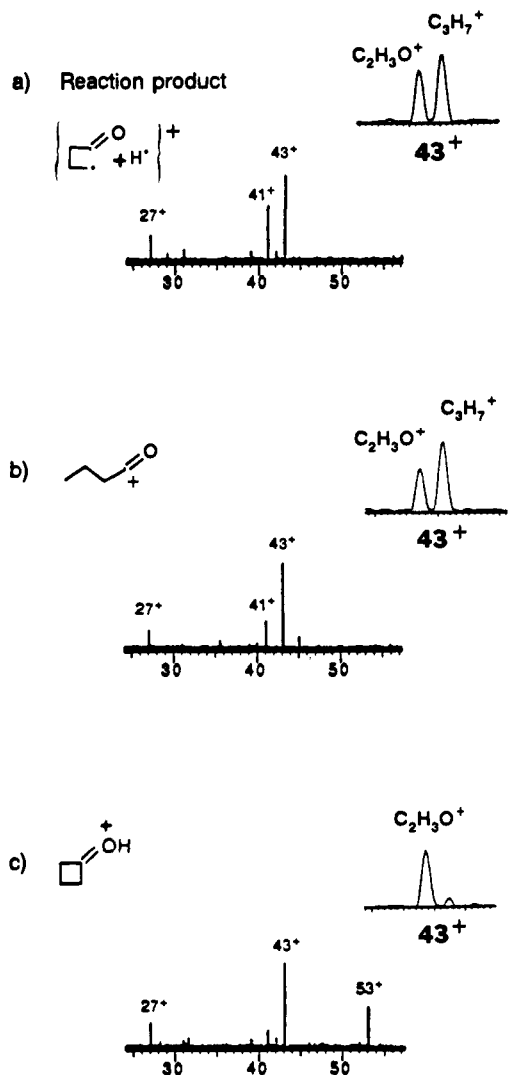
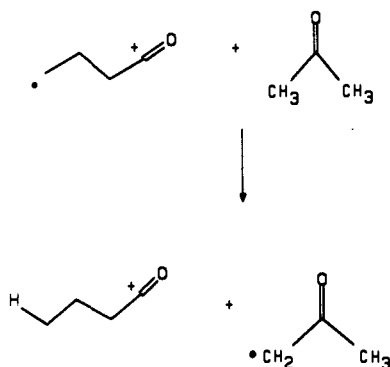


Figure 7. CAD spectra (30–50 eV) measured⁵ for (a) the product formed upon abstraction of a hydrogen atom by the ion $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ from acetone, (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}^+$ generated by loss of CH_3^+ from 2-pentanone, and (c) protonated cyclobutanone. The inserts are an expanded view of each spectrum around m/z 43. Comparison of the spectra shown in a and b indicates that upon hydrogen atom abstraction, bond formation occurred at the radical site in the ion $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$.

Scheme 18



culated at the UHF/6-31G level is shown in Figure 8. The ion $\cdot\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$ reacts with dimethyl disulfide through the same two channels observed for $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$: abstraction of a thiomethyl group (Scheme 19) and charge exchange.^{55,63}

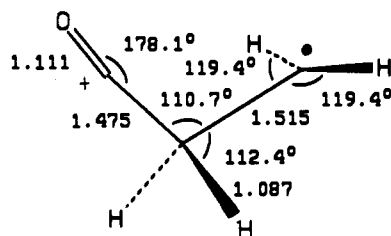
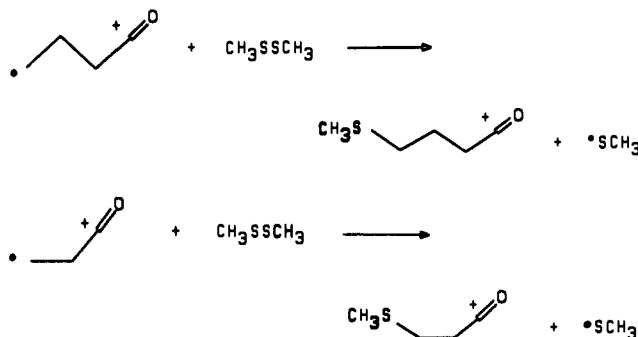


Figure 8.

Scheme 19



D. Halide Ions: $\text{CH}_2\text{ClCH}_3^{\cdot+}$, $\text{CH}_2\text{BrCH}_3^{\cdot+}$, $\text{CH}_2\text{ClH}^{\cdot+}$, and $\text{CH}_2\text{BrH}^{\cdot+}$

The distonic ions $\text{CH}_2\text{ClCH}_3^{\cdot+}$ and $\text{CH}_2\text{BrCH}_3^{\cdot+}$ are fragments of methyl chloro- and methyl bromoacetate, respectively.⁶⁵ Ab initio molecular orbital calculations^{65,66} (UMP2/6-31G**//STO-3G) indicate that the lowest energy structure of $\text{CH}_2\text{ClCH}_3^{\cdot+}$ can best be described as a complex of a chloromethyl radical (the odd spin located on the methylene carbon) and a methyl cation attracted to one of the chlorine lone pairs (Figure 9). These calculations⁶⁶ further suggest that the distonic ion $\text{CH}_2\text{ClCH}_3^{\cdot+}$ is higher in energy by 6.4 kcal mol⁻¹ than the conventional isomer, $\text{CH}_3\text{CH}_2\text{Cl}^{\cdot+}$. Experimental heats of formation, determined from appearance energies, confirmed the relative stability ordering predicted by theory for the distonic and the conventional structures, although the energy difference was found to be larger (15 kcal mol⁻¹) than the calculated value.⁶⁷ The experimental heat of formation of the ion $\text{CH}_2\text{ClH}^{\cdot+}$, generated by dissociation of ionized chloroacetic acid, and that of $\text{CH}_2\text{BrH}^{\cdot+}$, generated by dissociation of ionized 2-bromoethanol, indicate that both of these distonic ions are somewhat higher in energy than their conventional isomers, $\text{CH}_3\text{Cl}^{\cdot+}$ and $\text{CH}_3\text{Br}^{\cdot+}$.¹⁹

The reactivity of both the distonic radical cations $\text{CH}_2\text{ClCH}_3^{\cdot+}$ and $\text{CH}_2\text{BrCH}_3^{\cdot+}$ is different toward nucleophiles and toward electrophiles.⁶⁵ Upon reaction of $\text{CH}_2\text{ClCH}_3^{\cdot+}$ with acetonitrile, $\text{CH}_3\text{CN}^+\text{CH}_3$ is almost exclusively produced for both ions (Scheme 20).⁶⁵ The observation of a methyl cation transfer rather than transfer of $\text{CH}_2^{\cdot+}$ from these halogenated ions to acetonitrile is in accordance with the suggestion mentioned above that acetonitrile acts as a nucleophile toward the charged center in many distonic ions.

The electrophile NO^{\cdot} reacts at the radical site in the halogenated distonic ions $\text{CH}_2\text{ClCH}_3^{\cdot+}$ and $\text{CH}_2\text{BrCH}_3^{\cdot+}$, resulting in the transfer of $\text{CH}_2^{\cdot+}$ to NO^{\cdot} .⁶⁵ Similar findings were briefly reported⁶⁵ for the lower homologues, $\text{CH}_2\text{ClH}^{\cdot+}$ and $\text{CH}_2\text{BrH}^{\cdot+}$: transfer of ionized methylene occurs to NO^{\cdot} , while proton transfer

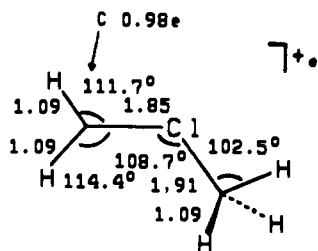
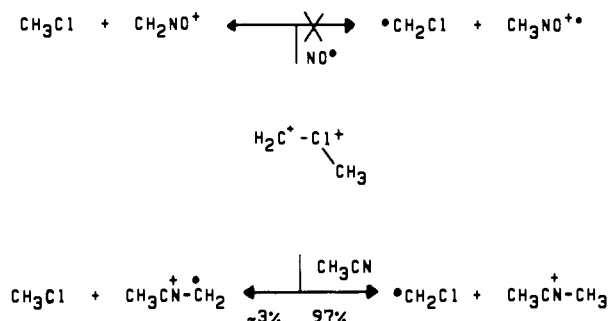


Figure 9.

Scheme 20



is observed to the nucleophiles CH_3CN , CH_2O , H_2O , and CF_2O .

E. Ester Ions

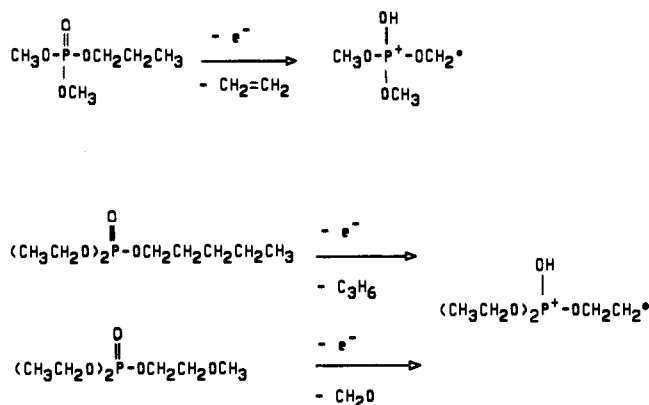
1. $(\text{CH}_3\text{O})_2\text{P}^+(\text{OH})\text{OCH}_2^\bullet$ and $(\text{C}_2\text{H}_5\text{O})_2\text{P}^+(\text{OH})\text{OCH}_2\text{CH}_2^\bullet$

Simple ionized organophosphorus esters have been shown to spontaneously isomerize to more stable distonic structures.⁴ Trimethyl phosphate, for example, isomerizes to $(\text{CH}_3\text{O})_2\text{P}^+(\text{OH})\text{OCH}_2^\bullet$.⁴ An ion with the same structure has been generated by dissociation of ionized dimethyl propyl phosphate by loss of ethylene.⁴ Ionized triethyl phosphate spontaneously isomerizes to $(\text{C}_2\text{H}_5\text{O})_2\text{P}^+(\text{OH})\text{OCH}_2\text{CH}_2^\bullet$;⁴ this ion is also formed by loss of C_3H_6 from ionized diethyl pentyl phosphate and by loss of CH_2O from ionized diethyl 2-methoxyethyl phosphate (Scheme 21).⁴

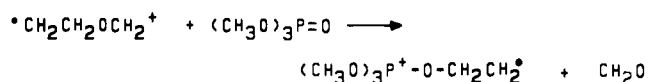
The structures of the molecular ions of trimethyl and triethyl phosphates were confirmed to be distonic through a comparison of the CAD spectra and the ion-molecule reaction products of these ions with those obtained for the respective distonic reference ions and for related radical cations with conventional, unreacted structures.⁴ The isomerization of the ionized methyl ester to the distonic form is estimated⁴ to have a barrier of about 6 kcal mol⁻¹ and to be exothermic by at least 23 kcal mol⁻¹.

The reactivity of the distonic ions $(\text{CH}_3\text{O})_2\text{P}^+(\text{OH})\text{OCH}_2^\bullet$ and $(\text{CH}_3\text{CH}_2\text{O})_2\text{P}^+(\text{OH})\text{OCH}_2\text{CH}_2^\bullet$ was found⁴ to be indistinguishable from that of their even-electron counterparts, protonated organophosphorus esters. For example, when reacted with deuterated ammonia, the ion $(\text{CH}_3\text{O})_2\text{P}^+(\text{OH})\text{OCH}_2^\bullet$ exchanges the acidic hydroxyl hydrogen with deuterium at about the same rate as $(\text{CH}_3\text{O})_3\text{P}=\text{OH}^+$. A related organophosphorus ester radical cation with a conventional structure, $(\text{CH}_3\text{O})_3\text{P}=\text{S}^+$, is unreactive toward deuterated ammonia.⁴ Neutral trimethyl phosphite reacts in a different and structurally characteristic manner with these conventional and distonic ester radical cations. Due to its low ionization energy, this molecule is able to

Scheme 21



Scheme 22



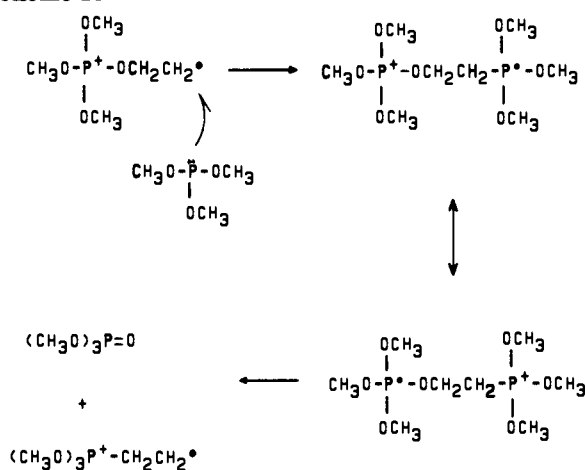
neutralize the molecular ions of many pentavalent organophosphorus esters with conventional structures, including $(\text{CH}_3\text{O})_3\text{P}=\text{S}^+$. However, trimethyl phosphite is also a strong Brønsted base, and it rapidly deprotonates the distonic isomers of ionized trimethyl and triethyl phosphates:⁴ 100% proton transfer was observed for $(\text{CH}_3\text{O})_2\text{P}^+(\text{OH})\text{OCH}_2^\bullet$ at a rate of 1.1×10^{-9} cm³ molecule⁻¹ s⁻¹ (both $(\text{CH}_3\text{O})_3\text{PH}^+$ and its fragment $(\text{CH}_3\text{O})_2\text{P}^+$ are formed)⁴ and for $(\text{CH}_3\text{CH}_2\text{O})_2\text{P}^+(\text{OH})\text{OCH}_2\text{CH}_2^\bullet$ at a rate of 1.3×10^{-9} cm³ molecule⁻¹ s⁻¹.⁴ Fast proton transfer was also observed⁶⁸ earlier upon reactions of the molecular ions of simple phosphorus esters with their neutral precursors. At that time, however, the ions were assumed to have the same connectivity as their neutral precursors.

2. $(\text{CH}_3\text{O})_3\text{P}^+\text{OCH}_2\text{CH}_2^\bullet$

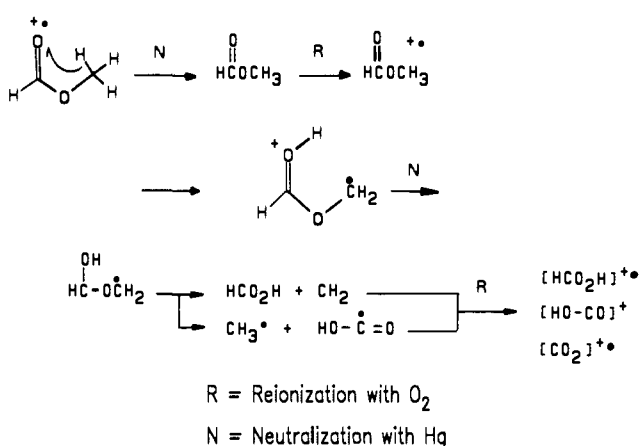
A third distonic organophosphorus ester ion has also been studied.²⁶ This distonic ion, $(\text{CH}_3\text{O})_3\text{P}^+\text{OCH}_2\text{CH}_2^\bullet$, was generated in an ion-molecule reaction involving the transfer of ionized ethylene from $\text{CH}_2\text{CH}_2\text{OCH}_2^\bullet$ to trimethyl phosphate (Scheme 22, Figure 1).²⁶ The structure of the distonic ion $(\text{CH}_3\text{O})_3\text{P}^+\text{OCH}_2\text{CH}_2^\bullet$ was verified by using several different approaches. Upon CAD, this ion shows behavior analogous to that observed for the other known distonic phosphorus ester ions discussed above.^{4,26} The fragmentation reactions of the distonic ion differ qualitatively from those observed for its conventional isomer, ionized dimethyl propyl phosphate.²⁶ Moreover, the ion $(\text{CH}_3\text{O})_3\text{P}^+\text{OCH}_2\text{CH}_2^\bullet$ undergoes a cleavage of the P-O(C₂H₄) bond when activated; this result demonstrates that the transferred ethylene group is covalently, rather than electrostatically, bonded to the phosphoryl oxygen in the ion.²⁶ The absence of CH_2O loss upon CAD indicates that the ion does not isomerize to $(\text{CH}_3\text{O})_2\text{P}^+(\text{OCH}_2\text{CH}_2\text{O})\text{CH}_3$.

The ion $(\text{CH}_3\text{O})_3\text{P}^+\text{OCH}_2\text{CH}_2^\bullet$ is one of the few known distonic radical cations that do not have acidic functional groups or unsaturation near the charge site. This ion was found to be quite unreactive toward strong bases, nucleophiles and reductants, in contrast to most known (distonic or conventional) radical cations.²⁶ The fundamental reasons behind the lack of reactivity were

Scheme 23



Scheme 24



not speculated upon,²⁶ although steric hindrance was proposed as a possible factor. The ion $(\text{CH}_3\text{O})_3\text{P}^+\text{OCH}_2\text{CH}_2^*$ was found to react very slowly ($k < 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) with organic phosphites by transfer of ionized ethylene; this reaction was proposed to lead to another novel distonic radical cation: $(\text{CH}_3\text{O})_3\text{P}^+-\text{CH}_2\text{CH}_2^*$.²⁶ Transfer of a methyl cation from $(\text{CH}_3\text{O})_3\text{P}^+-\text{OCH}_2\text{CH}_2^*$ to trimethyl phosphite was not observed, which rules out a cationic $\text{S}_{\text{N}}2$ mechanism for the ethylene transfer reaction. The reaction was proposed²⁶ to occur by the radical-type mechanism shown in Scheme 23. Support for this mechanism was obtained from the observation that the reaction only occurs for phosphorus-containing neutral reagents. For example, $(\text{CH}_3\text{O})_3\text{P}^+\text{OCH}_2\text{CH}_2^*$ does not transfer ionized ethylene to the strong nucleophiles triethylamine and *sec*-butylamine; both are molecules that cannot form an intermediate analogous to that shown in Scheme 23 for trimethyl phosphite.²⁶ The behavior of $(\text{CH}_3\text{O})_3\text{P}^+-\text{OCH}_2\text{CH}_2^*$ is similar to that of a related even-electron ion, $(\text{CH}_3\text{O})_4\text{P}^+$, in that both ions are quite unreactive in the gas phase.²⁶ For example, $(\text{CH}_3\text{O})_4\text{P}^+$ does not transfer a methyl cation to trimethyl phosphite despite the estimation that this reaction is exothermic.

3. $\text{HC}^+(\text{OH})\text{OCH}_2^*$, $\text{HC}^+(\text{OH})\text{OCH}_2\text{CH}_2^*$

In analogy with the phosphorus ester radical cations discussed above, certain carbon esters have also been proposed to isomerize to distonic structures in the condensed⁶⁹ as well as gaseous phases.⁷⁰⁻⁷³ For example,

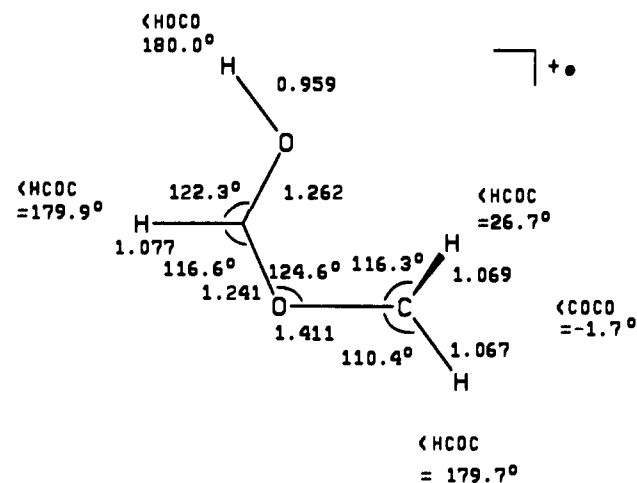


Figure 10.

gaseous methyl and ethyl formate radical cations have been cited⁷⁰⁻⁷³ as isomerizing to distonic structures before fragmenting. Evidence for the rearrangement of a "significant fraction" of the short-lived (microsecond time frame) methyl formate radical cations to the distonic ion $\text{HC}^+(\text{OH})\text{OCH}_2^*$ has been obtained^{73,74} from CAD and neutralization-reionization experiments (see Scheme 24).⁷²⁻⁷⁴ Recent ab initio calculations (QCISD-(T)/6-311G**//HF/6-31G*⁷⁵ and MP3/6-31G**//6-31G**+ZPVE⁷⁶) indicate that the ground-state-ionized methyl formate, HCOOCH_3^+ , has a barrier of 10-16 kcal mol⁻¹ for isomerization to the distonic isomer, $\text{HC}^+(\text{OH})\text{OCH}_2^*$ which is lower in energy by 14-15 kcal mol⁻¹.^{75,76} The optimized geometry⁷⁵ for this distonic ion is given in Figure 10. According to the calculations, the positive charge is shared by the central carbon and hydrogen atoms; spin density of the unpaired electron is located almost exclusively on the terminal carbon.^{75,76}

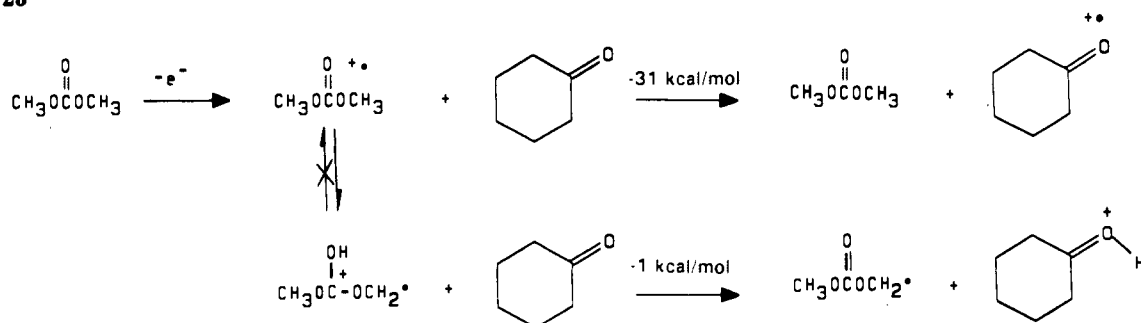
Recent work on the ion-molecule reactions of the gaseous methyl and ethyl formate radical cations demonstrates that the *long-lived* molecular ions exist as the distonic structures.⁷⁷ Like the other distonic ester ions discussed above, the distonic formate ions exhibit only acid-base chemistry, and their reactivity resembles that of protonated esters. For example, $\text{HC}^+(\text{OH})\text{OCH}_2\text{CH}_2^*$ reacts with cyclohexanone by fast proton transfer;⁷⁷ the same reaction occurs for related even-electron ions (protonated esters).⁷⁷ Ester radical cations demonstrated to have conventional, unrearranged structures, such as unsubstituted, ionized lactones, react with cyclohexanone by electron transfer.⁷⁷

Reactions of the distonic formate ions with dimethyl disulfide were of special interest since this neutral reagent is known to transfer a thiomethyl group to certain other distonic ions, presumably to the radical site.⁶³ However, the methyl formate distonic ion reacts by fast proton transfer with dimethyl disulfide.⁷⁷ The ethyl formate distonic ion undergoes fast dissociative charge exchange with CH_3SSCH_3 , and produces $\text{CH}_3\text{-SSCH}_3^+$, ethylene, and formic acid.⁷⁷

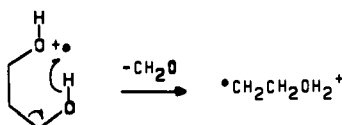
4. $\text{CH}_3\text{OC}^+(\text{OH})\text{OCH}_2^*$

The long-lived dimethyl carbonate radical cation has also been demonstrated to isomerize to a distonic structure: $\text{CH}_3\text{OC}^+(\text{OH})\text{OCH}_2^*$.^{55,77} This conclusion was based on the observation of exclusive proton transfer when the ion was allowed to react with

Scheme 25



Scheme 26



cyclohexanone (see Scheme 25); the unrearranged molecular ion of dimethyl carbonate is expected to react with cyclohexanone by charge exchange.^{55,77} The only other reaction studied thus far for the distonic dimethyl carbonate ion is the reaction with 2-propanol-*d*₃: exchange of the hydroxyl hydrogen with a deuterium atom was observed.^{54,77}

F. Alcohol Ion: $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$

The β -distonic isomer of the ethanol radical cation has been studied extensively. The ion $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$ can be generated for example by loss of CH_2O from ionized 1,3-propanediol⁷⁸ (see Scheme 26). This ion has been structurally characterized using several different approaches. One of the first studies on $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$ reported different CAD spectra for the ion and its two conventional isomers, $\text{CH}_3\text{CH}_2\text{OH}^+$ and $\text{CH}_3\text{OCH}_3^+$.⁷⁹ Other experiments have shown that the dominant metastable dissociation ($\text{C}_2\text{H}_6\text{O}^{+\bullet} \rightarrow \text{C}_2\text{H}_4^+ + \text{H}_2\text{O}$) has a very small kinetic energy release associated with it.⁸⁰ This suggests that the decomposing ion does not rearrange upon formation of the C_2H_4^+ fragment. The energy needed for the formation of $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$ from 1,3-propanediol has been measured, and ΔH_f^\ddagger ($\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$) was deduced to be $175 \pm 2 \text{ kcal mol}^{-1}$.⁸¹ Ab initio molecular orbital calculations (at the MP3/6-31G** level) have been carried out for several different $\text{C}_2\text{H}_6\text{O}^{+\bullet}$ isomers.⁸² The ion $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$ was calculated to have a relatively long C–O bond (Figure 11), but not as long as in the higher energy isomer, ionized ethanol. Both theoretical as well as experimental evidence provide support for the proposal⁸³ that the water molecule can freely shift between the carbon atoms in $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$. The barrier for this isomerization has been estimated to be about $2.4 \text{ kcal mol}^{-1}$.⁸⁴

The ion-molecule reactions of $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$, $\text{CH}_3\text{CH}_2\text{OH}^+$, and $\text{CH}_3\text{CH}_2\text{OH}_2^+$ with a few different neutral reagents were recently compared.⁷⁸ The ions $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$ and $\text{CH}_3\text{CH}_2\text{OH}_2^+$ react with 1-propanol by proton transfer at the same rate ($k = 1.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). $\text{CH}_3\text{CH}_2\text{OH}^+$ reacts in the same way, but at a slightly slower rate ($k = 0.9 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).⁷⁸ $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$ does not transfer ionized ethylene to 1-propanol in spite of the facts that this reaction would be exothermic by at least 20 kcal mol^{-1} ⁷⁸ and that other

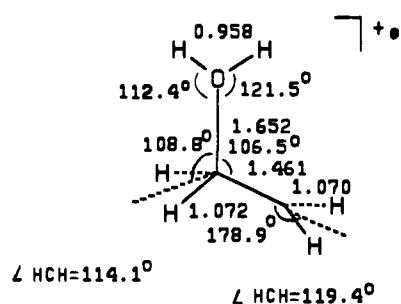


Figure 11.

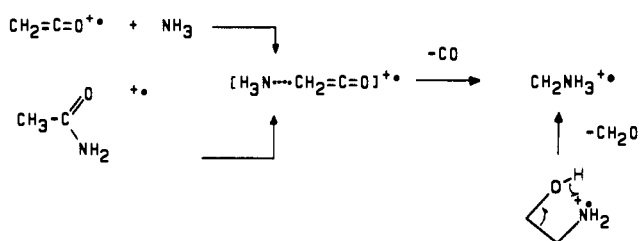
distonic ions with a heteroatom-bound ethylene group (e.g., $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$) readily transfer ionized ethylene to many nucleophiles.

The ions $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$, $\text{CH}_3\text{CH}_2\text{OH}_2^+$, and $\text{CH}_3\text{CH}_2\text{OH}^+$ react with acetonitrile in a different manner than with 1-propanol. Acetonitrile deprotonates the ion $\text{CH}_3\text{CH}_2\text{OH}^+$ ($k = 1.9 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).⁷⁸ Replacement of water with acetonitrile is observed for the other two ions. This reaction leads to transfer of ionized ethylene to acetonitrile for the ion $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$ ($k = 1.6 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $\Delta H_{\text{rxn}} = -31 \text{ kcal mol}^{-1}$) and to transfer of an ethyl cation to acetonitrile for $\text{CH}_3\text{CH}_2\text{OH}_2^+$. For the latter ion, fast proton transfer to acetonitrile is also observed ($k_{\text{total}} = 0.7 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $\Delta H_{\text{rxn}} = -15 \text{ kcal mol}^{-1}$).⁷⁸ Transfer of C_2H_4^+ from $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$ to acetonitrile is analogous to the replacement of CH_2O with acetonitrile in the distonic ion $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ (see the discussion above).

The different reactivity of $\text{CH}_3\text{CH}_2\text{OH}_2^+$ toward the neutral reagents 1-propanol and acetonitrile was explained on the basis of the energy difference between the reactants and the transition state for the ethyl cation transfer.⁷⁸ This energy difference is likely to be greater for the reaction with acetonitrile than for 1-propanol: the higher dipole moment of acetonitrile results in a deeper potential energy well for the ion-molecule complex. Thus, replacement of water is expected to compete more efficiently with proton transfer for the reaction with acetonitrile. On the other hand, the greater basicity of 1-propanol makes proton transfer to this reagent more favorable than to acetonitrile.⁷⁸ Similar arguments may explain the different reactivity of the distonic ion $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$ toward 1-propanol and acetonitrile.

When the ion $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$ is allowed to react with isotopically labeled water (D_2O and H_2^{18}O), exchange of a water molecule with labeled water is observed.⁷⁸ Protonated ethanol, however, shows two stepwise H/D exchanges with D_2O : $\text{CH}_3\text{CH}_2\text{OHD}^+$ is produced initially, and it undergoes H/D exchange to yield $\text{CH}_3\text{CH}_2\text{OD}^+$.

Scheme 27



$\text{CH}_2\text{OD}_2^{\bullet+}$.⁷⁸ Protonated ethanol does not react with ^{18}O -labeled water. The facile replacement of water with labeled water in the distonic ion was suggested⁷⁸ to be in accordance with the predicted⁸⁴ low barrier for the isomerization of this ion to an ion-dipole complex of ionized ethylene and water.

The behavior of the ion $^{\bullet}\text{CH}_2\text{CH}_2\text{OH}_2^+$ differs from that of the distonic ester ions in that some of the bimolecular reactions of the distonic ethanol ion do not resemble those of its even-electron analogue, $\text{CH}_3\text{-CH}_2\text{OH}_2^+$. However, the bimolecular reactions of all the distonic ions discussed thus far are distinctly different from those of their conventional isomers.

G. Amine Ions

1. $^{\bullet}\text{CH}_2\text{NH}_3^+$

Ion-molecule reactions of four distonic amine ions have been studied. The simplest one, $^{\bullet}\text{CH}_2\text{NH}_3^+$, is a product of the reaction of ionized cyclopropane and ammonia (see above).^{30,35} It can also be formed by reaction of ionized ketene, $\text{CH}_2\text{CO}^{\bullet+}$, with ammonia (Scheme 27).^{85,86} Further, ionized acetamide dissociates to give $^{\bullet}\text{CH}_2\text{NH}_3^+$.⁸⁵ Other routes to this distonic ion include the loss of CH_2O from ionized 2-aminoethanol^{86,87} and the loss of two ethylene molecules from ionized *n*-hexylamine.³ The structure of $^{\bullet}\text{CH}_2\text{NH}_3^+$ has been identified by collision-activated dissociation and by ion-molecule reactions.⁸⁵

On the basis of an experimental¹⁹ ΔH_f (deduced from a measured appearance energy), $^{\bullet}\text{CH}_2\text{NH}_3^+$ is higher in energy than $\text{CH}_3\text{NH}_2^{\bullet+}$ by 27 kcal mol⁻¹. Ab initio molecular orbital calculations at the UMP2/6-31G* level predict, however, that $^{\bullet}\text{CH}_2\text{NH}_3^+$ is lower in energy than $\text{CH}_3\text{NH}_2^{\bullet+}$ by 2 kcal mol⁻¹.^{88,89} A discrepancy to this extent is not expected since the agreement between the experimental and theoretical (high-level) determination of the heat of formation of distonic ions is usually good.^{18,19} However, the experimental appearance energy reported for $^{\bullet}\text{CH}_2\text{NH}_3^+$ was not obtained through a simple measurement, due to an isotopic interference from an abundant ion of one unit lower mass value. Indeed, it has been suggested⁸⁹ recently that this value should be redetermined. The optimized geometry⁸⁹ calculated for $^{\bullet}\text{CH}_2\text{NH}_3^+$ is given in Figure 12.

Drewello and others^{35,85} have studied the reactions of $^{\bullet}\text{CH}_2\text{NH}_3^+$ with a number of different electrophiles, including nitric oxide, bromine, phenyl bromide, and phenyl chloride. These experiments were designed to test the possible reactivity at the radical site of the ion. However, no reactions were observed with these neutral reagents.⁸⁵ Proton transfer from $^{\bullet}\text{CH}_2\text{NH}_3^+$ to ammonia has been reported.³⁵ The ion $^{\bullet}\text{CH}_2\text{ND}_3^+$ (formed by reaction of ketene with ND_3) transfers exclusively D^+ to NH_3 .⁸⁵

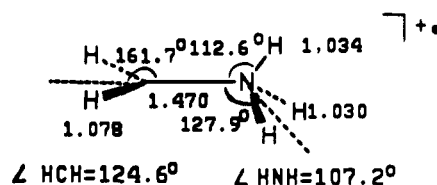


Figure 12.

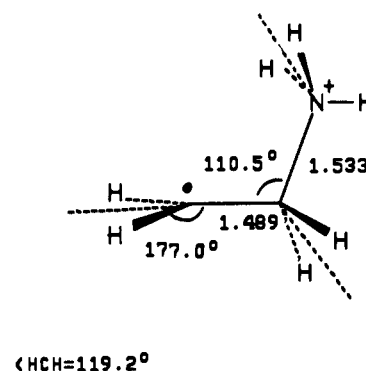


Figure 13.

2. $^{\bullet}\text{CH}_2\text{CH}_2\text{NH}_3^+$

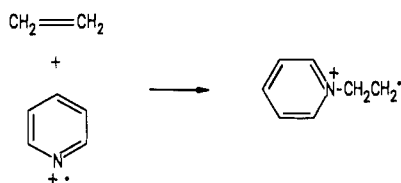
The higher homologue, $^{\bullet}\text{CH}_2\text{CH}_2\text{NH}_3^+$, can be generated in different ways, including fragmentation of ionized 3-aminopropanol by loss of CH_2O , fragmentation of ionized 1,3-propanediamine by loss of $\text{CH}_2=\text{NH}$, fragmentation of ionized 2-(benzyloxy)ethylamine by loss of benzaldehyde, and fragmentation of ionized *n*-alkylamines by loss of alkenes.⁹⁰ The distonic structure $^{\bullet}\text{CH}_2\text{CH}_2\text{NH}_3^+$ was assigned for the $\text{C}_2\text{H}_7\text{N}^{\bullet+}$ fragment ion formed in these reactions on the basis of collision-activated dissociation (formation of $\text{CH}_2=\text{NH}_2^{\bullet+} + \text{CH}_3^{\bullet}$ and $\text{NH}_4^+ + \text{C}_2\text{H}_3^{\bullet}$), comparison of the metastable ion dissociation characteristics of several $\text{C}_2\text{H}_7\text{N}^{\bullet+}$ isomers, dissociation of the partially labeled ion $^{\bullet}\text{CH}_2\text{CH}_2\text{ND}_3^+$, and the differences observed in the neutralization-reionization spectra of isomeric ions $\text{C}_2\text{H}_7\text{N}^{\bullet+}$.^{19,90-92} Examination of the dissociation reactions of $^{\bullet}\text{CH}_2\text{CD}_2\text{NH}_3^+$ and $^{\bullet}\text{CD}_2\text{CH}_2\text{NH}_3^+$ revealed that NH_3 readily shifts between the carbon atoms in $^{\bullet}\text{CH}_2\text{CH}_2\text{NH}_3^+$, suggesting that the barrier for 1,2- NH_3 shift is lower than the dissociation threshold (note the similarity to the β -distonic isomer of ionized ethanol).⁹⁰ Ab initio molecular orbital calculations (MP3/6-31G**/6-31G*) place the barrier at 29 kcal mol⁻¹.⁹¹ The measured dissociation threshold is 48.5 kcal mol⁻¹.⁹¹ The optimized geometry for the distonic ion is given in Figure 13.

The experiments carried out thus far on the bimolecular reactions of the ion $^{\bullet}\text{CH}_2\text{CH}_2\text{NH}_3^+$ show acid/base chemistry similar to that expected for protonated ethyl amine. The reactivity of $^{\bullet}\text{CH}_2\text{CH}_2\text{NH}_3^+$ is quite different from that observed for $^{\bullet}\text{CH}_2\text{CH}_2\text{OH}_2^+$, in spite of some structural similarity. For example, when $^{\bullet}\text{CH}_2\text{CH}_2\text{NH}_3^+$ is reacted³ with ND_3 , three stepwise H/D exchanges are observed; in contrast, the entire water molecule in $^{\bullet}\text{CH}_2\text{CH}_2\text{OH}_2^+$ is replaced by labeled water.

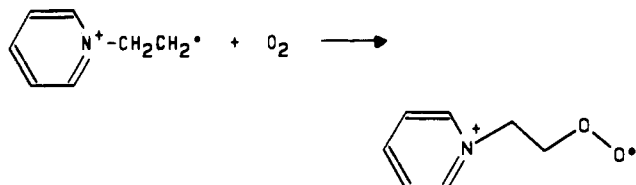
3. $\text{C}_5\text{H}_5\text{N}^+ - \text{CH}_2\text{CH}_2^{\bullet}$

Recently, Gross et al.⁹³ discovered a new route for the synthesis of certain pyridinium distonic ions. They introduced a new way to use an FT-ICR device under

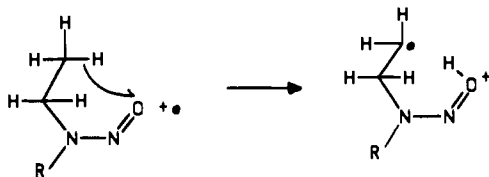
Scheme 28



Scheme 29



Scheme 30



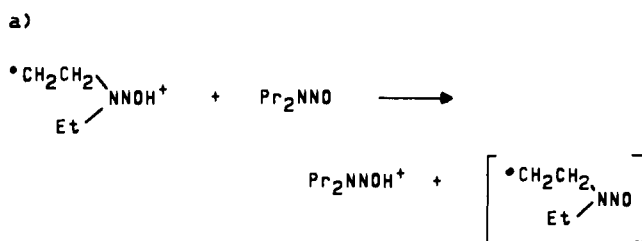
high-pressure conditions and utilized this approach to generate $C_5H_5N^+-CH_2CH_2^{\bullet}$ by addition of the pyridine radical cation to ethylene (Scheme 28). The reactivity of the radical site of $C_5H_5N^+-CH_2CH_2^{\bullet}$ was probed by allowing the ion to react with O_2 : the observed addition to O_2 was proposed to occur as shown in Scheme 29. However, the structures of the reactant ion and the product ion have not yet been conclusively verified.

4. $(^{\bullet}CH_2CH_2)(CH_3CH_2)NNOH^+$

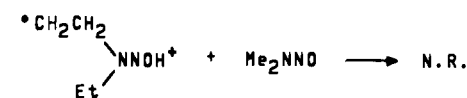
Jaffé, Billets, and Kaplan^{94,95} have reported a study on a different type of distonic amine radical cation. These ions were generated by rearrangement of ionized, long-lived dialkyl-*N*-nitrosamines via a six-membered intramolecular hydrogen atom transfer (Scheme 30) resembling the McLafferty rearrangement.⁹⁴ The distonic structure was suggested for these long-lived radical cations on the basis of their fragmentation reactions: loss of OH^{\bullet} was observed upon collisional activation (it also occurs upon electron ionization of the corresponding neutral molecules). The methyl derivative, dimethyl-*N*-nitrosamine was the only ion studied that did not lose OH^{\bullet} upon activation. This observation was explained on the basis of the inability of this radical cation to undergo intramolecular hydrogen atom transfer via a six-membered transition state.⁹⁴

The ion-molecule reactions observed for the ionized dialkyl-*N*-nitrosamines further support the structural assignment. Protonated dialkyl-*N*-nitrosamines react by proton transfer with neutral alkyl-*N*-nitrosamines if the neutral reagent is more basic than the conjugate base of the ion ($Me_2NNO < Et_2NNO < n-Pr_2NNO < n-Bu_2NNO$).^{94,95} The alkyl-*N*-nitrosamine radical cations were found to react with neutral alkyl-*N*-nitrosamines in a similar manner as protonated dialkyl-*N*-nitrosamines. For example, the distonic diethyl-*N*-nitrosamine radical cation transfers a proton to Pr_2NNO , but not to Me_2NNO (see Scheme 31). Thus, the presence of a radical site does not seem to affect the basicity of these molecules.⁹⁵

Scheme 31



b)



Charge transfer was also observed when the dialkyl-*N*-nitrosamine radical cations were allowed to react with a neutral dialkyl-*N*-nitrosamine with a longer chain or a more branched chain (leading to a lower ionization potential). These reactions are likely to occur via isomerization to the conventional structures.

V. Conclusions

The general reactivity characteristics of distonic radical cations are not readily defined on the basis of the current knowledge. For most distonic radical cations, few different reactions have been examined. Often no attempt has been made to relate the reactivity observed for different distonic ions or to compare the reactivity of distonic ions to that of isomeric conventional radical cations or related even-electron ions. Nevertheless, a few general trends are apparent. For example, it is clear that distonic ions react quite differently from their conventional counterparts. Many distonic ions are characterized by the occurrence of structurally informative reactions involving transfer of charged odd-electron groups (e.g., $CH_2^{+\bullet}$), and by the absence of fast charge exchange reactions common for conventional radical cations.

Bimolecular reactions of distonic radical cations appear to be directed, at least to some extent, by the presence of a protonated heteroatom at the charge site. According to the studies dealing with this type of distonic ions, their bimolecular reactions predominantly involve the charged site. Thus, most of the ions that can be considered as protonated radicals behave like the related even-electron ions. As an example, $(CH_3O)_2P^+(OH)OCH_2^{\bullet}$ reacts with trimethyl phosphite exclusively by proton transfer, and this reaction occurs at the same rate as for the even-electron analogue, $(CH_3O)_3P=OH^+$. On the other hand, the related conventional radical cation $(CH_3O)_3P=S^+$ reacts with trimethyl phosphite by exothermic charge exchange. In a similar manner, the distonic formate ion $HC^+(OH)OCH_2CH_2^{\bullet}$ and its even-electron analogue, protonated ethyl formate, react with cyclohexanone by proton transfer, while conventional ester radical cations react by charge exchange. The known exceptions to this generalization include the β -distonic isomer of ethanol, $^{\bullet}CH_2CH_2OH_2^+$, which has a low barrier for isomerization to an electrostatically bound ion-molecule complex.

In those cases where the charge site of a distonic ion is unreactive toward the neutral reagent, one might

expect the distonic ion to react as a free radical rather than a cation. Indeed, radical-type reactions have been observed for certain distonic ions, including the ions $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$, $\cdot\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$, $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$, $\text{C}_5\text{H}_5\text{N}^+-\text{CH}_2\text{CH}_2\cdot$, and $\text{CH}_3\text{ClCH}_2^+$. In a few cases, these reactions have been verified to involve bond formation at the radical site. Since research has only recently been directed toward the identification of reactions involving the radical site of distonic ions, many more examples are likely to emerge in the near future.

The mechanisms of the radical-type reactions observed thus far are not well understood. For example, the role of the charge site must be important but it has not been addressed. The relative energies of the distonic ions and their conventional isomers may also play a role in controlling the bimolecular reactions of the distonic ions. While many distonic ions are lower in energy than the corresponding conventional ions, some distonic ions, like $\text{CH}_3\text{ClCH}_2^+$, are higher in energy and may rearrange to the low energy isomer prior to or during reaction.

As mentioned above, a bimolecular reaction commonly observed for distonic ions involves transfer of a charged odd spin group to neutral reagents. This reaction is indicative of a $\cdot\text{CHR}$ or $\cdot\text{CH}_2\text{CH}_2$ group in the ion, and hence of a distonic ion structure. Besides serving as a useful diagnostic tool, these reactions provide a powerful synthetic tool for forming new distonic ions, such as $(\text{CH}_3\text{O})_3\text{P}^+\text{OCH}_2\text{CH}_2\cdot$. Although the mechanisms of these reactions must still be considered unknown, the general picture that is slowly starting to emerge involves nucleophilic attack of the entering neutral reagent to a carbon bound to the leaving group in the distonic ion.

Finally, it should be pointed out that studies of several distonic ions, including $\cdot\text{CH}_2\text{OCH}_2^+$, $\cdot\text{CH}_2\text{CH}_2\text{-CH}_2\text{C}\equiv\text{O}^+$, $(\text{CH}_3\text{O})_2\text{P}^+(\text{OH})\text{OCH}_2\cdot$, and $\text{HC}^+(\text{OH})\text{-OCH}_2\text{CH}_2\cdot$, suggest that it may be common for long-lived molecular ions of organic compounds to spontaneously rearrange to their distonic forms. These distonic radical cations are readily distinguished from their conventional counterparts by differences in bimolecular reactions. For this reason alone, it is obvious that the study of the ion-molecule reactions of distonic radical cations is an important emerging area of research.

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