Formation and Identification of Ionized and Neutral Cumulenes, RN=C=C=C=NH, by Tandem Mass Spectrometry

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Using a combination of mass spectrometric techniques, it is shown that 5-amino-4-cyanoisoxazole molecular ions $(1^{+\cdot})$, lose isocyanic acid HNC=O, not fulminic acid, HC≡N → O. Metastable ion fragmentations (unimolecular and collision induced) and deuterium-labelling experiments are in agreement with the formation of a cumulenic structure, HN=C=C=C=NH $(3a^{+\cdot})$. The hitherto unreported molecules HNCCCNH are also shown to be stable when formed in the low-pressure gas phase of the mass spectrometer by using the technique of neutralization–reionization mass spectrometry. The arguments developed for the characterization of $3a^{+\cdot}$ have also been extended to the methylated and phenylated analogues $3b^{+\cdot}$ and $3c^{+\cdot}$ $[RN=C=C=C=NH^{+\cdot}$, R = CH$_3$ or C$_6$H$_5$]. On flash-vacuum pyrolysis at 700 °C, 1 also loses HN=C=O producing the cumulene 3a, which is in turn readily tautomerized into malononitrile via wall collisions.

INTRODUCTION

Reactive organic molecules possessing a C=C=C connectivity have received considerable attention in recent years. The parent compound, tricarbon, C_3, has been exhaustively described in a recent review.[1] Introduction of heteroatoms on the tricarbon skeleton leads to heterocumulenes presenting a wide variety of stability. Thus, whereas carbon suboxide, O=C=C=C=O, is a stable compound under ordinary conditions,[2] tricarbon oxide, C=C=C=O, has only been observed at low pressure in the gas phase by microwave spectroscopy,[3] by low-temperature matrix IR spectroscopy[4] or by neutralization–reionization mass spectrometry (NRMS).[5] In this last technique, a beam of ions is produced by dissociative ionization of an appropriate precursor molecule and then subjected to collisional neutralization followed by reionization.[6] The appearance of the resulting spectrum provides information on the stability and the structure of the intermediate neutral species.

Another class of compounds belonging to the C_3 family, the methylene ketenes $R_1R_2C=C=C=O$, is of considerable interest in terms of their high reactivity and remarkable molecular transformations.[7] Recent work has also proved the usefulness of these compounds in the gas-phase production of new organic molecules such as C_2S_2[8] and acylketenimines.[9]

Iminopropadienones, RN=C=C=C=O, have recently been identified during flash-vacuum pyrolyses (FVP) of pyrimidinones and Meldrum's acid derivatives using complementary techniques such as tandem mass spectrometry (MS/MS),[10] matrix isolation IR spectroscopy and trapping experiments.[11] Although remarkably stable, these compounds react readily with nucleophiles to produce malonic acid imides.[11] HN=C=C=C=O has also been observed in NRMS experiments, but under FVP conditions it rapidly tautomerizes to cyanoketene, N≡CCH=C=O, probably because of collisions with the wall.

We report here on the generation of a new class of heterocumulenes, formally the diimines of carbon suboxide, RN=C=C=C=NH. They are produced as radical cations by fragmentation of 5-amino-4-cyano-isoxazole molecular ions and as neutral molecules in NRMS.

RESULTS AND DISCUSSION

The mass spectrum of 5-amino-4-cyanoisoxazole (1) features an intense molecular ion peak at m/z 109 (Fig. 1) and a base peak at m/z 66 corresponding to $[C_3H_2N_2]^{+\cdot}$ ions. Aminoacylium ions, $NH_2C^+=O$, are also observed, but this cleavage competes only at high internal energy. Metastable molecular ions undergo mainly the m/z 109 → 66 cleavage with a minor contribution of the m/z 109 → 29 reaction.

Ionized 5-amino-4-cyanoisoxazole-N-d_2 (1a) loses specifically CDNO (m/z 111 → 67), thereby showing that the fragment ions retain the hydrogen atom at position 3 and that the exocyclic nitrogen atom is lost in the fragmentation. For the monodeuterated isotopomer 1b, one observes eliminations of CHNO and CDNO with identical abundances. The neutral species lost is therefore isocyanic acid, HN=C=O, not fulminic acid,
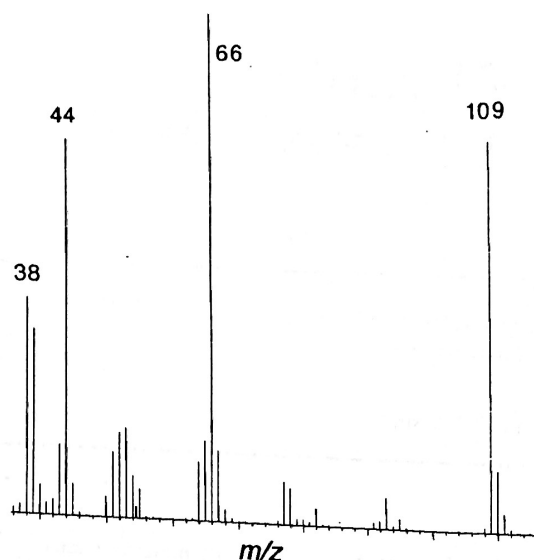
Figure 1. Mass spectrum (electron impact, 70 eV) of 5-amino-4-cyanoisoxazole (1).

$HC\equiv N \rightarrow O$. The considerable stability difference of these neutral species ($\Delta H_f°$ (HNCO) $= -105$ kJ mol^{-1} and $\Delta H_f°(HC\equiv N \rightarrow O) = 218$ kJ mol^{-1})[12] justifies the occurrence of a mechanism more complex than a [1, 3] dipolar cycloreversion.

The mechanism of this transformation probably involves first the cleavage of the N—O bond. The nascent nitrene undergoes a [1, 2] shift of the hydrogen atom in position 3 to generate the keteneimine ions $2^{+\cdot}$. Hydrogen transfer from the amino group to the nitrile moiety and loss of HN=C=O completes the reaction, producing [HN=C=C=C=NH]$^{+\cdot}$ ions, $3a^{+\cdot}$, which are cumulogues[13] of carbodiimide ions, [HN=C=NH]$^{+\cdot}$. This mechanism is very similar to that proposed recently to explain the formation of iminopropadienone ions, [RN=C=C=C=O]$^{+\cdot}$, from 5-amino-4-methoxycarbonylisoxazoles.[10]
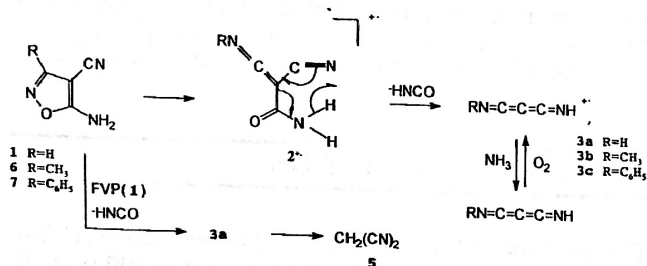
The two main reactions induced by collisional activation of the $3a^{+\cdot}$ ions produce m/z 39 ($-$CHN) and m/z 38 ($-$CH$_2$N) fragments [Fig. 2(a)]. These fragments are also present in the mass spectrum of 3. The collisional activation (CA) spectra of these ions are consistent with the [HN=C=C]$^{+\cdot}$ and [N=C=C]$^+$ structures, respectively. In particular, in the case of [N=C=C]$^+$, the CA and NRMS data (Fig. 3) are in complete agreement with the data recently published by Sülzle et al.[14] Similar CA spectra are obtained for [HN=C=C]$^{+\cdot}$ and [N=C=C]$^+$ ions produced by MS/MS of $3a^{+\cdot}$. Deuterium exchange of the acidic hydrogens also confirms the HNCCCNH connectivity of the $3a^{+\cdot}$ ions. Indeed, for 1a and 1b, the splitting of the m/z 51 signal
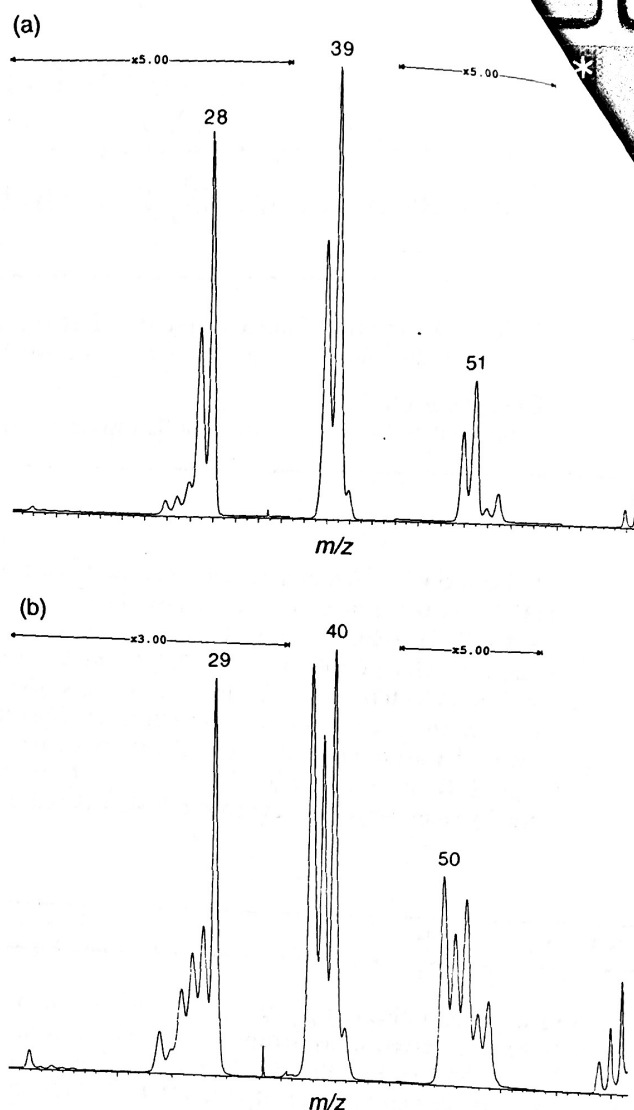

Figure 2. CA mass spectra of (a) the [C$_3$H$_2$N$_2$]$^{+\cdot}$ ions (m/z 66) of 1 and (b) the [C$_3$HDN$_2$]$^{+\cdot}$ ions (m/z 67) of 1b.

observed in the case of 1 indicates collision-induced losses of NH and ND with a nearly identical probability. The loss of CHN (from 1) is also replaced by losses of CHN and CDN [Fig. 2(b)].

These labelling results exclude a significant contribution of isomeric 2-aminomethylene-2H-azirine ions, $4^{+\cdot}$. The existence of these azirine ions has been demonstrated recently, however, in our laboratories by FVP/electron impact of some 4-methyleneisoxazole-5-one derivatives.[15] It is therefore possible that the small peak observed at m/z 53 (loss of CH) in the CA spectrum shown in
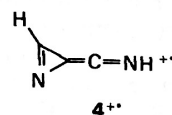

$4^{+\cdot}$

Fig. 2(a) is not due to post-collisional isomerization of ions $3a^{+\cdot}$, but to a reduced contribution of ions $4^{+\cdot}$.

[C$_3$H$_2$N$_2$]$^{+\cdot}$ ions are also produced by electron impact ionization of malononitrile, CH$_2$(CN)$_2$ (5). The
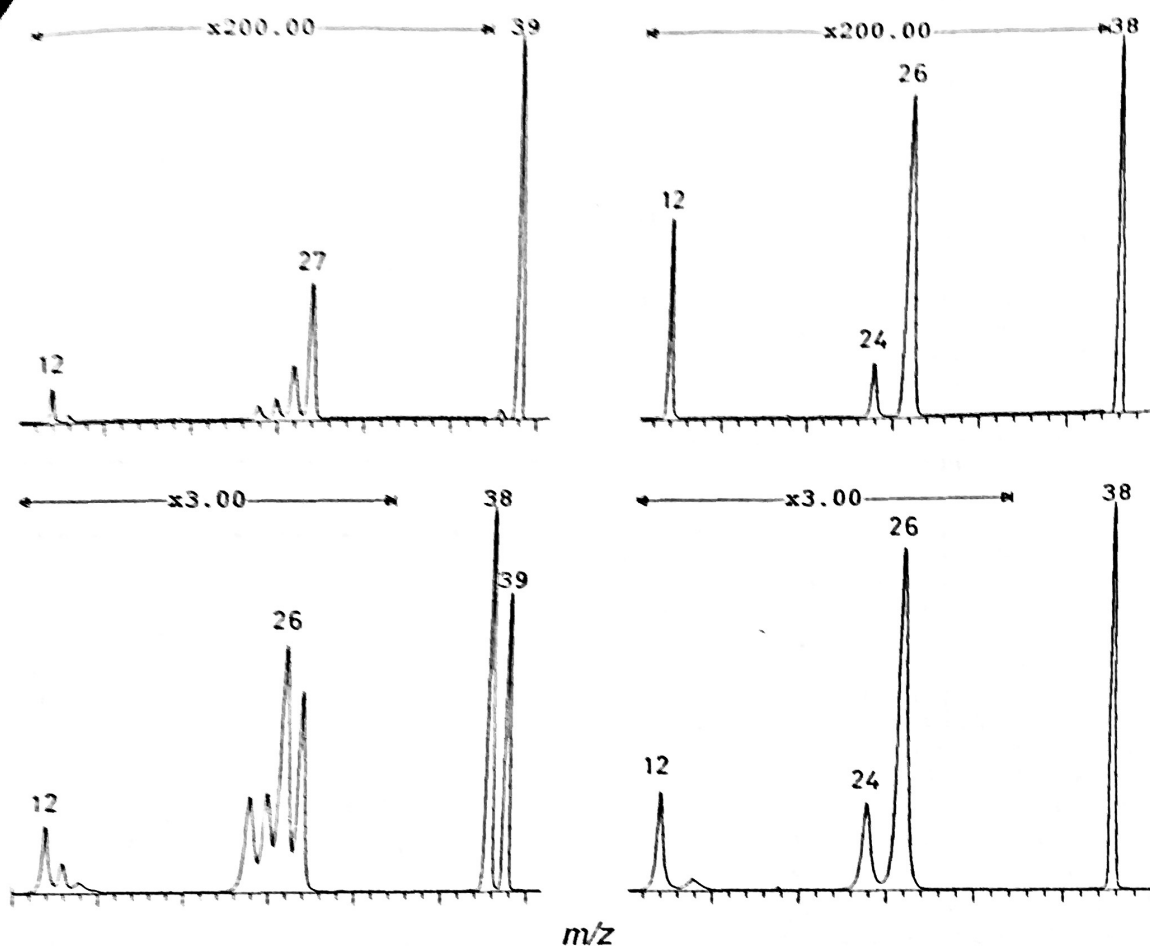
Figure 3. CA and NR mass spectra of m/z 39 and 38 ions derived from 1[+·].

CA spectra (He or O_2 collision gas) are very similar to the spectra of the 3a[+·] ions. However, there are some noticeable differences (Table 1): an increased abundance of the m/z 40 fragment ions (loss of CN'); a different distribution of the intensities in the m/z 50–53 region; a higher m/z 28/27 ratio; and the complete absence of charge stripping for the 5[+·] ions. These differences, which are more pronounced when oxygen is used as the collision gas, confirm that 1 and 5 produce isomeric $[C_3H_2N_2]$[+·] ions which do not equilibrate.

The above conclusion is confirmed by the NR mass spectra using NH_3 and O_2 in sequence (Fig. 4). Significant differences are again observed for 3 and 5. Moreover, the NR spectrum of 3a[+·] is characterized by a strong recovery signal, indicating that the neutral diimine, 3, is also a stable molecule in the rarefied gas phase of the spectrometer. Tautomerization of 3 into 5 involves a 1,3-shift, which is formally forbidden in the wall-less experiment.

Another argument favouring the formation of the cumulene 3 originates from the behaviour of 1 towards FVP[16] conditions. The relative abundances of some significant signals in the mass spectra of 1 at 200 and 800 °C are reported in Table 2. The structure of the m/z 43 and 66 ions, which are obvious pyrolysis products of 1, are established as HNCO and $CH_2(CN)_2$, respectively using CAMS (the CA spectrum of HNCO ions has already been described[17]). It therefore appears that

Table 1. CA mass spectra (He and O_2) of $[C_3H_2N_2]$[+·] (m/z 66) ions from 1 and 5[a]

Compound	Gas	65	64	53	52	51	50	40	39	38	33	28	27	26	25	24
1	He	*25*	*4*	8	4	37	24	*7*	*100*	63	2	100	50	9	5	4
5	He	*12*	*5*	4	5	25	16	*16*	*100*	50	—	100	27	16	10	4
1	O_2	*27*	*5*	8	10	30	17	*8*	*100*	65	27	100	39	12	6	6
5	O_2	*16*	*2*	<1	5	15	4	*17*	*100*	52	—	100	11	3	1	<1

[a] Spectra normalized relative to the signal at m/z 28, except the regions m/z 65/64 and m/z 40/38, normalized relative to m/z 39 (values in italics).
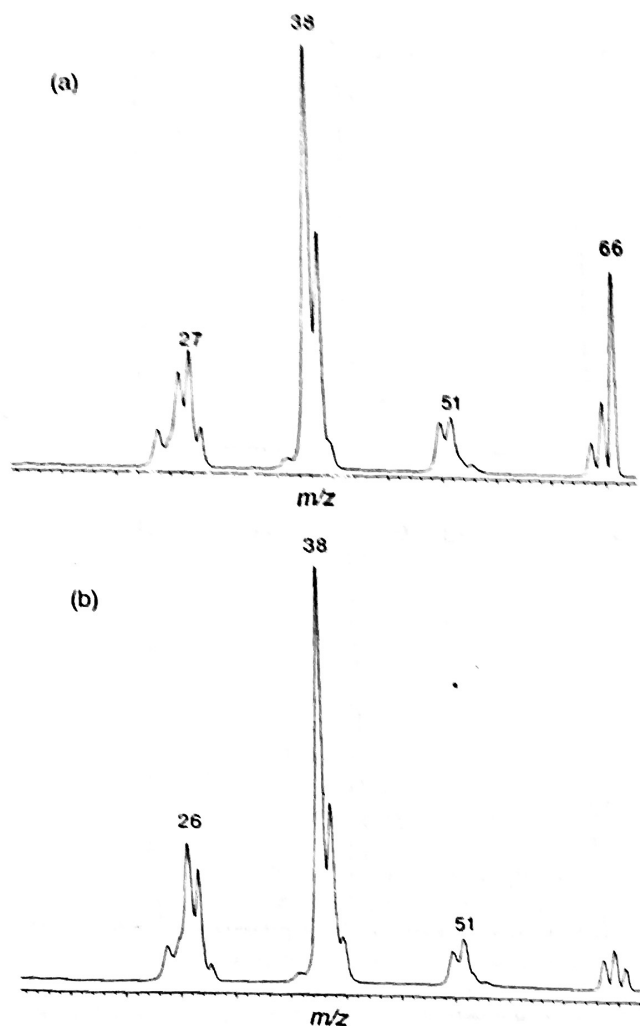
(a)

Figure 4. NR mass spectra of m/z 66 ions produced by (a) dissociative ionization of **1** and (b) ionization of malononitrile (**5**).

Figure 5. CA mass spectra (He) of (a) m/z 80 ions of **6** and (b) m/z 81 ions of **6b**.

FVP of **1** produces the cumulene **3**, but collisions with the reactor walls rapidly tautomerize **3** into malononitrile (**5**).

A similar behaviour on electron impact is also found for the substituted analogues, 5-amino-4-cyano-3-methyl- and 5-amino-4-cyano-3-phenylisoxazoles (**6** and **7**). For example, in the case of **6**, the metastable molecular ions only lose HN=C=O. The CA mass spectrum of the $[M - HNCO]^{+\cdot}$ ions (m/z 80) shows significant peaks at m/z 65 (loss of $CH_3^\cdot$) and m/z 15 (CH_3^+). Appropriate mass shifts are observed for the isotopomers **6a** and **6b** (Fig. 5).

An intense recovery signal at m/z 80 is again observed in the NR mass spectrum, together with fragment ions at m/z 65 (Fig. 6). All these data confirm that the
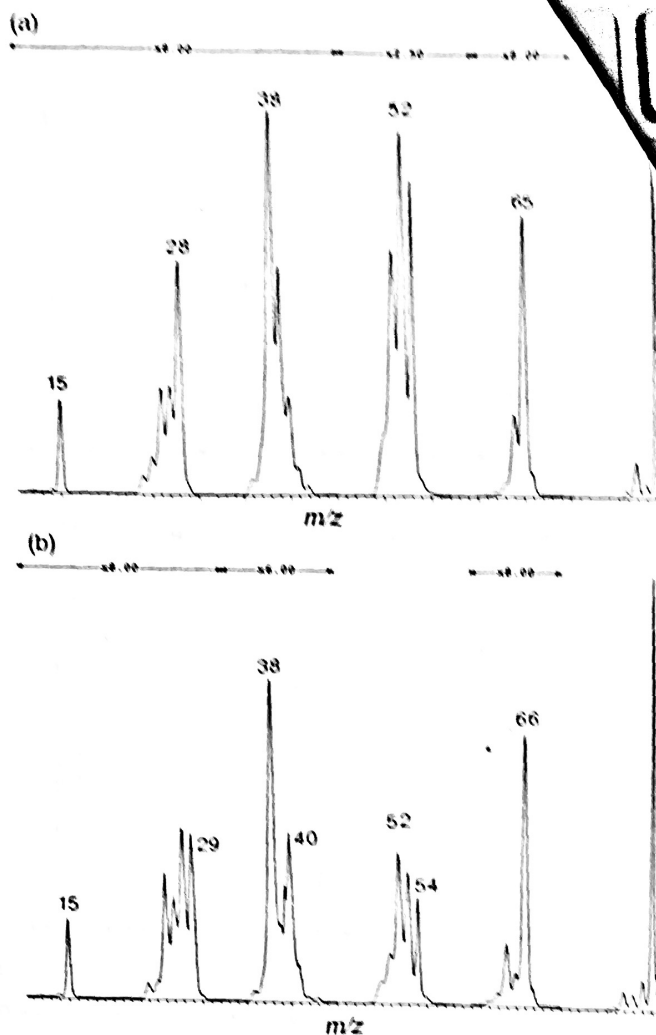
$CH_3N=C=C=C=NH^{+\cdot}$ ions and the corresponding neutral species, $CH_3N=C=C=C=NH$, are stable in the mass spectrometer gas phase.

The phenylated compound **7** likewise loses $HN=C=O$ after ionization (m/z 142, 100%). The CA mass spectrum of these ions [Fig. 7(a)] indicates the composition $[C_6H_5, C_3, N_2, H]$, given the presence of an intense signal at m/z 77 ($C_6H_5^+$). This CA mass spectrum was also recorded using linked E/B/E scanning in order to improve the mass resolution. The other important fragmentations are losses of CHN (m/z 115) and CH_2N (m/z 114). The observation of an intense recovery signal for the survivor ions (m/z 142) in the NR mass spectrum [Fig. 7(b)] and the observation of a fragmentation pattern very close to that observed in the CA mass spectrum confirm that ions and neutral species have the same atom connectivity. A significant difference between the CA and NR mass spectra appears at m/z 65; these ions arise from reionization of open-shell NCCCNH radicals formed in the neutralization cell. This peculiar behaviour has been noted already in the analogous case of phenyliminopropadienone, $C_6H_5N=C=C=C=O.^{[10]}$

Overall, these data indicate that dissociative ionization of **7** produces $C_6H_5N=C=C=C=NH^{+\cdot}$ ions

Table 2. Significant peaks in the mass spectra of 1 (200 and 800 °C) and malononitrile (5)

Compound	T (°C)	109	66	44	43	40	39	38
1	200	67	100	72	11	6	30	36
	800	23	100	31	42	8	33	38
5	200	—	100	—	—	11	30	33

Figure 6. CA (O_2) and NR mass spectra of m/z 80 ions from 6.

and, after neutralization by collision with NH_3, stable $C_6H_5N=C=C=C=NH$ molecules.

CONCLUSIONS

Dissociative ionization of the 5-amino-4-cyano-isoxazoles 1, 6 and 7 induces a loss of isocyanic acid which incorporates the exocyclic nitrogen atom. This dissociation produces new radical cations possessing the cumulene structure $RN=C=C=C=NH^{+\cdot}$ (3''').

The corresponding neutral molecules, $RN=C=C=C=NH$ (3), are also stable when produced by neutralization in the gas phase. These hitherto unreported cumulenes are formally diimines derived from carbon suboxide, C_3O_2.

On FVP of 1, 3a is also formed by thermal loss of $HN=C=O$, but it rapidly tautomerizes into malononitrile (5) by collision with the reactor walls.

As a general rule, our results indicate that, whatever the nature of the substitution at position 3 (R = C_6H_5, CH_3 or H), ionized isoxazole derivatives (4-cyano-5-amino and also 4-methoxycarbonyl-5-amino[10]) undergo a facile [1, 2] shift after the cleavage of the NO bond producing N-R-substituted keteniminos. This situation contrasts with the thermal behaviour of other isoxazole derivatives which, depending on the nature of the precursor molecule, the nature of substituent at position 3 and temperature, can yield cumulenes,[11] oxazoles[11] or iminomethylene-2H-azirines.[15]

EXPERIMENTAL

The mass spectra (electron impact, 70 eV) were recorded on a VG AutoSpec 6F spectrometer of $E_1B_1E_2E_3B_2E_4$ geometry (E = electric sector, B = magnetic sector) at

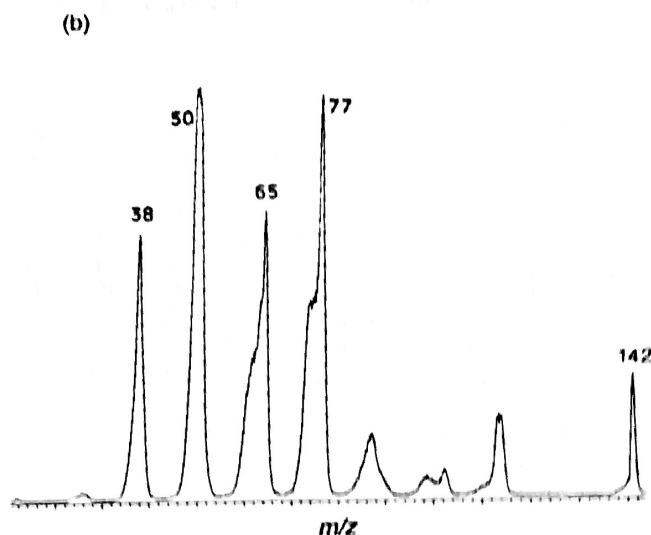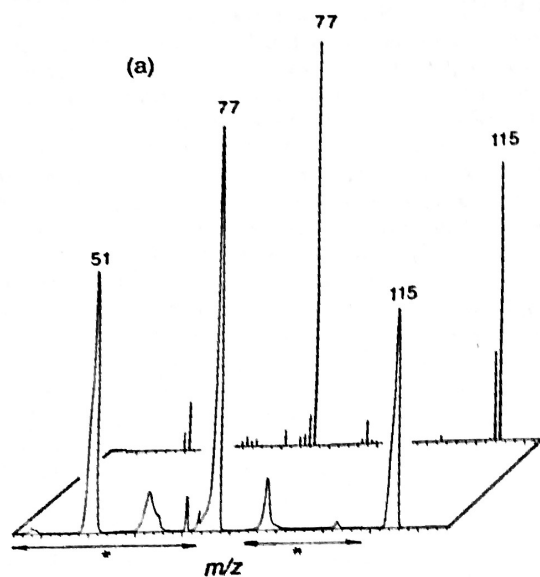

Figure 7. (a) CA mass spectra (resolved and unresolved, see text) of m/z 142 ions from 7 and (b) NR mass spectrum of the same ions. * = signals amplified by a factor 3.

an accelerating voltage of 8 kV.[5] In the CA experiments, a beam of ions is selected by a combination of three sectors ($E_1B_1E_2$) and submitted to collisional activation with O_2 (80% transmission). In the NR experiments, neutralization of the ions with NH_3 (80% T) precedes reionization with O_2 (also 80% T), unreacted ions being removed by applying a potential of 9 kV to the intermediate calibration ion source inserted between the two cells. The two kinds of spectra were recorded by scanning E_3 and collecting the ions in the fourth field-free region.

The flash vacuum pyrolysis device, consisting of a quartz tube (3 mm i.d., 50 mm length) installed in the source housing, has been described elsewhere.[9b]

The isoxazoles 1, 6 and 7 were prepared according to the literature.[18] The isotopomers 1a, 1b, 6a, 6b, 7a and 7b were prepared by exchange with CD_3OD in the ion source of the spectrometer.

Acknowledgements

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