

Characterization of Iminopropadienone Ions and Neutrals in a Tandem Mass Spectrometer

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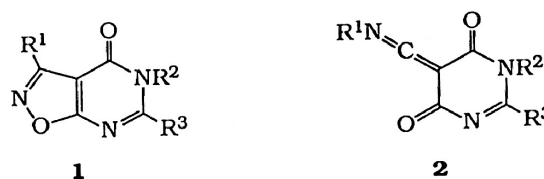
Radical-cations of iminopropadienones ($RN=C=C=C=O^{+\cdot}$) have been generated by dissociative ionization of isoxazole precursors and structurally characterized by collisional activation mass spectrometry; the corresponding neutral cumulenes have also been produced in a tandem mass spectrometer by neutralization and/or flash-vacuum pyrolysis experiments.

Dissociative ionization of heterocyclic compounds constitutes a virtually inexhaustible source of new ionic systems.¹ This is again exemplified in this report which describes the production from isoxazole derivatives of hitherto unreported heterocumulenes; ionized as well as neutral iminopropadienones, $RN=C=C=C=O$. Structural analysis of these new molecules has been performed using tandem mass spectrometry techniques,² viz collisional activation (CA)³ and neutralization-reionization (NR) mass spectrometry.⁴

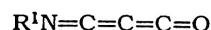
RESULTS

The electron ionization mass spectra of 3-phenylisoxazolo[5,4-d]pyrimidine-4(5H)-ones **1a-d** invariably feature a base peak at m/z 143 (Table 1). This common behaviour together with high resolution mass measurement suggest the composition C_9H_5NO for this ion. This can be further specified as $[C_6H_5, C_3, N, O]$ because the base peaks of the CA spectra of the mass-selected m/z 143 ions correspond to the phenyl cation (m/z 77, see Table 2 and inset in Fig. 1(a)). A competitive loss of CO from m/z 143 (giving m/z 115) indicates the interconnection of the atoms to be that of the iminopropadienone structure **3a⁺**. The other possible candidate, ionized phenylcyanoketene, **4⁺**, can be excluded on the basis of the CA data. This ketene was produced directly in the ion source of the spectrometer by flash-vacuum pyrolysis (FVP) of ethyl phenylcyanoacetate $C_6H_5CH(CN)CO_2C_2H_5$ (**5**). Although **4** was not the major FVP product (losses of C_2H_4 and CO_2 are favoured over the C_2H_5OH loss at $800^\circ C$ ⁵), the signal at m/z 143 was sufficiently intense that its CA spectrum, which is very different from that of **3a⁺**, could be recorded. In particular, a much weaker peak at m/z 77 and a much stronger one at m/z 115 are observed for **4⁺** (Table 2). All the data thus indicate that the phenyliminopropadienone radical cation is a stable species in the gas phase in the mass spectrometer.

Neutralization of a fast beam of these m/z 143 ions (**3a⁺**) with ammonia followed by reionization with oxygen in a separate collision cell afforded the NR mass spectrum shown in Fig. 1(a). The observation of a strong recovery signal at m/z 143 ('survivor ions') and the close similarity of the NR and CA mass spectra prove that neutral phenyliminopropadienone is also



- a: $R^1 = Ph; R^2 = R^3 = H$
 b: $R^1 = Ph; R^2 = Me; R^3 = H$
 c: $R^1 = Ph; R^2 = H; R^3 = Me$
 d: $R^1 = Ph; R^2 = R^3 = Me$
 e: $R^1 = Me; R^2 = R^3 = H$
 f: $R^1 = Me; R^2 = H; R^3 = Me$



3

- a: $R^1 = Ph$
 b: $R^1 = Me$
 c: $R^1 = H$

stable in the rarefied gas phase on the microsecond time scale of the mass spectrometer. One significant difference between the CA and NR spectra is observed at m/z 66, which corresponds to reionization of the open-shell NCCCCO radical formed by unimolecular dissociation in the neutralization step. This peculiar behaviour has also been noted and used in the characterization of analogous compounds, the carbon suboxide diimines, $RNCCCNR$.⁶

Table 1. Relative intensities of significant peaks in the 70 eV mass spectra of 3-phenylisoxazolo[5,4-d]pyrimidine-4(5H)-ones (**1**, $R^1 = C_6H_5$)^a

Precursor	$M^{+\cdot}$	m/z 143	m/z 77
1a	213 (47)	100	40
1b	227 (48)	100	35
1c	227 (58)	100	25
1d	241 (40)	100	56

^a $M^{+\cdot}$ data are given as m/z (relative intensity).

Table 2. Collisional activation of $[C_9H_5NO]^{+\cdot}$ ions^a

Precursor	T(°C)	115	103	88	m/z 77	62	51	38
1a	200	18	2	9	54	4	12	2
1a	800	18	1	9	54	5	12	1
5(4)	800	66	—	15	4	8	4	3
6	200	21	2	6	52	4	13	2

^a Oxygen was used as collision gas. Relative intensities are reported.

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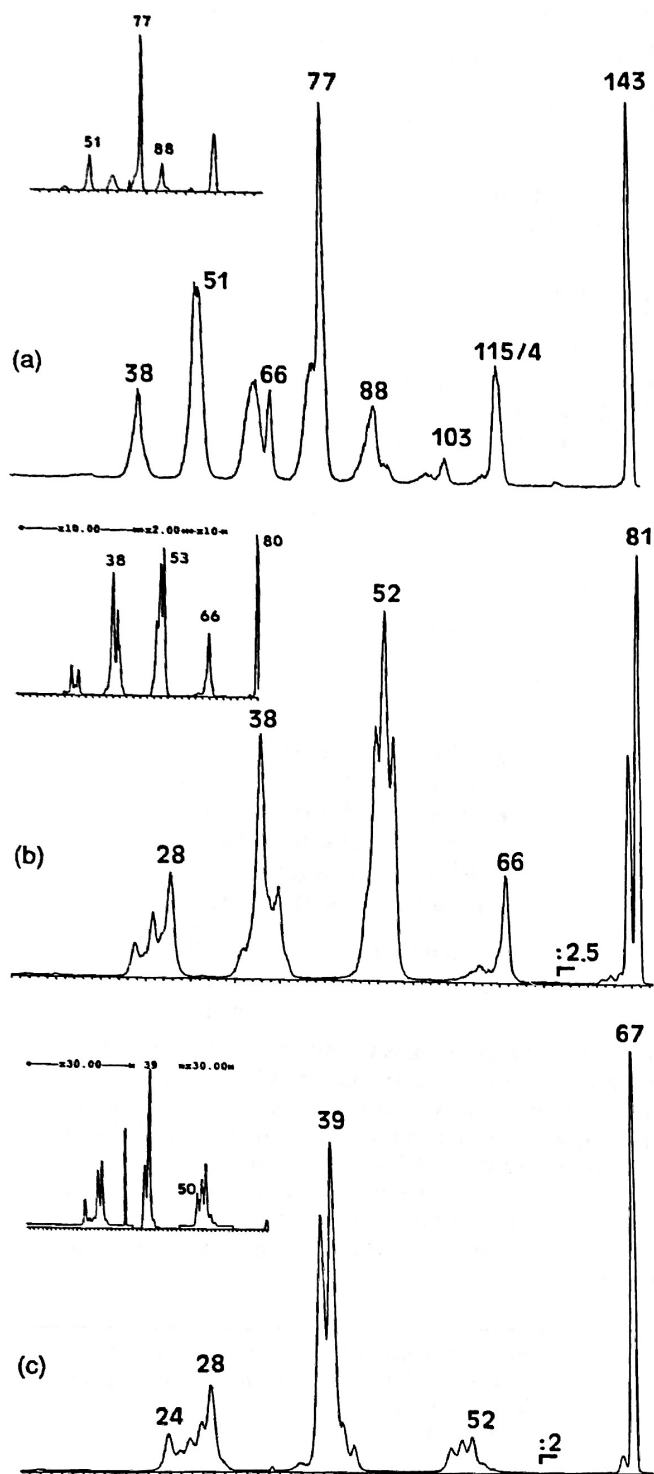
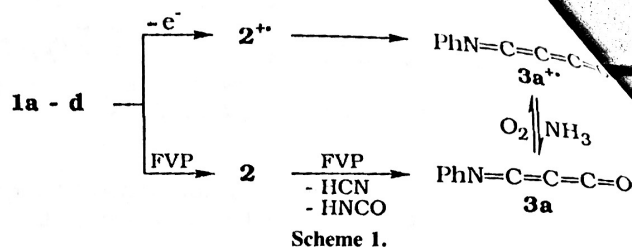


Figure 1. Neutralization-reionization mass spectra of $\text{RN}=\text{C}=\text{C}=\text{C}=\text{O}^+$ ions. The insets show, respectively, the collisional activation (CA) spectra of the ions. (a) PhNCCCO^+ , m/z 143. (b) $\text{CH}_3\text{NCCCO}^+$, m/z 81. (c) HNCCCO^+ , m/z 67.

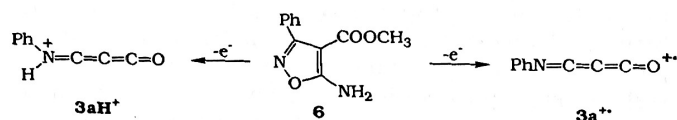
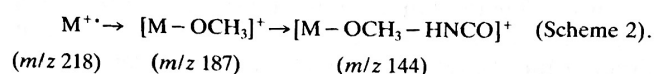
That neutral **3** is indeed a long-lived species outside the mass spectrometer is also shown by complementary techniques such as FVP/low temperature infra-red spectrometry and FVP/trapping experiments, which are described separately.⁷ In the present work, it was shown that the CA mass spectrum of m/z 143 produced by FVP of **1a** followed by ionization, remained unchanged up to 800 °C (Table 2), thus confirming that the neutral **3a** identified above, and hence also the ion



Scheme 1.

3a^+ , possess the structure $\text{C}_6\text{H}_5\text{N}=\text{C}=\text{C}=\text{C}=\text{O}$ (**3a**, Scheme 1).

$\text{C}_6\text{H}_5\text{N}=\text{C}=\text{C}=\text{C}=\text{O}^+$ ions are also produced in quite high abundance (43%) by dissociative ionization of 3-phenyl-4-methoxycarbonyl-5-aminoisoxazole (**6**), probably by consecutive losses of methanol and isocyanic acid. The fragmentation of 6^+ is, however, dominated by the formation of m/z 144 ions ascribed to protonated ions 3aH^+ , $[\text{C}_6\text{H}_5\text{NH}=\text{C}=\text{C}=\text{C}=\text{O}]^+$ through the sequence:



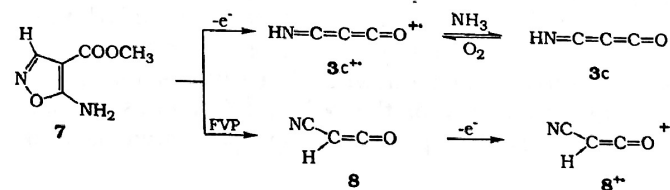
Scheme 2.

The arguments developed for the characterization of 3a^+ and **3a** can be extended to the analogue **3b**. The CA spectrum indeed indicates a CH_3NCCCO structure for the $[\text{C}_6\text{H}_5\text{NO}]^+$ ions (m/z 81) produced from **1e** and **1f** and the NR mass spectrum clearly establishes the stability of the corresponding neutrals (see Fig. 1(b)).

Although unsubstituted isoxazolopyrimidinone **1g** is unavailable, we have been able to prepare the parent iminopropadienone ions $\text{HN}=\text{C}=\text{C}=\text{C}=\text{O}^+$, 3c^+ , by dissociative ionization of 4-methoxycarbonyl-5-aminoisoxazole (**7**). Atom connectivity is confirmed by the CA mass spectrum which is characterized by an intense loss of CO and a small but significant peak at m/z 52 (loss of NH , see inset in Fig. 1(c)). The cyanoketene structure, $\text{N}\equiv\text{CCH}=\text{C}=\text{O}^+$, can be excluded as its CA spectrum shows additional m/z 53 ($-\text{N}$) and m/z 41 ($-\text{CN}$) peaks.

The NR mass spectrum (Fig. 1(c)) again demonstrates that $\text{HN}=\text{C}=\text{C}=\text{C}=\text{O}$ is a stable molecule in the gas phase when produced in a wall-less experiment. However, upon FVP at 800 °C, the isoxazole **7** decomposed into MeOH , HNCO and cyanoketene (**8**). It is likely that iminopropadienone is also formed thermally but readily tautomerizes to **8** via wall collision in the FVP experiments (Scheme 3).

Besides iminopropadienone production, FVP also induces a competitive isomerization process of isoxazo-



Scheme 3.

Table 3. Collisional activation of $[C_{11}H_7N_3O_2]^{++}$ ions (m/z 213)^a

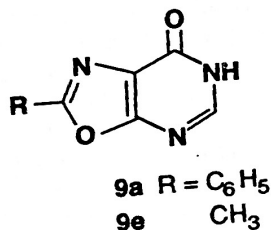
Precursor	186	185	157	143	m/z 130	115	105	88	77	51
1a 200 °C	—	6	2	100	4	5	3	1	9	1
1a 800 °C	93	—	8	100	5	15	29	4	17	2
9a 200 °C	100	—	5	3	4	10	24	3	5	1

^a Oxygen collision gas (80% transmission).Table 4. Collisional activation of $[C_6H_5N_3O_2]^{++}$ ions (m/z 151)^a

Precursor	124	121	96	81	m/z 63	53	52	43	38	28
1e 200 °C	41	100	8	51	11	5	5	1	1	1
1e 800 °C	100	34	9	19	7	6	5	3	1	1
9e 200 °C	100	—	3	4	1	4	4	4	1	1

^a Oxygen collision gas (80% transmission).

lopyrimidinones **1**, which is clearly shown by the strong modifications observed in the CA spectra of the 'residual' molecular ions at 800 °C (see Tables 3 and 4). For example, the appearance of peaks at m/z 105 ($C_6H_5C=O^+$) and 43 ($CH_3C=O^+$) in the CA spectra of **1a**⁺⁺ and **1e**⁺⁺, respectively, suggests that the corresponding neutrals have been isomerized into the corresponding oxazolopyrimidinones **9a** and **9e**. Further investigations on this isomerization process will be reported.



Finally, trapping of the pyrolyzate of **1a** in methanol allows the observation of m/z 207 ions in the mass spectrum. These ions originate from the addition of two methanol molecules to **3a** yielding a malonic acid imide **10**.⁷ The CA spectrum of the **10**⁺⁺ ions (Fig. 2) fully supports the proposed structure.

EXPERIMENTAL

The electron ionization mass spectra were recorded on a new six-sector VG AutoSpec 6F spectrometer (VG Analytical, Manchester, UK) of $E_1B_1E_2E_3B_2E_4$ geometry (E = electric sector; B = magnetic sector) at an accelerating voltage of 8 kV.⁸ In the CA experiments, a beam of ions is mass selected by the combination of the first three sectors ($E_1B_1E_2$) and submitted to collisional activation with oxygen (80% transmission). In the NR experiments, neutralization of the ions with ammonia (80% transmission) precedes reionization with oxygen (also 80% transmission), unreacted ions being eliminated by floating at 9 kV 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 4th field-free region.

The FVP device consists of a quartz tube (3 mm ID, 50 mm length) installed in the source housing of the

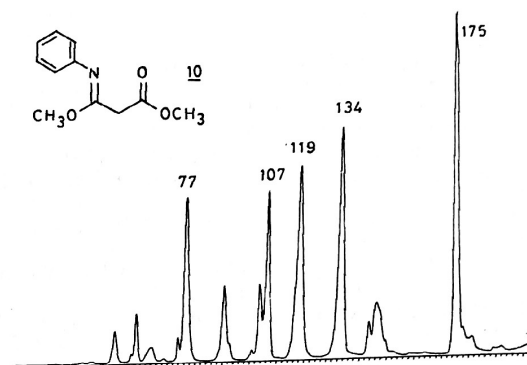
Figure 2. CA spectrum of m/z 207 ions obtained after ionization of the methanol trapping products of **3a** (see text).

Table 5. Melting points and NMR spectra of the pyrimidinones

	Melting point	¹ H NMR: (δ (ppm), DMSO-d ₆):
1a	241–242° (lit.: 237–239) ¹²	8,5(1H, s, C ₆ H); 8,3–8,1 (2H, m, φ); 7,7–7,4 (3H, m, φ)
1b	170–171°	8,7(1H, s, C ₆ H); 8,3–8,1 (2H, m, φ); 7,7–7,4 (3H, m, φ); 3,5 (3H, s, CH ₃)
1c	296–297°	8,3–8,1 (2H, m, φ); 7,7–7,4 (3H, m, φ); 2,6 (3H, s, C ₆ –CH ₃)
1d	200–202°	8,3–8,1 (2H, m, φ); 7,7–7,4 (3H, m, φ); 3,5 (3H, s, CH ₃); 2,6(3H, s, C ₆ –CH ₃)
1e	222–223° (lit.: 214–218) ¹²	8,3 (1H, s, C ₆ H); 7,2 (1H, br, NH); 2,5 (3H, s, CH ₃)
1f	269–270°	6,2 (1H, br, NH); 2,5 (3H, s, CH ₃); 2,4 (3H, s, C ₆ –CH ₃)
9a	319–320° (lit.: 320–321) ¹³	8,6 (1H, s, C ₆ H); 8,2–7,9 (2H, m, φ); 7,7–7,4 (3H, m, φ)
9e	281–282° (lit.: 281–282) ¹⁴	8,1 (1H, s, C ₆ H); 2,5 (3H, s, CH ₃)

spectrometer.⁹ Semi-preparative FVP experiments were performed by using a similar pyrolysis device (alumina tube) installed in a modified source housing of a Varian MAT 311A spectrometer (Bremen, Germany).¹⁰ The pyrolyzates were condensed on a liquid-nitrogen-cooled receptor and rapidly dissolved in methanol before reaching room temperature.

Some pyrimidinones were prepared according to the literature: **1a**,¹¹ **1e**,¹¹ **9a**,¹² **9e**.¹³ The methylated pyrimidinones **1b**, **1c**, **1d** and **1f** were synthesized by two-step reactions starting with 3-substituted-5-amino-4-methoxyisoxazoles, by using slightly modified literature methods.¹⁴ The first step involves the formation of imidates by the condensation of orthoesters and these imidates were cyclized by ammonia or methylamine (Table 5).

Acknowledgements

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