A Mass-Spectrometric Investigation of C_xNO_2 (x = 1, 2) Ions and Neutrals

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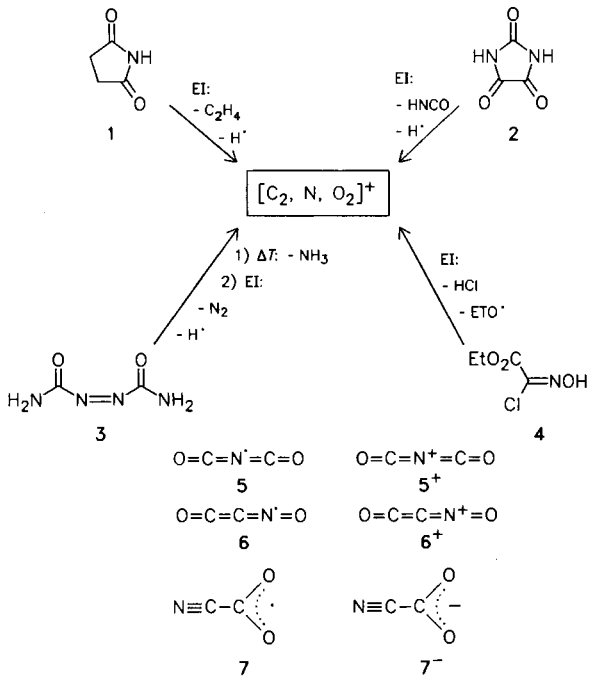
The isomeric $[C_2,N,O_2]^+$ ions $OCNCO^+$, $OCCNO^+$, and $NCCO_2^-$ have been generated and structurally characterized on the basis of their collisional activation, charge reversal, and neutralization-reionization mass spectra. The open-shell neutrals formed in the neutralization step undergo facile unimolecular decomposition. A recovery signal is obtained only for OCCNO.

In recent years, we have used the technique of neutralization-reionization mass spectrometry[1] to characterize cumulenes of theoretical and cosmochemical interest[2]. Much of this work has concentrated on sulfides, oxides, and nitrides of carbon. A logical extension of this work is a study of cumulenes containing multiple heteroatoms. However, the more heteroatoms the molecule of interest contains, the more difficult it becomes to distinguish between isomeric species. In such instances it is desirable to generate and study several structural isomers.

Here we report that three different $[C_2,N,O_2]^+$ ions may be clearly distinguished by using collisional mass-spectrometry techniques. Surprisingly, the smaller $[C,N,O_2]^+$ system is less clear.

Results and Discussion

A number of compounds give rise to $[C_2,N,O_2]^+$ ions. For instance, the cyclic amides succinimide (**1**) and parabanic acid (**2**) as well as azoformamide (**3**) and ethyl chlorohydroxyiminoacetate (**4**) all display an intense signal at m/z = 70 upon electron impact in the positive-ion mode of our three-sector mass spectrometer[3]. Even poly(n-hexyl isocyanate) affords a $[C_2,N,O_2]^+$ ion on pyrolysis[4]. Simple bond cleavages can account for the formation of this ion from compounds **1**, **2**, and **4**. Compound **3**, however, most likely cyclizes first to an unstable triazolinedione[5], this species then fragments to yield the $[C_2,N,O_2]^+$ ion. In the pyrolysis of poly(n-hexyl isocyanate), a cyclic amide is postulated to be the ultimate precursor of this ion.



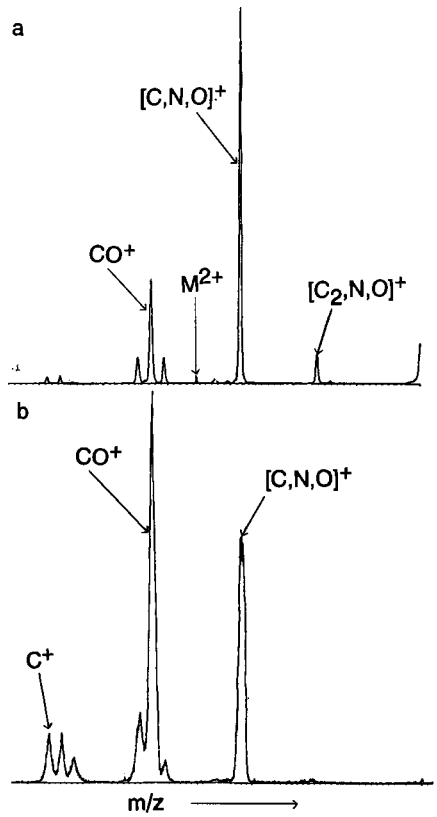


Figure 1. a) CA mass spectrum of $[C_2,N,O_2]^+$ generated on electron impact of compound **1** [helium, 80% transmission (T)]; b) NR mass spectrum of $[C_2,N,O_2]^+$ (xenon, 80% T // helium, 80% T)

  0009–2940/92/0101–0279 $ 3.50+.25/0

When the ion $m/z = 70$ was generated from precursors **1**, **2**, or **3** and mass-selected with *BE* followed by collisional activation (CA)[6] and detection with *B*(2) the spectrum shown in Figure 1a was obtained. The CA mass spectrum of $m/z = 70$ generated from precursor **4** is shown in Figure 2a.

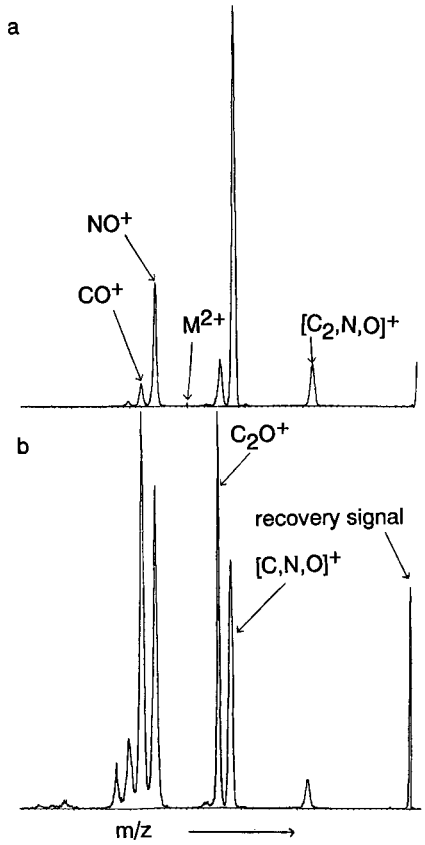


Figure 2. a) CA mass spectrum of $[C_2,N,O_2]^+$ generated on electron impact of compound **4** [helium, 80% transmission (*T*)]; b) NR mass spectrum of $[C_2,N,O_2]^+$ (xenon, 80% *T* // helium, 80% *T*)

It is readily apparent that these ions have the atomic composition $[C_2,N,O_2]$. Of the conceivable linear, branched, or cyclic structures for $[C_2,N,O_2]^+$ we are most inclined to propose a linear connectivity for the two ions observed in these experiments (vide infra). There are two chemically reasonable isomeric linear structures for the $[C_2,N,O_2]^+$ ion: $O=C=\overset{+}{N}=C=O$ (**5**$^+$) and $O=C=C=\overset{+}{N}=O$ (**6**$^+$). These are closed-shell cations, isoelectronic with carbon suboxide (OCCCO).

Although the spectra (Figures 1a and 2a) do exhibit peaks at common m/z values, there are several striking differences between the two spectra. In Figure 1a the dominant peaks are at $m/z = 42$ ($[C,N,O]^+$) and $m/z = 28$ (CO^+). Smaller peaks are observed at $m/z = 54$ ($[C_2,N,O]^+$), $m/z = 30$ (NO^+), 26 (CN^+), and at $m/z = 35$ a charge-stripping peak, corresponding to $[C_2,N,O_2]^{2+}$. In Figure 2a the largest peak is also at $m/z = 42$, the intensities of the peaks at $m/z = 30$ and $m/z = 28$ are, however, *reversed* relative to that observed in Figure 1a. Additionally, there is a peak at $m/z = 40$ (CCO^+) in Figure 2a that is not observed in Figure 1a.

On the basis of the presence of CCO^+ and the intensity of the NO^+ peak in Figure 2a we assign this spectrum to the ion $O=C=C=\overset{+}{N}=O$ (**6**$^+$) and the spectrum in Figure 1a to ion $O=C=\overset{+}{N}=C=O$ (**5**$^+$). If this assignment is correct, then the peak at $m/z = 42$ in Figure 1a should be due to OCN^+, and in Figure 2a this peak should be due to CNO^+. In fact, we can distinguish the isocyanate ion (NCO^+) from the cyanate ion (CNO^+) through an MS/MS/MS experiment. Here, $m/z = 42$ is produced by collisional activation of $m/z = 70$ as generated from precursor **1**, selected with *E*, and its CA spectrum recorded with *B*(2). This spectrum is shown in Figure 3a. A similar experiment with $m/z = 42$ as generated from precursor **4** afforded the CA spectrum shown in Figure 3b. While *partial* collision-induced isomerization $OCN^+ \rightleftarrows CNO^+$ cannot be ruled out in the multicollision event, on the basis of the intensities of the peaks at $m/z = 30$ (NO^+) and $m/z = 28$ (CO^+) it can be seen that the peak at $m/z = 42$ in Figure 1a is due to NCO^+ (more CO^+ than NO^+) and that the same peak in Figure 2a is due to the isomeric CNO^+ ion (more NO^+ than CO^+). The experiments further substantiate our structural assignments for the ions **5**$^+$ and **6**$^+$.

The structural difference between the two ions **5**$^+$ and **6**$^+$ becomes even more apparent when their neutralization-reionization mass spectra (NRMS) are examined. The NR mass spectrum of ion **5**$^+$ is shown in Figure 1b, and that of ion **6**$^+$ is shown in Figure 2b. By comparing the CA and NR mass spectra we can get a glimpse of the neutral mol-

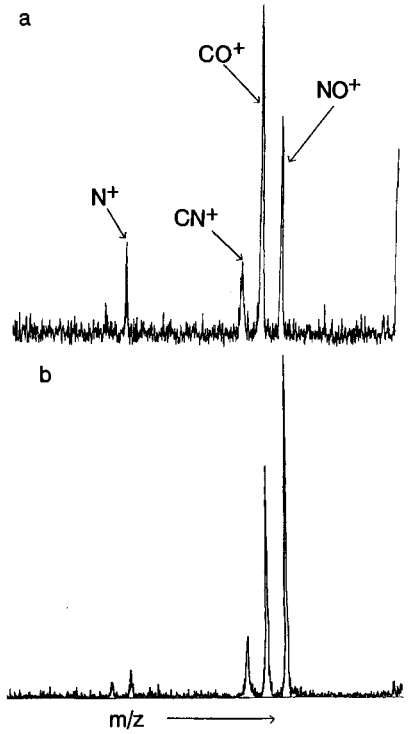


Figure 3. a) CA/CA mass spectrum of $[C,N,O]^+$ generated from compound **1** (helium, 80% *T* // helium, 80% *T*); b) CA/CA mass spectrum of $[C,N,O]^+$ generated from compound **4** (helium, 80% *T* // helium, 80% *T*)

ecules **5** and **6**. It is important to keep in mind that these neutrals are open-shell free radicals and may be undergoing unimolecular rearrangements or fragmentations on the NRMS time scale (ca. 0.5 μs, 10^8 molecular vibrations).

The most obvious difference between Figure 1b and Figure 2b is that a strong recovery signal is observed in Figure 2b and not in Figure 1b. The absence of such a signal in Figure 1b can have several origins. It may be that the neutral molecule O=C=N–C˙=O (**5**) is simply not a chemically bound species and spontaneously decomposes. However, a priori, it is difficult to rationalize why O=C=C˙–N=O (**6**) is a chemically bound species and **5** is not. It may be that **5** has completely reacted before it can be detected. Alternatively, if the geometries of the cation and the neutral are very different, poor Franck-Condon overlap in the neutralization step (a vertical process) would explain the absence of a recovery signal. Presently, it is difficult to state which factor is responsible for the lack of a recovery signal in Figure 1b.

There are significant differences between the CA (Figure 1a) and the NR mass spectra (Figure 1b) of ion 5^+. The peak at m/z = 54 (C_2NO^+) has disappeared and the relative intensities of the peaks at m/z = 28 and 42 are reversed in the NR relative to the CA mass spectra. As expected, the charge-stripping peak at m/z = 35 is absent in the NR experiment. These observations are best explained by a simple fragmentation of the neutral OCNCO˙ (**5**) to CO and OCN˙. Thermochemically, this fragmentation is expected to be favored over fragmentation to C_2NO and atomic oxygen or to two molecules of CO and atomic nitrogen[7]. These neutrals (CO and OCN˙) are then reionized and detected. More CO is observed in the NR spectrum than in the CA spectrum because on thermodynamic grounds the cation 5^+ will prefer to fragment to OCN^+ and CO (ΔH_f° = 281 kcal/mol) rather than OCN˙ and CO^+ (ΔH_f° = 334 kcal/mol).

In the NR mass spectrum of $OCCNO^+$ (6^+) (Figure 2b) a strong recovery signal is registered. With the exception of the charge-stripping peak (m/z = 35), all of the ions that are present in the CA spectrum (Figure 2a) also occur in the NR spectrum, and a new peak at m/z = 24 (C_2^+) has appeared. This peak (m/z = 24) suggests a CC connectivity in **6** and further supports our connectivity assignment for this species. The relative intensities of the ions are, however, quite different in the NR relative to the CA experiment. Particularly striking is the increase in the intensities of the peaks at m/z = 40 (CCO^+) and m/z = 28 (CO^+). These differences can be attributed to the partial unimolecular decomposition of the neutral. Two primary decomposition pathways are conceivable for neutral OCCNO˙ (**6**). Cleavage of the CN bond would afford the neutrals NO and CCO, and cleavage of the CC bond would afford CNO and CO. These same fragmentation pathways are available to the cation 6^+; however, for thermochemical reasons, the charge will prefer to stay on the NO and (presumably[8]) the CNO fragments. Thus, the CCO and CO fragments are not observed in as large intensities in the CA as those of their NO and CNO counterparts. In the NRMS experiment all neutrals are reionized and detected.

A third [C_2,N,O_2] (m/z = 70) isomer has been described by McMahon[9]. The anion $NCCOO^-$ (7^-) can be generated upon electron impact of ethyl cyanoformate ($NCCO_2Et$). We have recorded the charge-reversal (CR)[10] mass spectrum (Figure 4a) and the $^-NR^+$ mass spectrum (Figure 4b) of this ion. Both spectra are quite different from the spectra of 5^+ and 6^+ (Figures 1 and 2), and, clearly, this is a structurally different [C_2,N,O_2] ion. Immediately apparent from the charge-reversal spectrum is the absence of a charge-reversal signal at m/z = 70. Once again, this may be due to either an inherent instability of the cation or to poor Franck-Condon overlap in going from the anion to the cation. Familiar peaks are observed at m/z = 54, m/z = 42, m/z = 28, and m/z = 26. The peak at m/z = 44 (CO_2^+) is not present in either Figure 1 or 2. This peak and the absence of a signal for NO^+ (m/z = 30) are diagnostic for the assignment of an atomic connectivity to this ion.

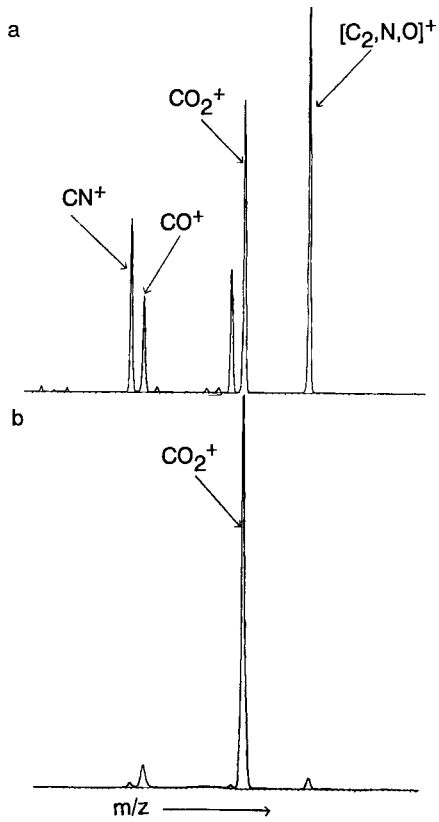


Figure 4. a) CR mass spectrum of $[C_2,N,O_2]^-$ generated on electron impact of ethyl cyanoformate [helium, 80% transmission (T)]; b) NR mass spectrum of $[C_2,N,O_2]^-$ (xenon, 80% T // helium, 80% T)

In contrast to the CR spectrum, very few signals are observed in the NR spectrum of 7^- (Figure 4b). There is no recovery signal, and the presence of an intense peak at m/z = 44 (CO_2^+) is compatible with the formation of a neutral with the same connectivity as 7^- that rapidly decomposes to the neutrals CN and CO_2. Reionization of CO_2 affords the peak at m/z = 44.

In connection with the above study of C_2NO_2 isomers, we were stimulated by the recent report by Bowie et al.[11] on

the oxoisocyanate anion ($ONCO^-$). Particulary interesting was the prospect of neutralizing this species to form the aza analog of the long-sought after ethylenedione (OCCO), one of the most elusive of all molecules[12]. In the event, $ONCO^-$ (m/z = 58) was obtained from methyl *N*-hydroxycarbamate as described by Bowie et al.[11]. This ion was mass- and energy-selected with *BE*, subjected to collision experiments in the third field-free region, and detected with *B*(2). The CR and NR spectra are shown in Figures 5a and 5b. The two spectra are quite similar. Fortunately, both a charge-reversal signal and a recovery signal are obtained. In the NR mass spectrum (Figure 5b) more NO^+ (m/z = 30) is observed relative to CO^+ (m/z = 28), and more CO_2^+ (m/z = 44) is detected relative to CNO^+ (m/z = 42) than in the CRMS (Figure 5a). Here too, these differences are most likely attributable to chemical reactions occurring at the level of the neutral.

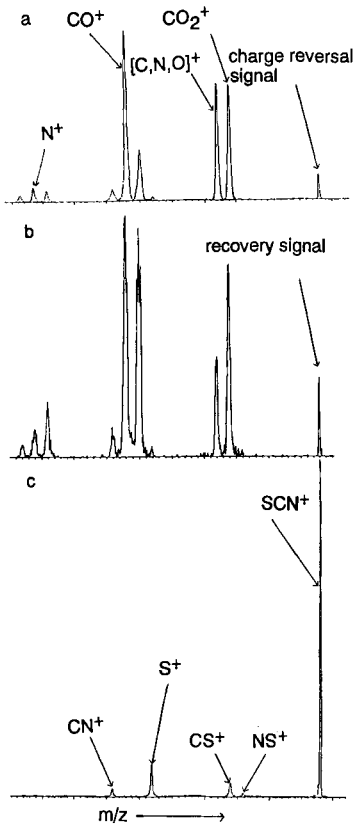


Figure 5. a) CRMS of $[C,N,O_2]^-$ generated from methyl *N*-hydroxycarbamate (oxygen, 80% *T*); b) NRMS of $[C,N,O_2]^-$ (oxygen 80% *T* // oxygen 80% *T*); c) CRMS of SCN^- (oxygen, 80% *T*)

The charge-reversal and recovery signals in Figures 5a and 5b may, however, be due to the isobaric isothiocyanate ion, SCN^-. This species gives rise to both an intense charge-reversal signal as well as an intense recovery signal in the $^-NR^+$ experiment, and the ion is a common mass in our machine. As a reference, the CR mass spectrum of this species is shown in Figure 5c. The NR mass spectrum of SCN^- is identical to the CR spectrum and is not shown. This spectrum (Figure 5c) is clearly different from those spectra shown in Figures 5a und 5b, yet we cannot be absolutely sure that the signals at m/z = 58 in Figures 5a und 5b are due to $ONCO^+$ and not SCN^+[13]. Our charge-reversal spectrum is in accord with Bowie's; however, in that work it is unclear whether a charge-reversal signal was observed or not.

The intense signal for CO_2^+ at m/z = 44 in the spectra of ONCO is somewhat mystifying, and sheds some doubt on the linear structure for the cationic and neutral species. If these species are in fact linear, then the barrier to isomerization and extrusion of CO_2 and N cannot be very high. Note that CO_2^+ is not observed in significant amounts in Figures 1 and 2.

A potentially second isomer of ONCO is the branched species CNO_2. A precursor ion to this neutral is the nitrocarbyne anion, CNO_2^-. In fact, on electron impact, in the anion mode of our four-sector mass spectrometer[14], tetranitromethane gives rise to an intense signal at m/z = 58 $[C,N,O_2]^-$. The charge-reversal and neutralization-reionization mass spectra of this ion, however, are identical with those obtained by using methyl *N*-hydroxycarbamate as the precursor. Conspicuously absent from these spectra is a signal at m/z = 46 (NO_2^+)[15]. Since rearrangement processes are of minor importance in radical anions[16], it is likely that the CNO_2 species rearranges at the level of the cation, and perhaps also at the level of the neutral.

In summary, we have shown that three different ionic $[C_2,N,O_2]$ species are accessible in the gas phase and easily distinguished using collisional mass-spectrometry experiments. Of the three isomers studied, only $OCCNO^+$ ($\mathbf{6}^+$) gives rise to a recovery signal in the NRMS experiment. The smaller $[C,N,O_2]$ system is less clear-cut, for $ONCO^-$ and CNO_2^- afford identical CR and NR mass spectra. An additional complication in these experiments is the possible contribution of SCN^- to the CR and the NR mass spectra.

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Experimental

Methyl *N*-hydroxycarbamate[17], parabanic acid (**2**)[18], and ethyl chlorohydroxyiminoacetate (**4**)[19] were prepared according to literature procedures. Ethyl cyanoformate, tetranitromethane, azoformamide (**3**), and succinimide (**1**) were purchased from Aldrich Chemical Co. All mass-spectrometric experiments were carried out by using standard techniques (see text).

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