Formation and Characterization of Acetonitrile *N*-Methylide [CH₃CNCH₂]•⁺ and *N*-Methylketenimine [CH₃NCCH₂]•⁺ Radical Cations in the Gas Phase

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Acetonitrile *N*-methylide radical cations [CH₃CNCH₂]•⁺, **a**•⁺, and *N*-methylketeneimine [CH₃NCCH₂]•⁺, **b**•⁺, have been prepared by ion−molecule reactions between ionized cyclobutanone or ionized ketene and acetonitrile or methyl isocyanide. Ion structures have been identified using different experimental conditions including Fourier transform ion-cyclotron resonance experiments, high- and low-energy collisional processes, and reactions within a quadrupole (rf-only) collision cell installed in a large-scale tandem mass spectrometer. All experiments demonstate that **a**•⁺ and **b**•⁺ are stable distonic species that do not easily interconvert. Ab initio molecular-orbital calculations at the QCISD(T)//UMP2 level with a 6-31G(d,p) basis set show that ions **a**•⁺ and **b**•⁺ are of comparable stability, and a heat of formation of 970 kJ/mol is proposed for both species.

Introduction

Chemical ionization[1] is usually considered as a method of production of even-electron ions. However, over the years, it has been recognized that radical cations can also be produced in a high-pressure ion source. In particular, the transfer of CH₂•⁺ to various substrates containing a wide variety of functions has been extensively described.[2−5] The most common reagent gases used to achieve these reactions were cyclopropane[2] and oxirane,[3] which readily undergo ring opening[2,6] upon electron ionization giving rise to a "distonic" ion[7] able to transfer a methylene group. Ionized ketene[4] and ionized cyclobutanone[5] have been also reported as efficient methylene transfer reagents. In fact, upon ionization, cyclobutanone spontaneously undergoes ring opening to generate the distonic ion [CH₂CH₂CH₂CO]•⁺.[8] This has been predicted by molecular-orbital calculations[8a] and was also suggested on the basis of ESR results.[8c]

In the present paper, we report results concerning the generation of acetonitrile *N*-methylide [CH₃CNCH₂]•⁺, **a**•⁺, and *N*-methylketeneimine [CH₃NCCH₂]•⁺, **b**•⁺, radical cations by ion−molecule reactions using the ions formed by electron ionization of cyclobutanone and, as neutral reagents, acetonitrile or methyl isocyanide. Various experimental approaches were used: conventional high-pressure chemical ionization, Fourier transform ion-cyclotron resonance (FT-ICR), and hybrid (sectors/rf-only-quadrupole/sectors configuration) mass spectrometry. Collisional activation at both high- and low-energy regimes, neutralization−reionization experiments, and associative ion−molecule reactions were used to characterize the actual structure of the so-produced ions. For the sake of interpretation, ab initio molecular-orbital calculations on the [C₃, H₅, N]•⁺ system have also been performed.

Results and Discussion

1. Ab Initio Molecular-Orbital Calculations. We have carried out ab initio molecular-orbital (MO) calculations using the Gaussian 94 set of programs.[9] The dp-polarized 6-31G-(d,p) basis set was employed throughout this work. Stationary points were initially located and characterized by harmonic vibrational analysis at the unrestricted Hartree−Fock (UHF) level. Geometrical parameters of the relevant equilibrium and transition structures were subsequently reoptimized by use of second-order perturbation theory. The UMP2/6-31G(d,p) geometries were then utilized in single-point electronic-energy calculations in conjunction with the quadratic configuration-interaction method. Unless otherwise noted, the relative energies given hereafter refer to the estimates obtained from QCISD(T)/6-31G(d,p) total energies and corrected for zero-point energies (ZPE).

A detailed exploration of the [C₃, H₅, N]•⁺ potential energy surface reveals that the two most stable forms among the various isomers considered are ions **a**•⁺ and **b**•⁺.[10] Both ions exhibit nonclassical structures in which charge and radical centers are formally separated. The ion **a**•⁺ under consideration possesses a linear structure (Figure 1) that can be described by the formula [CH₃CN⁺CH₂•]. The terminal radical carbon center is found to be planar. The second structure, **b**•⁺, can be obtained by simply switching the positions of both C and N atoms within the linear frame (Figure 1). It can be seen that either the CN bond length or the distance between the terminal carbons remains almost unchanged in both structures **a**•⁺ and **b**•⁺. The ion **b**•⁺ can thus be described as [CH₃N⁺CCH₂•] also having a planar radical center.
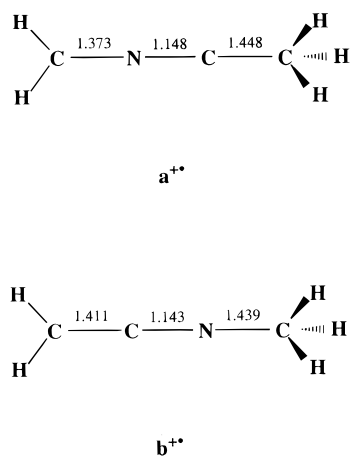
a⁺•

b⁺•

Figure 1. Optimized geometries of acetonitrile *N*-methylide (a) and *N*-methylketenimine (b) radical cations.

TABLE 1: Calculated Total Energies (hartree) and Zero-Point Vibrational and Relative Energies (kJ/mol) of the Stationary Points Considered

| structures	QCISD(T)/6-31G(d,p)[a]	ZPE[b]	ΔE[c]
	Radical Cations		
CH_3CNCH_2•⁺ **a**•⁺	−171.258 55	176	0
CH_3NCCH_2•⁺ **b**•⁺	−171.259 78	178	−1
CH_3CH_2CN•⁺ **c**•⁺	−171.174 14	180	226
CH_3CH_2NC•⁺ **d**•⁺	−171.167 54	184	247
$CH_2CH-CNH^+ + H$•	−171.182 37	157	181
$CH_2CNCH_2^+ + H$•	−171.151 59	155	260
$CH_2CN^+ + CH_3$•	−171.094 76	153	407
$CH_2NC^+ + CH_3$•	−171.089 79	154	421
CH_2CN• $+ CH_3^+$	−171.106 41	155	378
CH_2NC• $+ CH_3^+$	−171.068 71	155	477
	Neutral Species		
CH_3CNCH_2	−171.504 40	181	235
CH_3NCCH_2	−171.538 03	184	150
CH_3CH_2CN	−171.596 46	188	0
CH_3CH_2NC	−171.559 56	187	96

[a] Based on (U)MP2/6-31G(d,p) optimized geometries. [b] Zero-point energies based on (U)HF/6-31G(d,p) harmonic vibrational wavenumbers and scaled by 0.9. [c] Relative energies including QCISD(T)/6-31G(d,p) values and ZPE corrections.

An important piece of information provided by MO calculations is that both ions have practically the same energy (Table 1).

Two reference structures, for which accurate experimental thermochemical data are available,[11,12] are $[C_2H_5CN]$•⁺, **c**•⁺, and $[C_2H_5NC]$•⁺, **d**•⁺. Results presented in Table 1 show that structures **a**•⁺ and **b**•⁺ are more stable than their conventional isomers **c**•⁺ and **d**•⁺ by at least 220 kJ/mol. Moreover, the QCISD(T)/6-31G** calculations corrected for the ZPE contribution (Table 1) combined with the experimental $\Delta_fH°_{298}[C_2H_5$-NC]•⁺ = 1222 ± 10 kJ/mol[11] and $\Delta_fH°_{298}[C_2H_5NC]$•⁺ = 1194 ± 3 kJ/mol[12] lead to an estimate of the heat of formation of both distonic ions $\Delta_fH°_{298}[CH_3CNCH_2]$•⁺ ≈ $\Delta_fH°_{298}[CH_3$-NCCH_2]•⁺ = 970 kJ/mol.

The fragments H• + $[CH_2CNCH_2]^+$, the direct dissociation products from both ions **a**•⁺ and **b**•⁺, lie about 260 kJ/mol above the ground state of both species. Attemps to locate the transition structures for loss of hydrogen atoms from both ions **a**•⁺ and **b**•⁺ failed because the dissociations show a monotonic increase of potential energy. We note that the cation $[CH_2CNCH_2]^+$ has a linear cumulenic structure and that its calculated heat of formation is about 1000 kJ/mol by reference to $\Delta_fH°_{298}[CH_2$-CHCNH]$^+$ = 920 kJ/mol.[12]

SCHEME 1
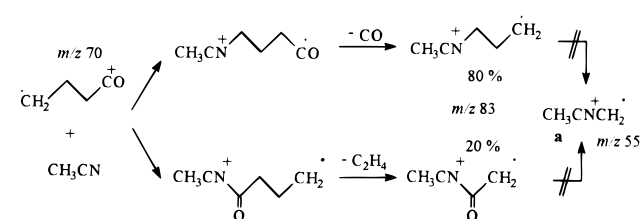
The products of methyl-radical losses and methyl-cation formations from **a**•⁺ and **b**•⁺ have been also investigated. The calculation demonstrates a better stability of the cyano form CH_2CN with respect to its isocyano isomer for both neutral and ionized species. The energy difference is equal to 99 kJ/mol for the neutrals and reduces to 14 kJ/mol for the ions. From the data quoted in Table 1, heats of formation values of $\Delta_fH°_{298}[CH_2CN]$• = 260 kJ/mol and $\Delta_fH°_{298}[CH_2CN]^+$ = 1236 kJ/mol may be proposed (using $\Delta_fH°_{298}[CH_3]$• = 146 kJ/mol and $\Delta_fH°_{298}[CH_3]^+$ = 1093 kJ/mol, and by reference to $\Delta_fH°_{298}[C_2H_5NC]$•⁺ = 1222 kJ/mol[11]). These estimates are in good agreement with the tabulated values: $\Delta_fH°_{298}[CH_2CN]$• = 245 ± 10 kJ/mol and $\Delta_fH°_{298}[CH_2CN]^+$ = 1214 kJ/mol.[12]
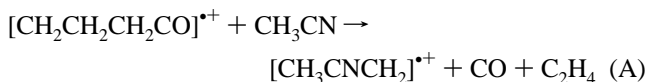
Finally, molecular-orbital calculations have been performed for some relevant neutral C_3H_5N species (Table 1). Structures **a** and **b** correspond to characterized minima on the singlet C_3H_5N potential energy surface (QCISD(T)/6-31G(d,p)//MP2/6-31G(d,p) level). In addition, the calculation predicts that **b** is more stable than **a** by 85 kJ/mol but that both structures are less stable than their more conventionnal isomers C_2H_5CN and C_2H_5NC. Note that, for the last two molecules, the calculated relative energy matches correctly the experimental difference in heat of formation (90 kJ/mol[12]).

2. FT-ICR Experiments. Electron ionization of cyclobutanone in the external ion source of the FT-ICR mass spectrometer yields two major ions: *m/z* 70, $[CH_2CH_2CH_2$-CO]•⁺, and *m/z* 42, $[CH_2CO]$•⁺. Each of these species was separately allowed to react inside the ICR cell with either CH_3-CN or CH_3NC.

Acetonitrile. The reaction of the $[CH_2CH_2CH_2CO]$•⁺ ion, originating from electron ionization of cyclobutanone in the external ion source of the FT-ICR mass spectrometer, with acetonitrile gives essentially three ionized products for which high-resolution measurements give the following: $[C_2H_4N]^+$, $[C_4H_5NO]$•⁺, and $[C_5H_9N]$•⁺. The first ion corresponds to protonated acetonitrile, while the last two isobaric (*m/z* 83) ions correspond to the elimination of ethene and CO, respectively, from the collision complex. These two eliminations occur in a ratio of 20/80 nearly independently of the reaction time.

The formation of a mixture of ions $[C_4H_5NO]$•⁺ and $[C_5H_9N]$•⁺ (*m/z* 83) may be readily explained by the formation of two intermediate adducts able to eliminate either C_2H_4 or CO. This may result from the reaction of both reactive sites of the distonic ion on the nitrogen atom of the acetonitrile molecule (Scheme 1). The major formation of $[C_5H_9N]$•⁺ ions indicates that the radical site is more reactive than the positively charged center. The favored efficiency of the radical-like addition of the distonic $[CH_2CH_2CH_2CO]$•⁺ ion to CH_3CN is in keeping with other results concerning gas-phase reactions between radical cations and unsaturated neutrals.[3a,8,13]

It is noteworthy that the overall process leading to $[CH_3$-CNCH_2]•⁺ ions after both eliminations of C_2H_4 and CO is not observed under our operating conditions (Scheme 1 and reaction A).

$$[CH_2CH_2CH_2CO]^{\bullet+} + CH_3CN \rightarrow$$
$$[CH_3CNCH_2]^{\bullet+} + CO + C_2H_4 \quad (A)$$

This is in agreement with the thermochemistry of this reaction. By use of $\Delta_fH°_{298}[CH_3CNCH_2]^{\bullet+} = 970$ kJ/mol (see Ab Initio Molecular-Orbital Calculations section) and known heats of formation values,[12,14] it appears that reaction A is endothermic by ca. 64 kJ/mol. The methylene transfer from $[CH_2CH_2CH_2CO]^{\bullet+}$ to CH_3CN is thus completely forbidden when using reagents thermalized by a bath of argon at room temperature as performed in the present FT-ICR experiments (see Experimental Section).

The reaction of ionized ketene $[CH_2CO]^{\bullet+}$ with acetonitrile is rapid and exclusively leads to m/z 55 ions (high-resolution determination: 100% of C_3H_5N). The high efficiency of the reaction $[CH_2CO]^{\bullet+} + CH_3CN \rightarrow [CH_3CNCH_2]^{\bullet+} + CO$ is not surprising considering the high exothermicity of this process:

$$[CH_2CO]^{\bullet+} + CH_3CN \rightarrow [CH_3CNCH_2]^{\bullet+} + CO \quad (B)$$
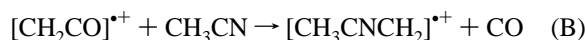
By use of tabulated[12] $\Delta_fH°_{298}$ values and $\Delta_fH°_{298}[CH_3CNCH_2]^{\bullet+} = 970$ kJ/mol, an exothermicity of 94 kJ/mol may be estimated for reaction B.

The low-energy (ca. 30 eV in the center-of-mass frame) CID spectrum of the m/z 55 ions $[CH_3CNCH_2]^{\bullet+}$ obtained after excitation of the ions of interest and collisional activation using a static pressure of argon is consistent with the data reported previously by Rusli and Schwarz.[15] Peaks are observed at m/z 54 (48%), 42 (20%), 28 (16%), 27 (13%), and 15 (3%). A signal is also observed at m/z 40 but is greatly obscured by the presence of ionized argon.

Methyl Isocyanide. A similar set of experiments has been done with methyl isocyanide as a neutral reagent. When neutral methyl isocyanide reacts with the selected $[CH_2CH_2CH_2CO]^{\bullet+}$ ions, three product ions were detected, namely, m/z 42 (C_2H_4N), m/z 55 (C_3H_5N), and m/z 83 (C_5H_9N). The most abundant of these three signals corresponds to m/z 55 ions at all the investigated reaction times. Thus, in contrast with the reaction between $[CH_2CH_2CH_2CO]^{\bullet+}$ and acetonitrile, a clear methylene transfer is observed with the methyl isocyanide isomer. Again, this is in perfect agrement with the thermochemistry of this reaction if ions of structure $\mathbf{b}^{\bullet+}$ $[CH_3NCCH_2]^{\bullet+}$ are produced:

$$[CH_2CH_2CH_2CO]^{\bullet+} + CH_3NC \rightarrow$$
$$[CH_3NCCH_2]^{\bullet+} + CO + C_2H_4 \quad (C)$$
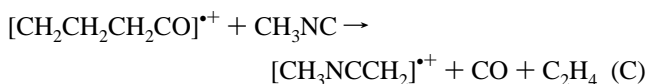
Available heats-of-formation values[12,14] demonstrates that reaction C is *exothermic* by 35 kJ/mol and is consequently allowed to occur from thermalized reactants.

The signal at m/z 42 is certainly the result of a proton transfer between the two reactants, thus giving rise to protonated methyl isocyanide. The reaction appears to be only sligthly efficient, suggesting a quasi-thermoneutral process.
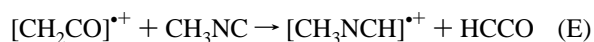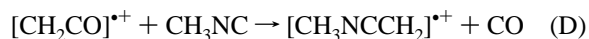
The observation of species with the molecular formula C_5H_9N at m/z 83 is of interest. This ion corresponds to the loss of CO from the collision complex, and its formation may be readily accounted for by the mechanism depicted in Scheme 2.

The first step of the reaction is a nucleophilic radical addition of the terminal methylene of the distonic $[CH_2CH_2CH_2CO]^{\bullet+}$ ion to the carbon of the isocyano group. It is noteworthy that this CC bond formation is in keeping with the known reactivity of isonitrile with respect to free-radical reagents and with the tendency of distonic ions to react with their radical center as mentioned above.[3a,8,13]

SCHEME 2
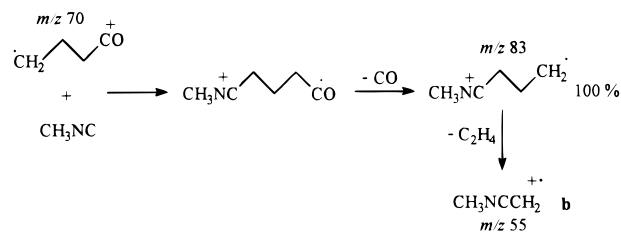
The second reaction investigated involves the $[CH_2CO]^{\bullet+}$ ions generated by dissociative ionization of cyclobutanone and neutral CH_3NC. After reaction, two ionized products are detected at m/z 55 $[C_3H_5N]^{\bullet+}$ and m/z 42 $[C_2H_4N]^{\bullet+}$ (ions that progressively replace the $[CH_2CO]^{\bullet+}$ species in the signal at m/z 42). The thermochemistry[12] of both reactions D and E

$$[CH_2CO]^{\bullet+} + CH_3NC \rightarrow [CH_3NCCH_2]^{\bullet+} + CO \quad (D)$$

$$[CH_2CO]^{\bullet+} + CH_3NC \rightarrow [CH_3NCH]^{\bullet+} + HCCO \quad (E)$$

reveals exothermicities of 193 and 16 kJ/mol, respectively. The methylene-cation transfer is consequently highly favored by its thermochemistry. The protonation of methyl isocyanide by ionized ketene observed here (reaction E) is in contrast with the experiments using the neutral isomeric acetonitrile. The absence of proton transfer in the latter case is due to the endothemicity of this reaction (reaction F, $\Delta H°_{298} = 40$ kJ/mol):

$$[CH_2CO]^{\bullet+} + CH_3CN \rightarrow [CH_3CNH]^{\bullet+} + HCCO \quad (F)$$

The characterization of ions $\mathbf{b}^{\bullet+}$, $[CH_3NCCH_2]^{\bullet+}$ coming from both ion−molecule reactions C and D in the FT-ICR cell has been done by means of collisional-activation experiments. The spectra are comparable and dominated by signals at m/z 54 (60%) and m/z 15 (30%). other peaks appear at m/z 28 (2%), 39 (1%), 41 (2%), and 42 (5%). Thus, compared to the CA spectrum of ions $\mathbf{a}^{\bullet+}$, $[CH_3CNCH_2]^{\bullet+}$ (from reaction B), significant differences emerge. Ions $\mathbf{a}^{\bullet+}$ are characterized by fragments m/z 27, 28, and 42, while for ions $\mathbf{b}^{\bullet+}$ the methyl-cation formation is significant. For both structures, however, the elimination of a hydrogen atom dominates the spectra. These observations are conveniently explained by the calculated energetics of H elimination and $[CH_3]^+$ formation (Table 1). For both structures, the H• loss needs 260 kJ/mol and is the lowest-energy dissociation process. Concerning $[CH_3]^+$ formation from $\mathbf{a}^{\bullet+}$ and $\mathbf{b}^{\bullet+}$, the predicted net critical energies are 477 and 379 kJ/mol, respectively, clearly favoring this reaction for the latter precursor.

3. Collisional Processes in a Hybrid Mass Spectrometer. As briefly summarized in the Introduction, methylenation of various functional groups under conditions of high-pressure chemical ionization has been reported in the literature.[2−5] In the present work, we have used a mixture of cyclobutanone and acetonitrile or methyl isocyanide in the chemical-ionization ion source of the Micromass Autospec 6F mass spectrometer (see Experimental Section) with the aim of generating either ions $\mathbf{a}^{\bullet+}$ or $\mathbf{b}^{\bullet+}$.

High-Energy CID. Experiments with acetonitrile indeed give rise to a very strong signal for $[CH_3CN + 14]^{\bullet+}$ ions, m/z 55 (50% of the base peak), which may be attributed to ions $\mathbf{a}^{\bullet+}$. Other significant peaks are observed at m/z 141 (15%: protonated cyclobutanone dimer), m/z 112 (30%: protonated cyclobutanone−acetonitrile heterodimer), m/z 84 (20%: [cyclob-
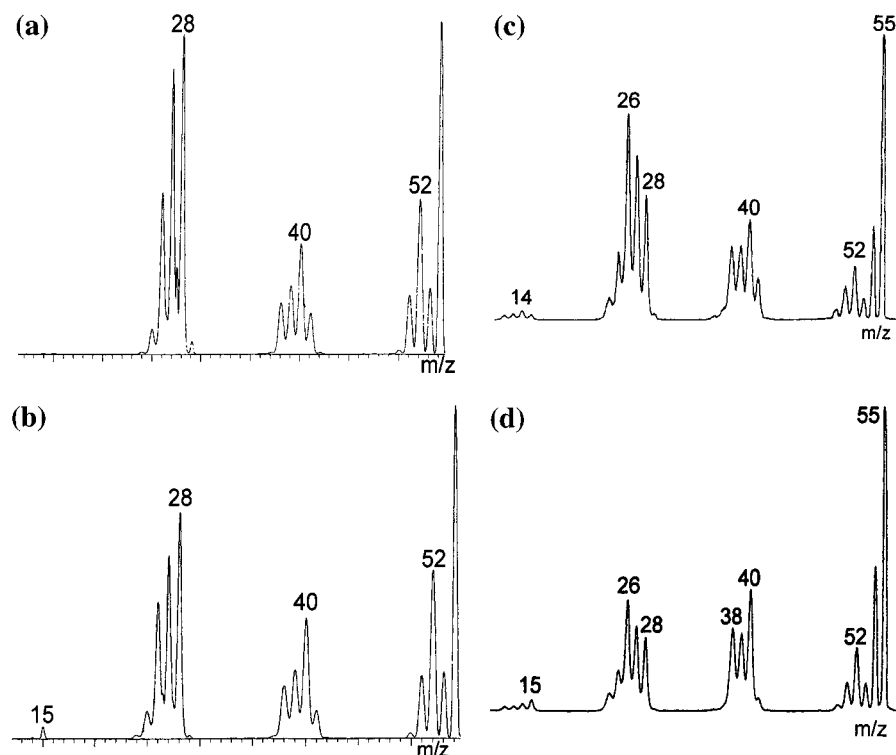
Figure 2. CA (O$_2$) and NR (NH$_3$/O$_2$) spectra of m/z 55 radical cations generated by chemical ionization (cyclobutanone reagent gas) of acetonitrile (a, c) and methyl isocyanide (b, d).

utanone + CH$_2$]$^{\bullet+}$), m/z 71 (100%: protonated cyclobutanone), m/z 70 (80%: ionized cyclobutanone), and m/z 42 (75%: a mixture of 37% ionized ketene, 13% [C$_3$H$_6$]$^{\bullet+}$ ions, and 50% protonated acetonitrile). Both ions m/z 84 and m/z 112 are the results of ion–molecule reactions between neutral and ionized cyclobutanone.[16]

The CA spectrum of ions **a**$^{\bullet+}$ is presented in Figure 2a. This spectrum is dominated by signals at m/z 54 and 28. Significant peaks also appear at m/z 52, 40 (methyl loss) and, in the low-mass region, m/z 14 and m/z 15. Note that the charge-stripping peak at m/z 27.5 is quite intense, a situation being frequently reported for distonic ions.[17] Surprisingly, this spectrum is not conclusive concerning the connectivity of the atoms; the loss of CH$_2$ is observed, but the corresponding peak (m/z 41) is of low intensity.

Radical cation **b**$^{\bullet+}$, [CH$_3$NCCH$_2$]$^{\bullet+}$ also appears to be efficiently prepared in the chemical-ionization source by electron bombardment of a mixture of cyclobutanone and methyl isocyanide. The chemical-ionization spectrum presents abundant peaks at m/z 141 (5%: protonated cyclobutanone dimer), m/z 112 (10%: [cyclobutanone + CH$_2$CO]$^{\bullet+}$), m/z 84 (14%: [cyclobutanone + CH$_2$]$^{\bullet+}$), m/z 71 (20%: protonated cyclobutanone), m/z 70 (60%: ionized cyclobutanone), m/z 55 (90%: [CH$_3$NC + 14]$^{\bullet+}$), and m/z 42 (75%: a mixture of 30% ionized ketene, 10% [C$_3$H$_6$]$^{\bullet+}$ ions, and 60% protonated methyl isocyanide).

The CA spectrum of the m/z 55 ions produced under high-pressure chemical ionization of a mixture of cyclobutanone and methyl isocyanide is quite similar to the spectrum of ions **a**$^{\bullet+}$ except that the CH$_3^+$ ions (m/z 15) are more abundant and that the m/z 27.5 peak due to a charge-stripping process is accompanied by a signal at m/z 26.5 of similar intensity (Figure 2b). Again, the observation concerning CH$_3^+$ is in line with calculated energies of the fragments (see Table 1 and the FT-ICR Experiments section).

We finally note that isomeric ions such as ionized propio-

nitrile and ethyl isocyanide exhibit distinct CA spectra[11] different from the CA spectra shown in parts a and b of Figure 2. However, large similarities are also apparent (dominant peaks at m/z 54, 40, 39, 38, 28, and 15), thus rendering difficult a clear structural characterization from these spectra.

Neutralization–Reionization Mass Spectrometry. To obtain more information on the actual structure of the m/z 55 ions, we have also recorded their neutralization–reionization (NR) mass spectrum. It is indeed recognized that with this technique more internal energy is deposited in the ions so that simple cleavage reactions often become predominant.[18] In fact, the NR spectrum of ions **a**$^{\bullet+}$ (Figure 2c) is not very different from the CA spectrum; in particular, no significant increase of the loss of CH$_2$ is observed. The reduction of intensity of the peak at m/z 28 may indicate that these ions result from a rearrangement reaction (HCN loss). The NR mass spectrum of radical cations **b**$^{\bullet+}$ is also very similar to that of ions **a**$^{\bullet+}$ with an increased intensity of the m/z 15 peak and a reduced intensity of the m/z 41 peak (Figure 2d).

The observation of an intense recovery signal corresponding to survivor ions in the NR spectra reported in parts c and d of Figure 2 indicates that both neutral molecules **a** and **b** are stable species in the gas phase. This corroborates the theoretical results demonstrating that both structures correspond to minima on the C$_3$H$_5$N potential-energy surface (Table 1).

Collisional Activation at Low Kinetic Energy. It has been reported in some instances that the CA spectra obtained in a low-kinetic-energy regime may complement the high-kinetic-energy results.[19] However, most of these conclusions are based on the sequence identification of peptides, and to the best of our knowledge, systematic studies on smaller organic ions are not available yet.

CA spectra of ions **a**$^{\bullet+}$ and **b**$^{\bullet+}$ obtained at low kinetic energy have been reported in the FT-ICR Experiments section. Low-energy CA spectra are usually recorded on multiquadrupole or hybrid (sectors–quadrupoles) instruments, and thus, the Mons'
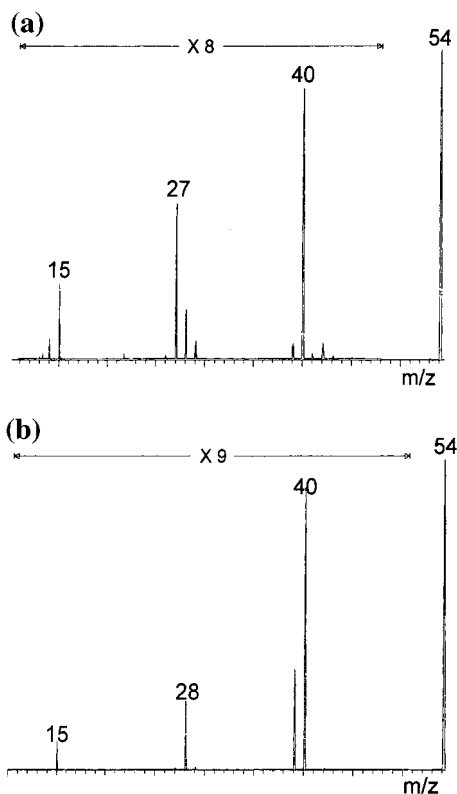
[CH₃CNCH₂]•⁺ and [CH₃NCCH₂]•⁺ | $[CH_3CNCH_2]^{\bullet+}$ and $[CH_3NCCH_2]^{\bullet+}$

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Figure 3. CA (Ar) spectra at low kinetic energy (ca. 30 eV) of *m/z* 55 ions generated by chemical ionization (cyclobutanone reagent gas) of acetonitrile (a) and methyl isocyanide (b).
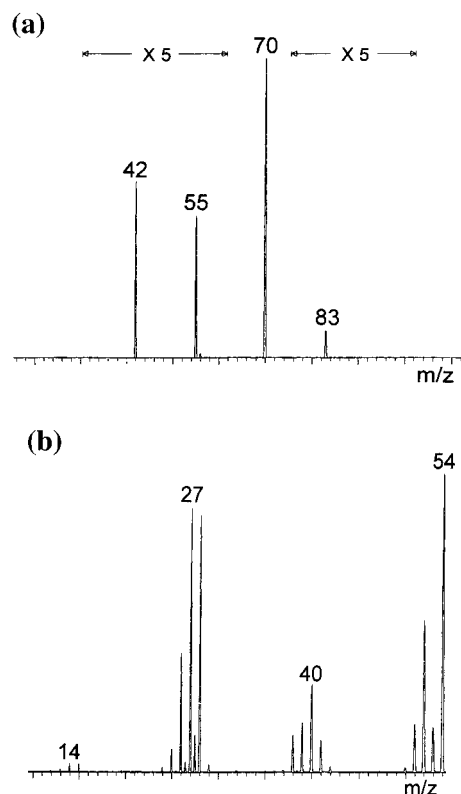

Figure 4. Reaction between ionized cyclobutanone and neutral acetonitrile in the rf-only collision cell: (a) mass spectrum of the ions produced and (b) CA (O₂) mass spectrum of the produced *m/z* 55 ions.

laboratory tandem mass spectrometer in its hybrid configuration is also appropriate for performing these kinds of experiments.

Parts a and b of Figure 3 show the CA spectra of the *m/z* 55 ions **a**•⁺ and **b**•⁺ generated in the CI source of a Micromass Autospec 6F and fragmented in the rf-only quadrupole at low kinetic energy (ca. 20 eV center-of-mass kinetic energy). Large similarities exist between these spectra and the homologuous data obtained from FT-ICR experiments. In both cases, the loss of H• (*m/z* 54) is by far the most intense process as expected from the favorable thermochemistry of this dissociation. Structure-significant peaks are clearly seen at *m/z* 15, *m/z* 27 (exclusively for **a**•⁺), *m/z* 28 (particularly for **b**•⁺), *m/z* 39 (exclusively for **b**•⁺), *m/z* 40, and *m/z* 42 (exclusively for **a**•⁺) in Figure 3. These observations compare perfectly with the FT-ICR results. A slight difference, however, concerns the larger relative abundance of peaks *m/z* 42 for **a**•⁺ and *m/z* 15 for **b**•⁺. This finding may be attributed to the larger kinetic energy used during the FT-ICR experiments.

Obviously, important differences appear between the low- and high-energy CA spectra of both ions **a**•⁺ and **b**•⁺. Secondary decompositions are virtually absent and charge stripping is inefficient, as would be expected for slow ions. Structure-significant peaks are also clearly seen at *m/z* 40 and 15.

4. Ion−Molecule Reactions in a Quadrupole rf-Only Collision Cell. *Formation of Ions a•⁺.* Recently, we have modified a large-scale tandem mass spectrometer to allow the study of reactive ion−molecule collisions and to allow the recording of CA spectra of mass-selected products at high kinetic energy (8 keV).[16]

The spectrum shown in Figure 4a results from the following sequence of operations. First, cyclobutanone is ionized by electron impact, and the molecular ions, *m/z* 70, accelerated at 8 keV are mass-selected with MS1 (see Experimental Section). These ions are then decelerated to ca. 5 eV and introduced in

the rf-only quadrupole cell pressurized to ca. 10⁻³ Torr with acetonitrile. The ions produced in the rf-only region are reaccelerated at 8 keV and recorded by scanning the last magnetic field (MS2). The reaction leads to the formation of *m/z* 55 and *m/z* 83 ions as shown in Figure 4a.

The characterization of these ions may be done in the following way. The *m/z* 55 ions are focused in a collision cell (O₂ as collision gas) preceding MS2 (EBE). The fragments of the mass-selected *m/z* 55 ions are then collected by a linked scanning of the field of the last three sectors. The CA spectrum obtained in such a way with acetonitrile (Figure 4b) is quite similar to that shown in Figure 2a, except, of course, for the resolution, which is increased in the linked scanning mode. The ions produced in the chemical-ionization source and in the rf-only quadrupole collision cell have therefore the same structure as **a**•⁺ and arise from an ion−molecule reaction between ionized cyclobutanone and neutral acetonitrile probably via the mechanism depicted in Scheme 1. The formation of *m/z* 83 ions in the rf-only cell strengthens this proposal. It is interesting to recall that the *m/z* 70 ions of cyclobutanone were not found to be reactive toward acetonitrile under ICR conditions. It is therefore apparent that endothermic reactions may occur in the rf-only collision cell owing to the absence of thermalization of the ions prior to reaction.

Analogous experiments have been undertaken with [CH₂-CO]•⁺ ions produced in the ion source from dissociative ionization of cyclobutanone (vide supra). Mass-selected [CH₂-CO]•⁺ ions and neutral acetonitrile leads exclusively to the formation of [C₃H₅N]•⁺ radical cations in the rf-only collision cell. The CA spectrum of these ions unambiguously confirms the CH₃CNCH₂ connectivity and thus the formation of ions **a**•⁺ in complete agreement with the thermochemistry of the reaction (reaction B) and in keeping with the ICR results.

Formation of Ions b•⁺. Identical experiments were performed

TABLE 2: Products of Ion–Molecule Reactions between [C₃H₅N]•⁺ Isomers and Neutral Reagents

	neutral reagents	
ions	pyridine-d_5	DMDS
[CH₃CH₂CN]•⁺	m/z 84, charge exchange (30%)	m/z 94, charge exchange (99.5%)
	m/z 85, protonation (70%)	m/z 102, CH₃S transfer (0.5%)
[CH₃CH₂NC]•⁺	m/z 84, charge exchange (60%)	m/z 94, charge exchange (98%)
	m/z 85, protonation (40%)	m/z 102, CH₃S transfer (2%)
a•⁺	m/z 85, protonation (62%)	m/z 94, charge exchange (7%)
	m/z 98, CH₂•⁺ transfer (38%)	m/z 102, CH₃S transfer (93%)
b•⁺	m/z 85, protonation (61%)	m/z 94, charge exchange (92%)
	m/z 98, CH₂•⁺ transfer (39%)	m/z 102, CH₃S transfer (8%)

with methyl isocyanide as the reagent gas. Hence, m/z 55 ions were generated by ion–molecule reaction between mass-selected [CH₂CH₂CH₂CO]•⁺ or [CH₂CO]•⁺ ions and methyl isocyanide in the rf-only collision cell. Collisional activation experiments confirm that the m/z 55 ions possess the [CH₃NCCH₂]•⁺, **b**•⁺, structure. No significant production of m/z 83 ions is observed.

*Ion–Molecule Reactions of Ions **a**•⁺ and **b**•⁺.* An alternative to collisional activation for the characterization of isomeric stable ions is the study of associative ion–molecule reactions.[20] Again, we take advantage of the capabilities of the hybrid mass spectrometer. Mass-selected m/z 55 ions of low kinetic energy (less than 5 eV) are monitored in the rf-only quadrupole cell and allowed to react with a neutral. To characterize ions **a**•⁺ and **b**•⁺, we have selected two different reagent gases: dimethyl disulfide[21] (CH₃SSCH₃, DMDS), which is recognized as an excellent trapping agent of distonic ions, and deuterated pyridine. For the purpose of comparison, the two conventional isomers [C₂H₅CN]•⁺, **c**•⁺, and [C₂H₅NC]•⁺, **d**•⁺, were also considered. The results are collected in Table 2.

The reactions between ionized ethyl cyanide [C₂H₅CN]•⁺, **c**•⁺, or ionized ethyl isocyanide [C₂H₅NC]•⁺, **d**•⁺, and pyridine-d_5 lead to the protonation of the neutral deuterated pyridine (m/z 85) and to charge exchange (m/z 84). In addition to the proton-transfer reaction, the distonic ions **a**•⁺ and **b**•⁺ significantly react by transferring CH₂•⁺ to pyridine-d_5 (no charge exchange is observed). The CA spectra of the so-produced m/z 98 ions [pyridine-d_5 + CH₂]•⁺ unambiguously confirm the pyridine *N*-methylide[22] structure in both cases. As long as distonic ions are recognized to be able to transfer charged odd-electron groups, such as CH₂•⁺, to a neutral molecule,[2–5] the preceding experiments definitively establish the distonic character of ions **a**•⁺ and **b**•⁺ and the difference between them and the conventional isomers **c**•⁺ and **d**•⁺. However, these experiments do not supply information on the possible occurrence of isomerization processes between ions **a**•⁺ and **b**•⁺. Evidence for the non-occurrence of such behavior was provided by considering another type of ion–molecule reaction.

Instead of performing reactions involving the transfer of a charged odd-electron species *from* **a**•⁺ and **b**•⁺, we have investigated ion–molecule reactions leading to the abstraction of an atom or a radical *by* the distonic ions **a**•⁺ and **b**•⁺. Indeed, if such reactions occur, it is expected that collisional activation of the ionized product will provide complementary information about the original atom connectivity of reactants. In line with previous observations,[21] dimethyl disulfide (DMDS) has been selected to react with the distonic species **a**•⁺ and **b**•⁺ and with the conventional radical cations [C₂H₅CN]•⁺ and [C₂H₅NC]•⁺.

The charge exchange reaction is the main process occurring when neutral DMDS interacts in the rf-only collision cell with the two conventional isomers [C₂H₅CN]•⁺, **c**•⁺, and [C₂H₅NC]•⁺, **d**•⁺. As a result of the large ionization energy differences between DMDS and the reactant ions, (IE(C₂H₅CN) = 11.84 eV, IE(C₂H₅NC) = 11.2 eV, and IE(DMDS) = 7.4 eV[12] − 8.0

eV,[27] the charge-exchange reactions are strongly exothermic and the [DMDS]•⁺ ions are produced with an excess of internal energy leading to fragmentations. That explains the observation of several fragments ions coming from dissociation of [DMDS]•⁺ molecular ions (m/z 47, 61, and 79, not included in Table 2). A closer analysis of the spectra reveals also the production of a very small amount of m/z 102 cations (CH₃S• transfer). These m/z 102 fragment ions correspond formally to [C₂H₅CN(NC) + CH₃S•]⁺ adducts. In the case of ethyl isocyanide ions, reference ions are readily accessible by chemical ionization of ethyl isothiocyanate using choloromethane as the reagent gas, leading to [CH₃CH₂NCSCH₃]⁺ cations (methyl transfer).[23] The CA spectrum of the so-produced m/z 102 ions is found to be very similar to the spectrum of the cations generated in the rf-only collision cell.

Ions **a**•⁺ react mainly with DMDS by CH₃S• abstraction (m/z 102), charge exchange (m/z 94) being a minor process (Figure 5a). The high-energy CA spectrum of the m/z 102 cations (Figure 5b) is quite characteristic of the expected structure, [CH₃−CN⁺−CH₂−S−CH₃], prominent peaks being observed at m/z 61 ([CH₃SCH₂]⁺ ions) and m/z 55 ([CH₃CNCH₂]•⁺ ions). Besides these simple cleavage reactions, some fragments must originate from more complex rearrangement processes or from the parallel formation of a second [**a** + CH₃S]•⁺ structure. For instance, the formation of m/z 59 ions (most probably thioacylium ions, [CH₃CS]⁺) and some of the m/z 87 ions could be initiated by the competitive formation of ions [**a** + CH₃S]•⁺ resulting from the CH₃S• abstraction by the carbon atom of the cyano moiety as proposed in Scheme 3.

Ions **b**•⁺ also react in the rf-only collision cell with DMDS by CH₃S• abstraction in addition to electron transfer. The degree of competition is, however, reversed compared to the case of ions **a**•⁺ (Figure 5c). The CA spectrum of the m/z 102 cations (Figure 5d) is different from the CA spectrum of the cations produced in the case of the ions **a**•⁺ and presents also fragments at m/z 61 and 55 characteristic of the [CH₃NCCH₂SCH₃]•⁺ structure. The absence of a peak at m/z 59 is also worthy of note. An identical CA spectrum has been obtained when m/z 102 ions are prepared by methylation of methylthioacetonitrile (chloromethane-chemical ionization conditions[23]).

Further confirmation of the intrinsic stability of ions **a**•⁺ and of the reaction mechanism indicated in Scheme 3 is found in the study of the isotopomer [CD₃CNCH₂]•⁺ radical cations, **a′**•⁺. These ions abstract also CH₃S• from DMDS, generating m/z 105 cations, and the peaks at m/z 55, 59, 74, and 87 (see Scheme 3) are clearly shifted to m/z 58, 62, 77, and 90. One may emphasize that if H/D exchange had been occurring between the two opposite sides of ions **a′**•⁺ giving rise to [CD₂-CNCDH₂]•⁺ radical cations, **b′**•⁺, then the resulting ions **b′**•⁺ should react with DMDS generating [CH₃SCD₂CNCDH₂]⁺ ions. Given the fact that the CA spectrum (Figure 5e) of these cations does not show [CH₃SCD₂]⁺ ions (m/z 63) at all, this experiment
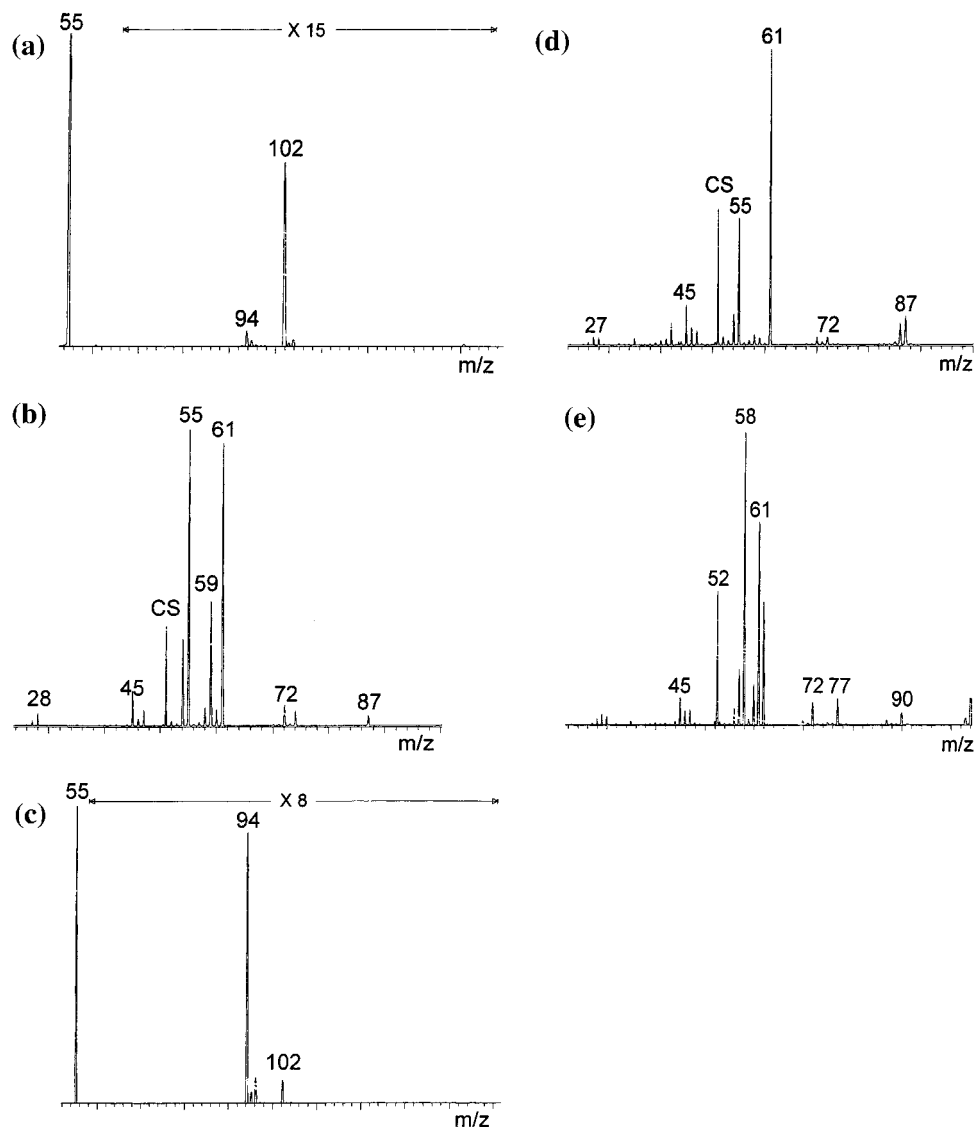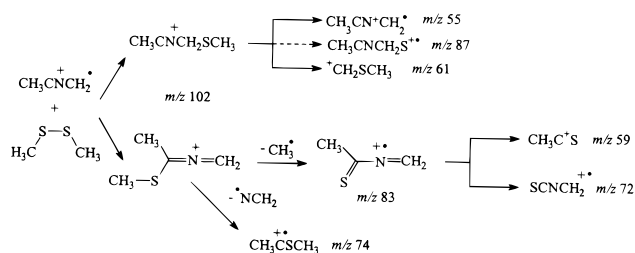
Figure 5. Reaction between **a**•⁺ and DMDS in the rf-only collision cell: (a) mass spectrum of the ions produced and (b) CA (O₂) spectrum of the m/z 102 cations. Reaction between **b**•⁺ and DMDS: (c) mass spectrum of the ions produced and (d) CA (O₂) spectrum of the m/z 102 cations. Reaction between **a′**•⁺ and DMDS: (e) CA (O₂) spectrum of the m/z 105 cations.

SCHEME 3

clearly indicates that the distonic ions **a**•⁺ and **b**•⁺ are distinct and stable species in the gas phase.

Conclusion

Transfers of the [CH₂]•⁺ radical cation to acetonitrile and methyl isocyanide from ions produced by electron ionization of cyclobutanone under different experimental conditions have been demonstrated. The structure of the product ions has been investigated by using collisional-activation, neutralization—reionization, and ion—molecule reaction experiments. These experiments establish the formation of stable distonic ions **a**•⁺,

[CH₃CNCH₂]•⁺, and **b**•⁺, [CH₃NCCH₂]•⁺. The distonic nature of ions **a**•⁺ and **b**•⁺ is clearly indicated by ion—molecule reactions in an rf-only quadrupole collision cell. These experiments also indicate that these ions are distinct species in the gas phase. The low-energy collisional-activation spectra (obtained in both FT-ICR and rf-only quadrupole instruments) are significantly different from the high-energy CA spectra. These differences could be only understood after examination of the possible isomerization processes accessible at high internal energy.

The energetics of ions **a**•⁺ and **b**•⁺ has been investigated by means of QCISD(T)//UMP2/6-31G(d,p) + ZPE molecular-orbital calculations. It appears that the two structures **a**•⁺ and **b**•⁺ are of identical stability and are the most stable in the [C₃, H₂, N]•⁺ series. A common heat of formation value of $\Delta_f H°_{298}[CH_3CNCH_2]^{•+} = \Delta_f H°_{298}[CH_3NCCH_2]^{•+} = 970$ kJ/mol has been proposed.

Experimental Section

FT-ICR experiments were performed on a Bruker Spectrospin CMS 47X mass spectrometer equipped with an external ion source.[24] The [CH₂CH₂CH₂CO]•⁺ and [CH₂CO]•⁺ cations were

generated by dissociative ionization of cyclobutanone in the external ion source (typical conditions: 4-A filament current, 30-eV electron energy, 10-ms ionizing pulse duration). All the ions were transferred to the reaction cell located inside the 4.7 T superconducting magnet. Selection of the ion of interest was done by ejection of unwanted ions by a combination of chirp and soft rf pulses. The reactants were relaxed to thermal energy ($T = 300$ K) by introducing argon inside the ICR cell at a pressure approximatively 1 order of magnitude greater than the pressure of the neutral reactant and by imposing a relaxation delay of 2−6 s after selection of the reacting ions. Next, the selected ions were allowed to react for a variable time with neutral acetonitrile or methyl isocyanide. Experiments were conducted at a constant pressure in the range 10^{-8}−10^{-7} mbar as indicated by the ionization gauge (Balzers-IMR-132) located between the high-vacuum pump and the cell housing. The intensities of the peaks were determined in the frequency domain after Fourier transformation of the corresponding time-domain signal. Collisional-activation experiments have been done at a total pressure of 10^{-7} mbar and a collision time of 200 ms. Under these conditions the center-of-mass kinetic energy imparted to ions m/z 55 by collision with argon is ca. 30 eV.

All the spectra shown in sections 3 and 4 have been recorded on a large-scale tandem mass spectrometer (Micromass AutoSpec 6F) combining six sectors of E′B1E2E3B2E4 geometry (E stands for electric sector and B for magnetic sector) already described elsewhere.[25] The optics transport lens between MS1 (E1B1E2) and MS2 (E3B2E4) can be removed and replaced by an rf-only quadrupole collision cell fitted with retardation and reacceleration lenses.[16] Typical conditions for electron impact were an 8-kV accelerating voltage, a 70-eV ionizing electron energy, and a 200-μA trap current. In the chemical-ionization experiments, cyclobutanone (∼3 μL) and the sample (∼1 μL) were injected in the source via a heated septum inlet (160 °C). This raises the pressure to 10^{-5} Torr as read on the ion gauge of the source housing. A 1-mA emission current has been used.

In the high-energy CA experiments, a beam of mass-selected ions by MS1 collided with oxygen in the fourth field-free region and the fragments were collected by a scanning of E3, collecting the ions in the fifth field-free region with an off-axis photo-multiplier detector. In the NRMS experiments, the beam of ions was first reduced by collision with ammonia before reionization with oxygen. Non-neutralized ions were removed by floating the intermediate calibration source inserted between the two collision cells at 9 kV. In the linked scan experiments, the fields of MS2 (E3B2E4) were simultaneously scanned after fixing B2 for the transmission of the selected precursor ions.

The low-energy CA spectra were recorded on an AutoSpec 6F fitted with the rf-only quadrupole cell. Fragmentation of mass-selected ions was performed in the quadrupole pressurized with argon (estimated pressure: 10^{-3} Torr), and fragment ions were separated by scanning the second magnetic field. The argon pressure and the floating voltage applied to the quadrupole (∼7970 V) were adjusted to maximize the yield of the fragments ions. If the floating voltage of the quadrupole is increased to ∼7995 V, ion−molecule reactions are favored, not collision-induced dissociations. The various reagent gases were also introduced in the quadrupole at an estimated pressure of 10^{-3} Torr.

All the samples were commercialy available except methyl and ethyl isocyanides, which were prepared according to the literature.[26]

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