

Ion–Molecule Reaction of Pyridine with CS_3 Radical Cations: Experimental Evidence for the Production of Pyridine *N*-Thiooxide Distic Ions

Pascal Gerbaux, Yves Van Haverbeke and Robert Flammang*

Organic Chemistry Laboratory, University of Mons-Hainaut, Avenue Maistriau 19, B-7000 Mons, Belgium

Chemical ionization of pyridine using carbon disulphide as the reagent gas leads to the formation of new distic ions, pyridine *N*-thiooxide radical cations, $2^{+\cdot}$. The origin of these ions is unambiguously attributed to the reaction of $CS_3^{+\cdot}$ ions with neutral pyridine owing to the use of a new hybrid mass spectrometer combining sectors and an r.f.-only quadrupole collision cell floated at a voltage similar to the accelerating voltage of the ions. Collisional activation (CA) of appropriate reference ions (the molecular ions of isomeric mercaptopyridines, $4-6^{+\cdot}$) demonstrates the actual structure of the ions, while neutralization–reionization experiments indicate the stability of the corresponding neutral dipole in the gas phase. Several reactions were performed in the quadrupole collision cell with molecules recognized as excellent trapping reagents of distic ions: dimethyl disulphide, dimethyl diselenide and nitric oxide. The $2^{+\cdot}$ ions react with nitric oxide generating NOS^+ ions; this reaction is not observed for the reference $4-6^{+\cdot}$ ions. Although the transfer of thiomethyl radicals or selenomethyl radicals is observed for all the radical cations, the resulting $[2(4-6) + S(Se)]^+$ cations are clearly differentiated by CA. It is also shown that the transfer of $S^{+\cdot}$ to perdeuterated pyridine is a specific reaction of the distic $2^{+\cdot}$ ions. © 1997 John Wiley & Sons, Ltd.

J. Mass Spectrom. 32, 1170–1178 (1997)

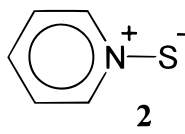
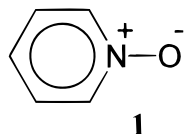
No. of Figures: 14 No. of Tables: 2 No. of Refs: 24

KEYWORDS: pyridine *N*-thiooxide; pyridine thiones; ion–molecule reactions; collisional activation; neutralization–reionization

INTRODUCTION

The stability and chemistry of *N*-oxides derived from pyridine, **1**, and related compounds is well established.¹ In contrast, the *N*-thiooxide (or *N*-sulphide) analogues are still elusive compounds and, to the best of our knowledge, only one paper dealing with theoretical considerations has appeared on pyridine *N*-thiooxide, **2**.² This is in keeping with the general instability of *N*-*S*-containing compounds as compared with their *N*-*O* analogues.³ Actually, *N*-*S* compounds, in contrast to their *N*-*O* analogues, contain a coordinate covalent bond between elements of the fifth and sixth groups in which the element bearing formal negative charge is less electronegative than the element bearing formal positive charge. The absence of more information on **2** is probably related to the lack of potential precursors, even in the gas phase.

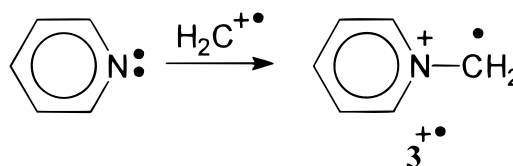
It is known that electron ionization of carbon disulphide under chemical ionization conditions (pressure



~1 Torr (1 Torr = 133.3 Pa)) leads to, besides the expected molecular and fragment ions of CS_2 , a series of heavier ions of composition C_xS_y ($0 \leq x \leq 2$ and $0 \leq y \leq 6$).^{4,5} Among these ions, the $CS_3^{+\cdot}$ species is the most abundant. Using collisional activation (CA) mass spectrometry (MS), and in relation to previous work by Sülzle et al.,⁶ we have recently shown that part of these ions have the carbon disulphide *S*-sulphide connectivity, $S=C=S^+-S^{\cdot}$.⁵ These ions are therefore distic ions.⁷

The transfer of an ionized methylene from distic reagent ions to pyridine has been thoroughly studied in recent years.⁸ Although the CA data were not easily interpreted, there is no doubt that the resulting ions have the pyridine *N*-methylidene structure, $3^{+\cdot}$. The ionized carbene is therefore specifically transferred from the distic ions (e.g. $H_2C^+-O^+=CH_2$ generated by ionization of oxacyclopropane⁹) on the nucleophilic nitrogen of pyridine (Scheme 1).

This paper describes a similar reaction of pyridine and related compounds with CS_3 radical cations. As already described for nitriles, ionized sulphur is readily transferred to nitrogen, generating the elusive pyridine



Scheme 1.

* Correspondence to: R. Flammang, Organic Chemistry Laboratory, University of Mons-Hainaut, Avenue Maistriau 19, B-7000 Mons, Belgium.

N-thioxide ions, $2^{+\cdot}$. Structural determination of these ions has made use of tandem mass spectrometric methodologies: collisional activation (CA) and neutralization–reionization (NR) mass spectrometry and also consecutive CA processes (MS/MS/MS). Ion–molecule reactions in an r.f.-only quadrupole collision cell were also investigated in order to prove the distonic nature of $2^{+\cdot}$ ions.

EXPERIMENTAL

The spectra were recorded on a large-scale tandem mass spectrometer (Micromass AutoSpec 6F) combining six sectors of EB©E©©EB©E (E stands for electric sector, B for magnetic sector and © for the collision cells used in this work).^{10a,b} General conditions were 8 kV accelerating voltage, 200 μ A trap current (in the electron impact mode), 1 mA (in the chemical ionization mode), 70 eV ionizing electron energy and 200 °C ion source temperature. The solid samples were introduced with a direct insertion probe, while the liquid samples were injected into the ion source via a heated (180 °C) septum inlet.

CA and NR spectra were recorded by scanning the field of the third electric sector and collecting the ions in the fifth field-free region with an off-axis photomultiplier detector.

The installation of an r.f.-only quadrupole collision cell inside the instrument has also been reported elsewhere.^{5,10b} Figure 1 shows the intermediate region of the spectrometer operating under 'normal' conditions (a) and in the hybrid mode (b). In this last mode, the neutralization cell is replaced by a demagnification lens, so that NRMS experiments are no longer accessible. Briefly, the experiments utilizing the quadrupole consist of the selection of a beam of fast ions (8 kV) with the three first sectors (EBE), the retardation of these ions to ~ 5 eV and the reaction with a reagent gas in the cell (the pressure of the reagent gas is estimated to be $\sim 10^{-3}$ Torr). After reacceleration to 8 kV, all the ions

present in the quadrupole are separated and mass measured by scanning the field of the second magnet. More interestingly, the high-energy CA spectra of the ions present in the quadrupole can be recorded by a linked scanning of the fields of the last three sectors (EBE) (resolved mode) or a conventional scanning of the field of the last electric sector after mass selection with the second magnet.

The quadrupole cell can be considered as a large field-free region and unimolecular decompositions within the quadrupole yield fragments with a low kinetic energy ($(m_2/m_1) < 5$ eV), which are then reaccelerated to ~ 8000 eV. It is therefore fairly easy to record their high-energy CA spectra without a loss of resolution and sensitivity whatever the mass difference between m_1 and m_2 .

All the samples used were commercially available, except for 3-mercaptopyridine, **5**, which was prepared according to Ref. 11.

RESULTS AND DISCUSSION

When a mixture of carbon disulphide (4 μ l) and pyridine (1 μ l) is ionized in the CI source, $[C_5H_5NS]^{+\cdot}$ ions are observed among several other products. That the $CS_3^{+\cdot}$ ions are the main reactive ions for the sulphur transfer reaction is established by ion–molecule reactions within the r.f.-only quadrupole collision cell. Indeed, if a beam of these m/z 108 ions is decelerated to ~ 5 eV before entering the cell containing pyridine, ion–molecule $[C_5H_5NS]^{+\cdot}$ (m/z 111) products are readily formed (Fig. 2). The same reaction was occurring between $CS_3^{+\cdot}$ and nitriles producing nitrile *N*-thioxides.⁵ It was therefore suggested that pyridine *N*-thioxide radical cations, $2^{+\cdot}$, are produced in these processes (Scheme 2).

Nevertheless, it is known that CS_3 radical ions are also able to attack ring carbons of heterocycles; for instance, neutral thiophene reacts with $CS_3^{+\cdot}$ generating 3-mercapthiophene radical cations.¹² Therefore,

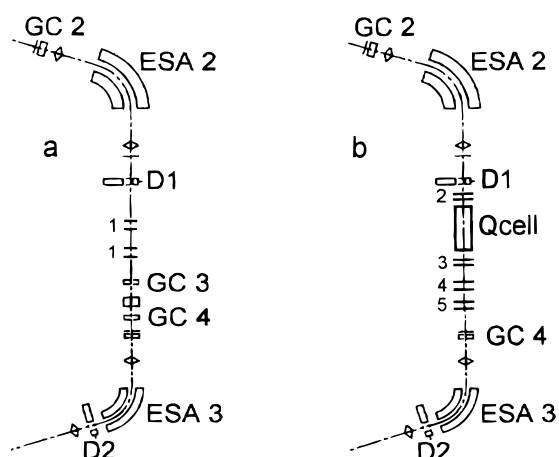


Figure 1. Schematic representation of the intermediate region of the AutoSpec 6F mass spectrometer in the 'normal' mode (a) and in the hybrid mode (b). GC, gas cell; D, off-axis photomultiplier detector; Qcell, quadrupole collision cell; 1, Y and Z lenses; 2, deceleration lenses; 3, acceleration lenses; 4, Y and Z lenses; 5, demagnification lens.

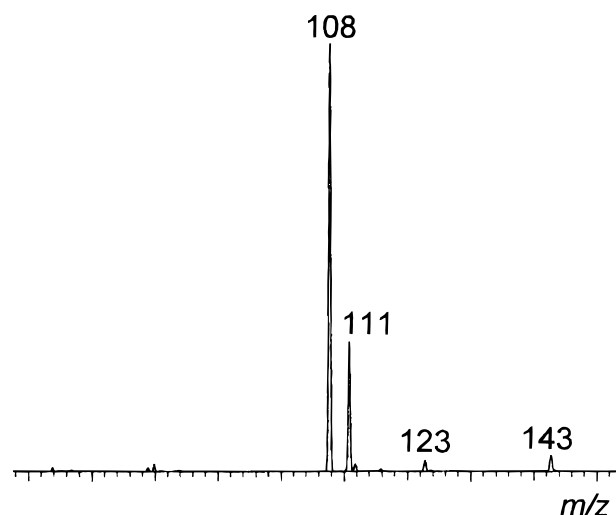
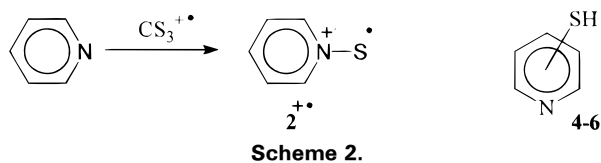


Figure 2. Mass spectrum (B scan) of the ions produced by reaction of $CS_3^{+\cdot}$ ions and pyridine in the Qcell.



other experimental data are required to confirm the production of $2^{+\bullet}$.

CA and NR experiments

The CA spectrum of $2^{+\bullet}$ ions is compared in Fig. 3 with the spectra of the molecular ions of 2-, 3- and 4-mercaptopyridine(4-6). Although some intense peaks are common for all four precursors, the spectra show important differences in the relative abundances, indicating the occurrence of different isomeric ions (or different mixtures of ions). In fact, the common peaks are those already seen without the collision gas (mass-analysed ion kinetic energy (MIKE) spectra). These unimolecular fragmentations are the competitive losses of CHN and CS giving, as indicated by MS/MS/MS experiments, the molecular ions of thiophene (m/z 84) and pyrrole (m/z 67), respectively. The relative peak

height ratios are 0.18 for $2^{+\bullet}$, 0.71 for $5^{+\bullet}$ and 0.22 for $6^{+\bullet}$; a notable exception is the metastable ion $4^{+\bullet}$, losing only CS.

A very important difference between the CA spectrum of $2^{+\bullet}$ and those of the reference ions is the loss of sulphur (m/z 79) for the former. This single bond cleavage is therefore characteristic of the proposed pyridine *N*-thioxide $2^{+\bullet}$ ions. Contrasting with the behaviour of acetonitrile *N*-thioxide,⁵ a significant peak corresponding to $S^{+\bullet}$ (m/z 32) is not observed; this is in keeping with a lower ionization energy (IE) of pyridine compared with the IE of acetonitrile (IE: pyridine 9.25, acetonitrile 12.2 and sulphur 10.3 eV).¹³

The NR mass spectrum of the pyridine *N*-thioxide ions is shown in Fig. 4. This spectrum is similar to the corresponding CA spectrum with the appearance of new peaks at m/z 44 and 32 resulting from the reionization of neutrals formed in the neutralization cell by unimolecular decomposition or collision-induced decomposition. The loss of sulphur remains an important process. Moreover, the recovery signal representing the survivor ions is the base peak of the NR mass spectrum. This indicates that the neutral pyridine *N*-thioxide dipole, **2**, is a stable molecule in the mass spectrometer gas phase for at least 1 μ s, which is the

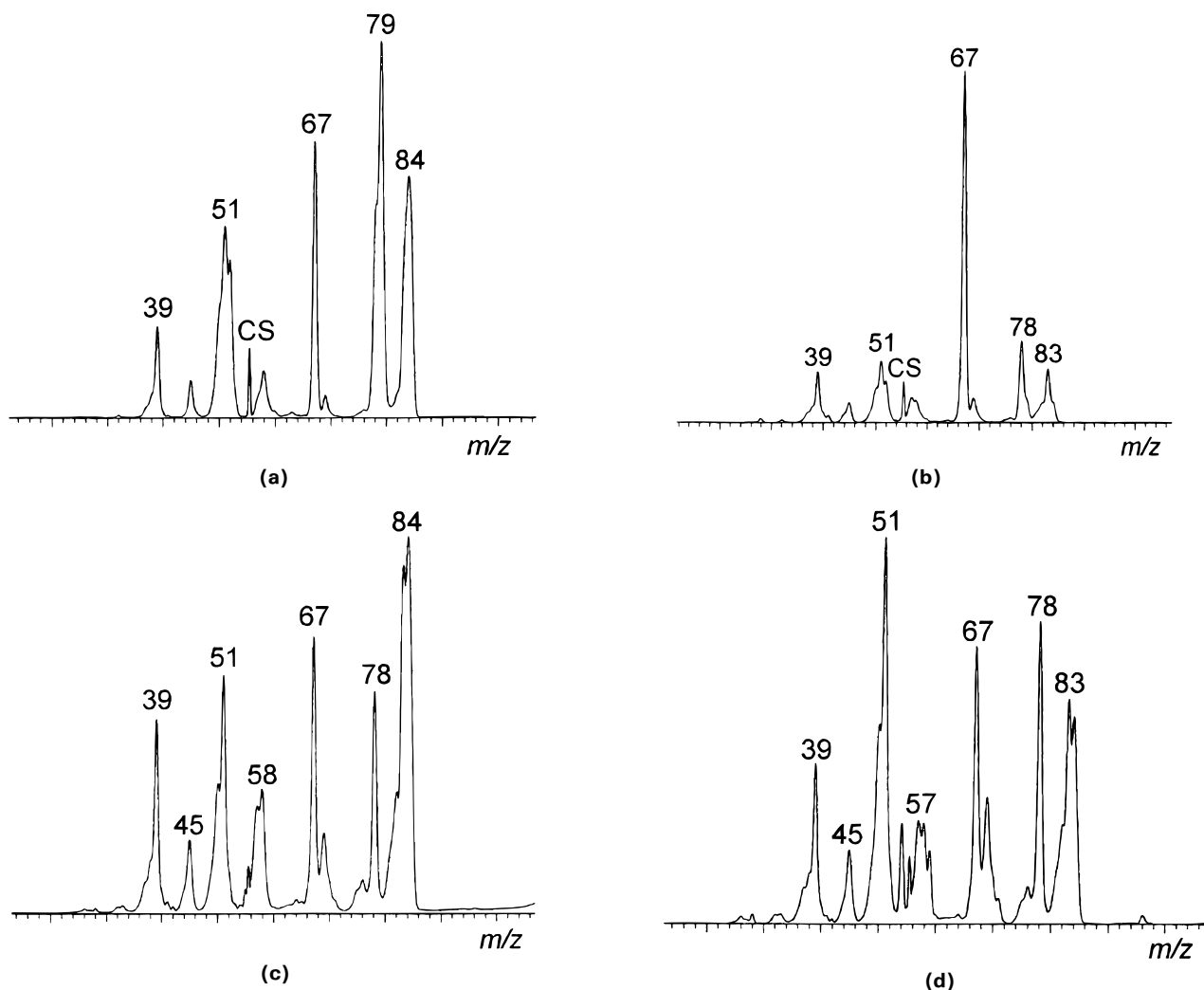


Figure 3. CA (O_2) spectra of the m/z 111 ions produced by chemical ionization (CS_2 reagent gas) of pyridine (a) and electron ionization of the mercaptopyridines 4-6(b-d).

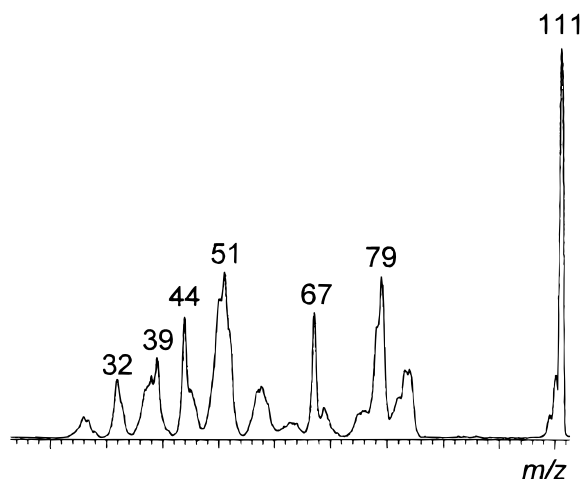


Figure 4. NR (NH_3/O_2) mass spectrum of m/z 111 ions produced by chemical ionization (CS_2) of pyridine.

time of flight between the neutralization and reionization cells.

Ion-molecule reactions with dimethyl disulphide

In contrast to conventional radical cations which usually undergo fast charge exchange with dimethyl disulphide (CH_3SSCH_3 , DMDS), distonic radical cations abstract $\text{CH}_3\text{S}^\bullet$ from DMDS. The observation of a $\text{CH}_3\text{S}^\bullet$ transfer may therefore be used as an indication of the occurrence of a distonic ion structure.¹⁴ This approach is unfortunately not applicable in all cases as some distonic ions react with DMDS by electron trans-

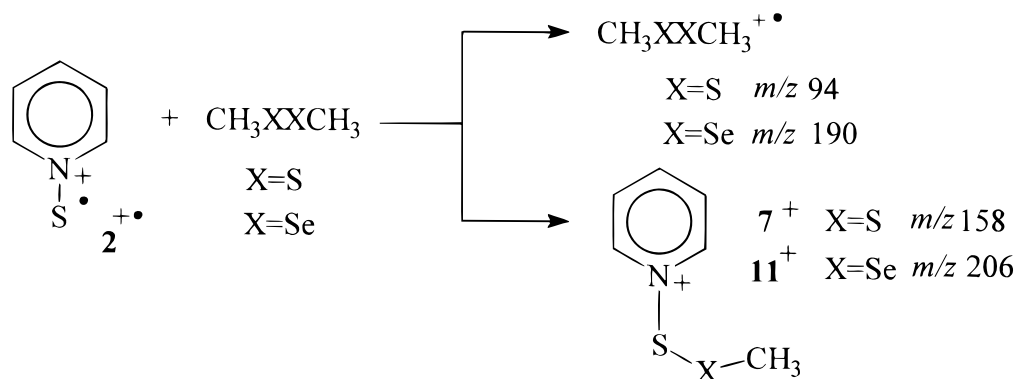
fer in addition to $\text{CH}_3\text{S}^\bullet$ abstraction.¹⁴ Further complications also arise from the fact that many distonic ions are unreactive towards DMDS¹⁵ and that the ions which undergo $\text{CH}_3\text{S}^\bullet$ abstraction react only very slowly (usually less than one out of five collisions leads to $\text{CH}_3\text{S}^\bullet$ abstraction).¹⁶ We decided, however, to perform the reactions between **2**, **4–6**⁺⁺ and DMDS in the r.f.-only quadrupole collision cell and the results are given in Table 1.

The pyridine *N*-thioxide molecular ions, **2**⁺⁺, react with DMDS by $\text{CH}_3\text{S}^\bullet$ abstraction and by charge exchange (Scheme 3, $\text{X} = \text{S}$). The other peaks at m/z 84 and 67 arise from the dissociation of metastable **2**⁺⁺ ions (Fig. 5(a)). Abstraction of a methyl radical is also an important competitive process leading to m/z 126 cations.

In order to obtain more information on the actual structure of the m/z 158 ions, their CA mass spectrum (Fig. 5(b)) was recorded. This spectrum is indicative of the proposed structure, **7**⁺. Indeed, the main fragmentations lead to the losses of CH_3^\bullet (m/z 143) and $\text{CH}_3\text{S}^\bullet$ (m/z 111) and to the production of m/z 79 ions. The interpretation of the peak at m/z 79 is, however, not straightforward as three different processes could be involved in their production: the loss of $\text{CH}_3\text{SS}^\bullet$ (formation of pyridine molecular ions), the loss of neutral pyridine (formation of isobaric CH_3SS^+ ions) and the formation of doubly charged **7**²⁺⁺ ions (charge stripping, CS). The effective competition between these processes is deduced from the use of pyridine- d_5 *N*-thioxide molecular ions (m/z 116). These ions react in the Qcell with CH_3SSCH_3 by $\text{CH}_3\text{S}^\bullet$ abstraction to produce m/z 163 cations which undergo, after collisional

Table 1. Products of ion-molecule reactions between $[\text{C}_5\text{H}_5\text{NS}]^+$ isomers and neutral reagents

Ions	Neutral reagent			
	CH_3SSCH_3	$\text{CH}_3\text{SeSeCH}_3$	NO^\bullet	Pyridine- d_5
2 ⁺⁺	m/z 80 $[\text{Pyr} + \text{H}]^+$ m/z 94 charge exchange m/z 126 $[\text{Pyr} + \text{CH}_3\text{S}^\bullet]^+$ m/z 141 $[\text{CH}_3\text{SSCH}_3 + \text{CH}_3\text{S}^\bullet]^+$ m/z 158 $[\mathbf{2} + \text{CH}_3\text{S}^\bullet]^+$	m/z 80 $[\text{Pyr} + \text{H}]^+$ m/z 174 $[\text{Pyr} + \text{CH}_3\text{Se}^\bullet]^+$ m/z 190 charge exchange m/z 206 $[\mathbf{2} + \text{CH}_3\text{Se}^\bullet]^+$ m/z 222 $[\text{CH}_3\text{SeSeCH}_3 + \text{CH}_3\text{S}^\bullet]^+$	m/z 62 ONS^+ m/z 141 $[\mathbf{2} + \text{NO}^\bullet]^+$	m/z 84 charge exchange m/z 85 $[\text{Pyr} - d_5 + \text{H}]^+$ m/z 116 $[\text{Pyr} - d_5 + \text{S}]^{++}$
4 ⁺⁺	m/z 94 charge exchange m/z 158 $[\mathbf{4} + \text{CH}_3\text{S}^\bullet]^+$	m/z 190 charge exchange m/z 206 $[\mathbf{4} + \text{CH}_3\text{Se}^\bullet]^+$	m/z 141 $[\mathbf{4} + \text{NO}^\bullet]^+$	m/z 84 charge exchange
5 ⁺⁺	m/z 94 charge exchange m/z 158 $[\mathbf{5} + \text{CH}_3\text{S}^\bullet]^+$	m/z 190 charge exchange m/z 206 $[\mathbf{5} + \text{CH}_3\text{Se}^\bullet]^+$	m/z 30 charge exchange m/z 141 $[\mathbf{5} + \text{NO}^\bullet]^+$	m/z 84 charge exchange
6 ⁺⁺	m/z 94 charge exchange m/z 158 $[\mathbf{6} + \text{CH}_3\text{S}^\bullet]^+$	m/z 190 charge exchange m/z 206 $[\mathbf{6} + \text{CH}_3\text{Se}^\bullet]^+$	m/z 30 charge exchange m/z 141 $[\mathbf{6} + \text{NO}^\bullet]^+$	m/z 84 charge exchange



Scheme 3.

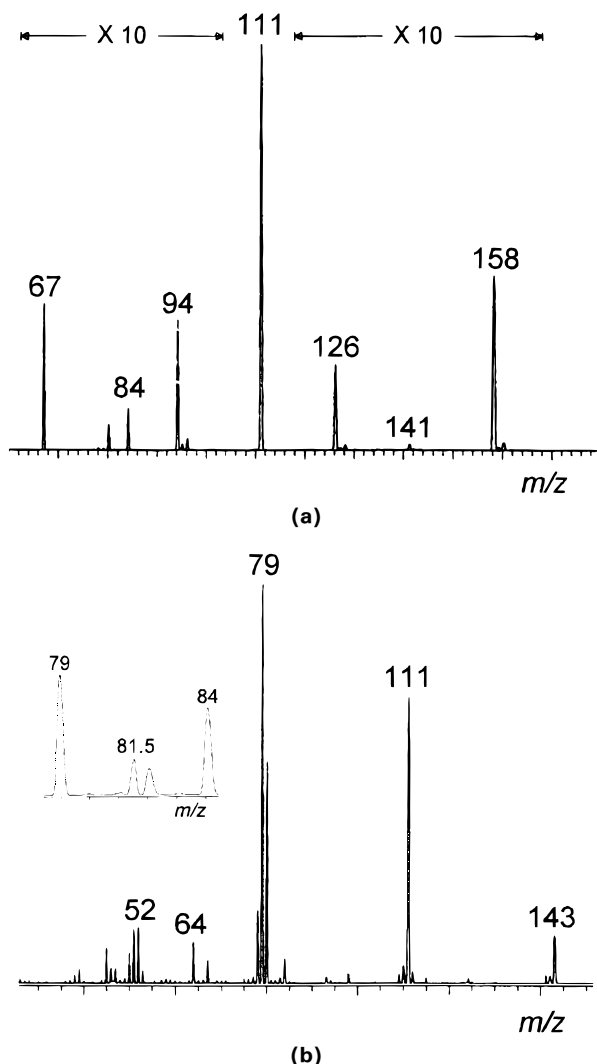
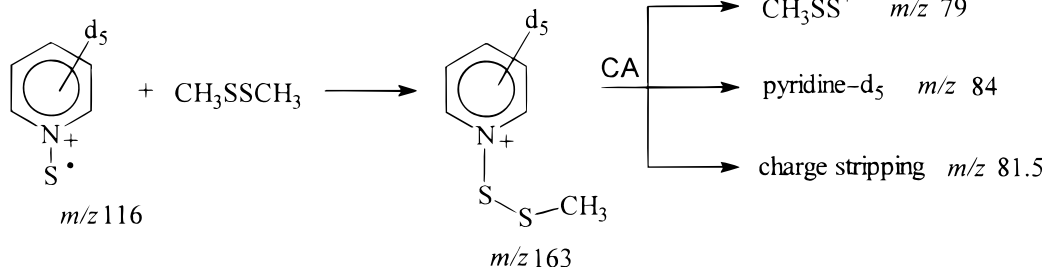


Figure 5. Reaction between 2^{++} ions and DMDS in the Qcell: (a) mass spectrum of the ion-molecule products and (b) CA (O_2) spectrum of the $[2 + \text{CH}_3\text{S}]^+$ (m/z 158) cations. Inset: part of the CA spectrum (m/z 84–79 region) of the m/z 163 ions produced by reaction of pyridine- d_5 *N*-thioxide and DMDS in the Qcell.

activation (inset in Fig. 5(b)), the loss of CH_3SS^+ (m/z 84, pyridine- d_5 molecular ions), the loss of pyridine- d_5 (m/z 79, CH_3SS^+) and collisional ionization (m/z 81.5) (Scheme 4).

It is surprising to observe that, in addition to the expected charge exchange reaction (relevant ionization energies are given in Table 2), a thiomethyl radical, $\text{CH}_3\text{S}^\bullet$, is also abstracted when DMDS reacts with the molecular ions of 2-mercaptopyridine, 4^{++} . In fact, neutral 2-mercaptopyridine, **4**, may exist in different tautomeric structures: the 2-mercaptopyridine, **4a**, and the pyridine-2-thione, **4b**, structures. In the gas phase,



Scheme 4.

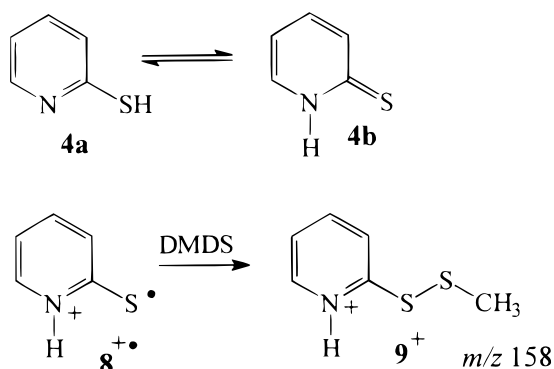
Table 2. Relevant ionization energies^{13a}

Neutral species	Ionization energy (eV)
2-Mercaptopyridine	8.7
Pyridine-2-thione	7.7
3-Mercaptopyridine	8.9
4-Mercaptopyridine	9.25
CH_3SSCH_3	8.0 ^{13b}
$\text{CH}_3\text{SeSeCH}_3$	7.9
NO^+	9.25
Pyridine	9.25

various approaches have indicated the co-existence of the two tautomers and the contribution of pyridine-2-thione, **4b**, has been estimated to be $\sim 10\%$.¹⁷ Vertical ionization of the mixture of the two tautomers will therefore produce in part pyridine-2-thione molecular ions, $4b^{++}$. It is not unexpected that the positive charge is localized in these ions on the nitrogen atom whereas the radical site is sulphur. Such a resonance structure, 8^{++} , is therefore distonic and could consequently rationalize the $\text{CH}_3\text{S}^\bullet$ abstraction (Scheme 5).

The CA spectrum of the m/z 158 ions, 9^+ , is shown in Fig. 6(a). Although the main fragmentations are identical with the fragmentations observed for the 7^+ ions (Fig. 5(b)), the relative intensities are different and therefore allow their differentiation. The two main processes are the loss of $\text{CH}_3\text{S}^\bullet$ (m/z 111) and the formation of m/z 79 ions. A sample of labelled 2-mercaptopyridine being unavailable, the actual structure of the m/z 79 ions cannot be derived from these data.

It is possible, however, to synthesize the m/z 158 ions, 9^+ , by using chemical ionization conditions. Indeed, when a mixture of DMDS and 2-mercaptopyridine/pyridine-2-thione is injected into the CI source, m/z 158 ions are generated and their CA spectrum unambiguously confirms that the same ions are produced in the CI source and in the Qcell. This experiment therefore offers the possibility of performing an MS/MS/MS experiment in order to characterize the structure of the m/z 79 ions. This peculiar experiment consists of the following operations: (i) preparation of the m/z 158 ions in the CI source as explained above, (ii) deceleration of these ions by floating the Qcell at a voltage appropriate to maximize collision-induced dissociation (argon collision gas) into m/z 79 ions, (iii) reacceleration of these ions at ~ 8 keV and (iv) collisional activation with oxygen and recording of the fragments by a linked scanning over MS2. The resulting CA spectrum is shown in Fig. 6(b). The very low intensity of the peaks at m/z 64 and 47 (S_2^{++} and CH_3S^+ , respectively) indicates that the m/z 79 ions are not CH_3SS^+ ions but instead



$[\text{C}_5\text{H}_5\text{N}]^+$ ions. Moreover, the perfect analogy of the spectrum depicted in Fig. 6(b) and the spectrum of the corresponding ions generated by dissociative ionization (loss of CO_2) of 2-picolinic acid confirms that the actual structure of the m/z 79 ions is azacyclohexadiene-2-ylidene radical cation, $10^{+\bullet}$ (Scheme 6, $\text{X} = \text{S}$).¹⁸

The interpretation of the contrasting behaviour of 7^+ and 9^+ is straightforward. Indeed, Lavorato et al.¹⁸ have recently calculated that neutral azacyclohexadiene-2-ylidene, 10 , is 50 kcal mol^{-1} ($1 \text{ kcal} = 4.184 \text{ kJ}$) less stable than neutral pyridine. In contrast, the relative stability of the corresponding radical cations has been found to be the inverse, the cyclic carbene ions, $10^{+\bullet}$, being more stable than the conventional pyridine molecular ions. Hence it is not surprising that the process leading to the generation of CH_3SS^+ cations plus the neutral carbene 10 in the fragmentation of 9^+ is thermodynamically disfavoured. Azacyclohexadiene-2-ylidene radical cations, $10^{+\bullet}$, can also be produced by protonation of the nitrogen atom of 2-chloropyridine using methanol chemical ionization followed by dechlorination of the so-produced cations by collisional activation with argon in the Qcell.

Similar experiments have been performed with the isomeric 3- and 4-mercaptopyridines, 5 and 6 (Table 1). $\text{CH}_3\text{S}^\bullet$ abstraction is again observed and collisional activation of the $[\mathbf{5(6)} + \text{CH}_3\text{S}]^+$ ions induces a loss of $\text{CH}_3\text{SS}^\bullet$ while formation of CH_3SS^+ ions is not observed.

Ion-molecule reactions with dimethyl diselenide

Dimethyl diselenide (DMDSe) has been demonstrated

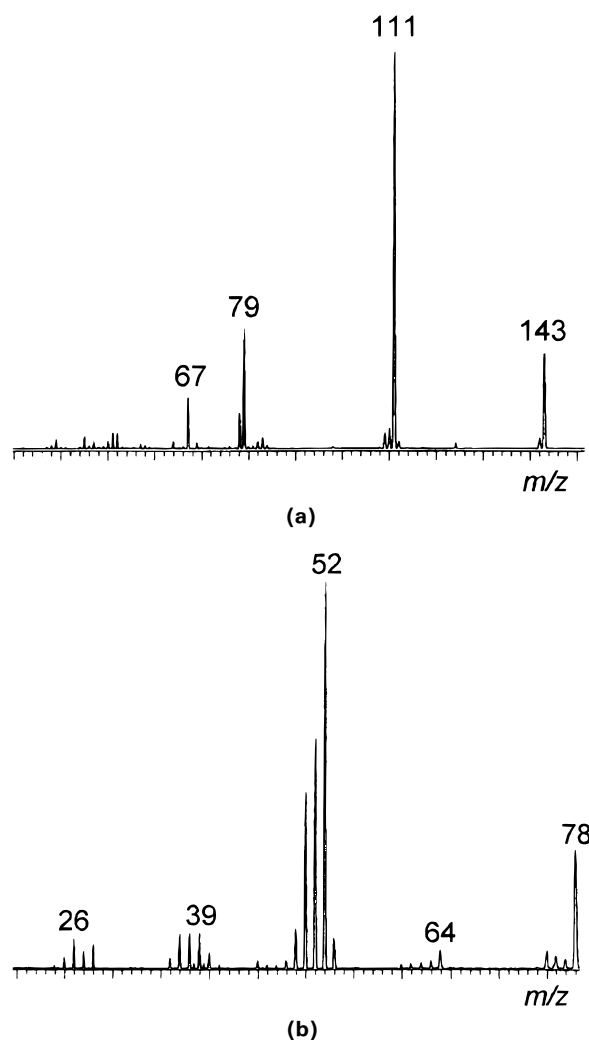
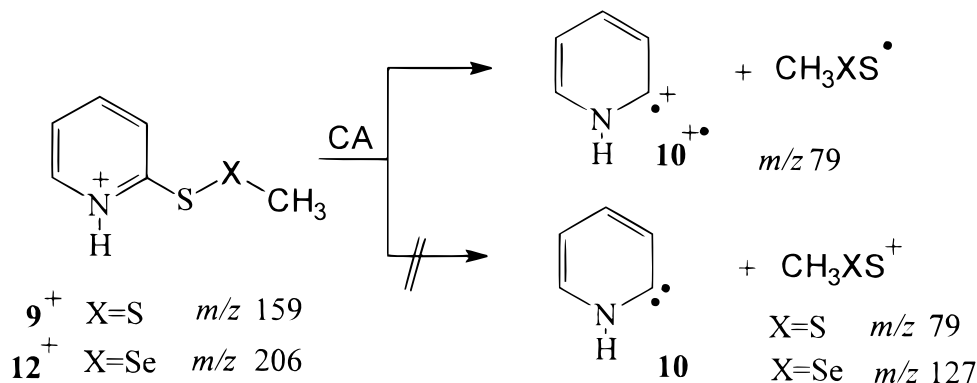


Figure 6. CA (O_2) spectrum of the $[\mathbf{4} + \text{CH}_3\text{S}]^+$ ions (m/z 158) generated by reaction of $4^{+\bullet}$ and DMDS in the Qcell (a) and CA (O_2) spectrum of the collision-induced (argon in Qcell) m/z 79 fragments of the m/z 158 cations (b). In this MS/MS/MS experiment, the precursor m/z 158 ions were prepared by chemical ionization of a mixture of DMDS and 2-mercaptopyridine/pyridine-2-thione.

to be one of the most powerful reagents for the identification of distonic radical cations. Indeed, these ions often readily abstract $\text{CH}_3\text{Se}^\bullet$ from DMDSe .¹⁹ The reaction is faster and more exclusive than $\text{CH}_3\text{S}^\bullet$ abstraction from CH_3SSCH_3 . Actually, in relation to

the sulphur–sulphur bond in CH_3SSCH_3 , the relatively large outer orbitals of selenium cause the Se–Se homolytic bond dissociation energy to be lower, thereby allowing this bond to be readily cleaved.²⁰ In sharp contrast to the reactivity of distonic ions, most conventional radical cations were found to react by exclusive electron transfer or to be unreactive towards DMDSe. Unfortunately, the complexity of the isotopic distribution makes the sensitivity lower and the spectra less easy to analyse.

Pyridine N-thioxide molecular ions, $2^{+\cdot}$, react with $\text{CH}_3\text{SeSeCH}_3$ by $\text{CH}_3\text{Se}^\cdot$ abstraction (Fig. 7(a), Table 1) in addition to electron transfer as depicted in Scheme 3 ($\text{X} = \text{Se}$).

The structure of the m/z 206 ions is clearly established by collisional activation, the main collision-induced fragments being observed at m/z 191 (loss of CH_3^\cdot), m/z 127 ($\text{CH}_3^{80}\text{SeS}^+$ ions) and m/z 111 (loss of $\text{CH}_3\text{Se}^\cdot$) (Fig. 7(b)). As expected, the molecular ions of 2-mercaptopyridine, **4**, also react by charge exchange and by $\text{CH}_3\text{Se}^\cdot$ abstraction in the Qcell (Table 1), confirming the distonic character of the ionized tautomeric structure of mercaptopyridine. The CA spectrum (Fig. 7(c)) shows a very strong decrease in the intensity of the

m/z 127 peak (CH_3SeS^+ cations). This corroborates the previous conclusions on the generation of the carbenic isomers of pyridine (Scheme 6, $\text{X} = \text{Se}$).

Ion–molecule reactions with nitric oxide

Further confirmation of the distonic structure, $2^{+\cdot}$, is found in the study of its reactivity towards nitric oxide. Instead of performing reactions involving a homolytic bond cleavage in the neutral reagent, leading to the abstraction of an atom or a radical by the ion, distonic ions are also recognized as potential reagents for the transfer of charged odd-electron groups to neutral molecules.²¹

Weiske et al.²² have shown using Fourier transform mass spectrometry that the reaction of $\cdot\text{CH}_2\text{—X}^+\text{—CH}_3$ distonic ions and nitric oxide (NO^\cdot) generates CH_2NO^+ cations. NO^\cdot therefore appears to be a versatile reagent for detecting non-conventional distonic ions and ion–molecule reactions in the r.f.-only quadrupole collision cell have been therefore realized starting from mass-selected $2^{+\cdot}$ and $4\text{--}6^{+\cdot}$ ions (Table 1).

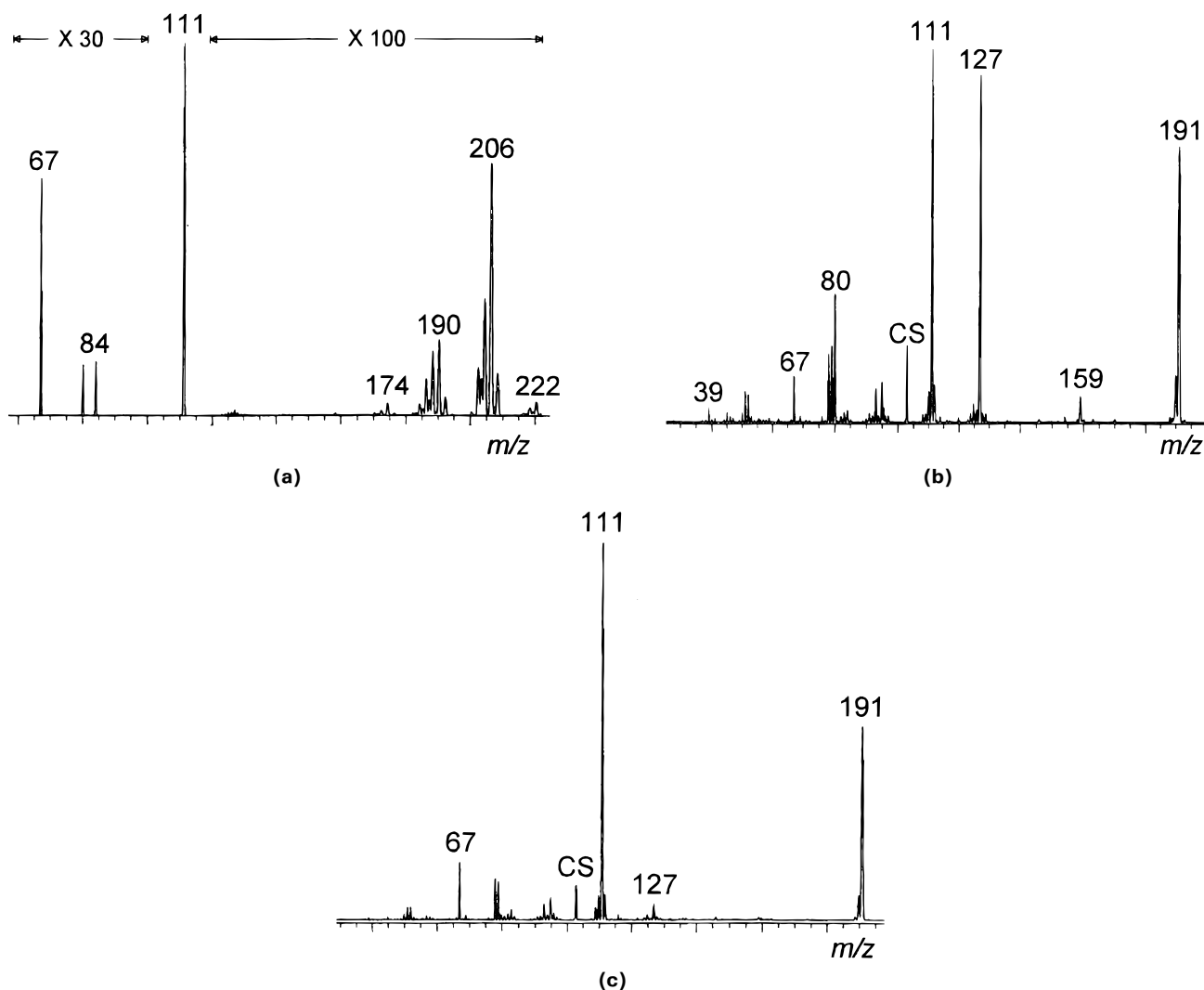


Figure 7. Reaction between $2^{+\cdot}$ ions and DMDSe in the Qcell: (a) mass spectrum of the ion–molecule products; (b) CA (O_2) spectrum of the $[2 + \text{CH}_3^{80}\text{Se}]^+$ (m/z 206) cations; (c) CA (O_2) spectrum of the $[4 + \text{CH}_3^{80}\text{Se}]^+$ (m/z 206) cations.

Two different products are detected in the reaction of $2^{+\bullet}$ ions with NO^\bullet corresponding, in order of increasing abundance, to the formation of NOS^+ by transfer of $\text{S}^{+\bullet}$ to NO^\bullet (m/z 62) and to the formation of $[\text{M} + \text{NO}]^+$ ions (m/z 141). The lone reaction observed during the interaction between $4^{+\bullet}$ ions and NO^\bullet leads to $[\text{M} + \text{NO}]^+$ (m/z 141) while $5^{+\bullet}$ and $6^{+\bullet}$ also react significantly by charge exchange. It is not surprising that, among the three isomeric mercaptopyrindines, only the 4-isomer produces NO^+ significantly, as its ionization energy matches exactly that of nitric oxide (Table 2). Given the fact that the ionization energy of 3-mercaptopyrindine (8.9 eV) is lower than that of nitric oxide (9.25 eV), the occurrence of the charge exchange reaction between $5^{+\bullet}$ and nitric oxide is more surprising.¹³ However, the uncertainty in the IE measurements and the fact that the ions are not thermalized in our experiments could perhaps justify this observation. Recall also that the mercaptopyrindines are tautomerizable compounds and that the real proportions of the tautomers will be dependent on the experimental conditions. Anyway, the production of NOS^+ in the specific case of $2^{+\bullet}$ strongly confirms their pyridine *N*-thioxide structure.

Ion-molecule reactions with pyridine- d_5

Yu et al.²³ performed a $\text{CH}_2^{+\bullet}$ abstraction reaction from pyridine *N*-methylidene ions, $3^{+\bullet}$, by a more nucleophilic pyridine, 2,6-dimethylpyridine, in order to ascertain the methylidene structure. We extended this interesting experiment to the $[\text{C}_5\text{H}_5\text{NS}]^{+\bullet}$ isomers, 2,4- $6^{+\bullet}$, looking at their reactivity toward pyridine- d_5 . The transfer of sulphur is only observed for $2^{+\bullet}$ ions as indicated in Fig. 8(a) by the appearance of a peak at m/z 116. The CA spectrum of these ions (Fig. 8(b)) presents the loss of sulphur as the main fragmentation. This is also the case if the m/z 116 ions are generated by chemical ionization (CS_2) of pyridine- d_5 .

$\text{CS}_3^{+\bullet}$ ions react also with the isomeric 2,4-picolines by sulphur transfer, and the CA spectra of the corresponding ions (m/z 125) are again characterized by an intense loss of sulphur. This reaction is, however, of minor importance for the product of sulphuration of 2-picoline which preferentially loses thioformaldehyde. Strong ortho-effects are thus occurring in this case. Transfer of ionized methylene to picolines has been recently described by Eberlin and co-workers²⁴ to produce the isomeric pyridine *N*-methylidene ions.

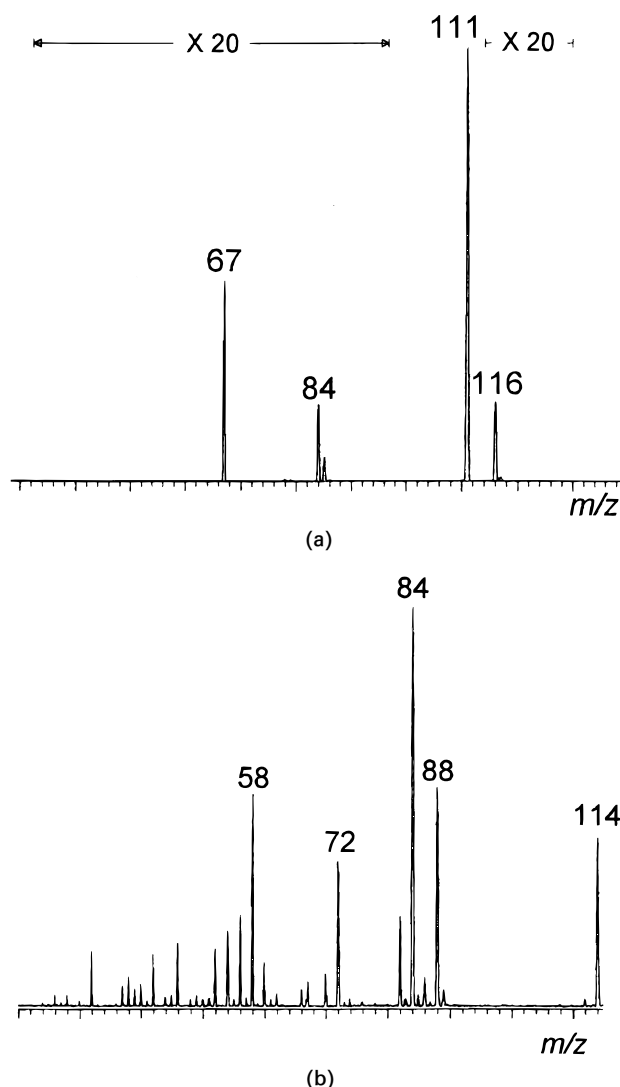


Figure 8. Reaction between $2^{+\bullet}$ and pyridine- d_5 in the Qcell: (a) mass spectrum of the ions produced and (b) CA (O_2) spectrum of the m/z 116 ions.

Acknowledgements

We thank the Fonds National pour la Recherche Scientifique for financial support for the acquisition of the tandem mass spectrometer (Micromass AutoSpec 6F) and for a fellowship for P.G. We also thank Dr C. Braybrook and Dr J. Brown (Micromass, Manchester, UK) for their contribution to the conception and installation of the r.f.-only quadrupole collision cell.

REFERENCES

1. A. R. Katritzky and J. M. Lagowsky, *Chemistry of Heterocyclic N-Oxides*. Academic Press, London (1971).
2. J. Fabian, *Izv. Akad. Nauk SSSR, Ser. Khim.* **20**, 562 (1987).
3. (a) C. Wentrup, S. Fischer, A. Maquestiau and R. Flammang, *J. Org. Chem.* **51**, 1908 (1986); (b) C. Wentrup and P. Kambouris, *Chem. Rev.* **91**, 363 (1991).
4. J. P. Delwiche and M. Praet, *Adv. Mass Spectrom.* **6**, 829 (1974).
5. P. Gerbaux, Y. Van Haverbeke, R. Flammang, M. W. Wong and C. Wentrup, *J. Phys. Chem.* **101** (1997).
6. D. Sülzle, H. Egsgaard, L. Carlsen and H. Schwarz, *J. Am. Chem. Soc.* **112**, 3750 (1990).
7. (a) S. Hammerum, *Mass Spectrom. Rev.* **7**, 123 (1988); (b) H. I. Kenttämaa, *Org. Mass Spectrom.* **29**, 1 (1994); (c) R. L. Smith, P. K. Chou and H. I. Kenttämaa, in *Structure, Energetics and Dynamics of Organic Ions*, edited by T. Baer, C. Y. Ng and I. Powis. Wiley, New York (1996).
8. (a) C. G. De Koster, J. J. Van Houte and J. Van Thuijl, *Int. J. Mass Spectrom. Ion Processes* **98**, 235 (1990); (b) S. J. Yu, M. L. Gross and K. R. Fountain, *J. Am. Soc. Mass Spectrom.* **4**, 117 (1993).
9. W. J. Bouma, J. K. MacLeod and L. Radom, *J. Chem. Soc., Chem. Commun.*, 724 (1978).
10. (a) R. H. Bateman, J. Brown, M. Lefevre, R. Flammang and

- Y. Van Haverbeke, *Int. J. Mass Spectrom. Ion Processes* **115**, 205 (1992); (b) R. Flammang, Y. Van Haverbeke, C. Braybrook and J. Brown, *Rapid Commun. Mass Spectrom.* **9**, 795 (1995).
11. N. Steiger, Br. Pat. 637130; *Chem. Abstr.* **44**, 8380 (1950).
 12. R. Flammang, M. Barbieux-Flammang, P. Gerbaux and C. T. Pedersen, *J. Chem. Soc., Perkin Trans.* **2**, 1261 (1997).
 13. (a) S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data* **17**, Suppl. 1 (1988); (b) D. T. Leeck and H. I. Kenttämää, *Org. Mass Spectrom.* **29**, 106 (1994).
 14. K. M. Stirk, J. C. Orłowski, D. T. Leeck and H. I. Kenttämää, *J. Am. Chem. Soc.* **114**, 8604 (1992).
 15. L. K. M. Kiminkinen, K. M. Stirk and H. I. Kenttämää, *J. Am. Chem. Soc.* **114**, 2027 (1992).
 16. R. L. Smith and H. I. Kenttämää, *J. Am. Chem. Soc.* **117**, 1393 (1995).
 17. (a) A. Maquestiau, Y. Van Haverbeke, C. De Meyer, A. R. Katritzky and J. Frank, *Bull. Soc. Chim. Belg.* **84**, 465 (1975); (b) A. Albert and G. B. Barlin, *J. Chem. Soc.* 2384 (1959); (c) P. Beak, F. S. Fry, Jr, J. Lee and F. Steele, *J. Am. Chem. Soc.* **98**, 171 (1976).
 18. D. Lavorato, J. K. Terlouw, T. K. Dargel, W. Koch, G. A. McGibbon and H. Schwarz, *J. Am. Chem. Soc.* **118**, 1189 (1996).
 19. (a) B. J. Beasley, R. L. Smith and H. I. Kenttämää, *J. Mass Spectrom.* **30**, 384 (1995); (b) K. K. Thoen, B. J. Beasley, R. L. Smith and H. I. Kenttämää, *J. Am. Soc. Mass Spectrom.* **7**, 1245 (1996).
 20. (a) M. Newcomb, *Tetrahedron* **49**, 1151 (1993); (b) M. Newcomb, T. R. Varich, C. Ha, M. B. Manek and X. Hue, *J. Am. Chem. Soc.* **114**, 8158 (1992).
 21. K. M. Stirk, L. K. M. Kiminkinen and H. I. Kenttämää, *Chem. Rev.* **92**, 1649 (1992).
 22. T. Weiske, H. van der Wel, N. M. M. Nibbering and H. Schwarz, *Angew. Chem., Int. Ed. Engl.* **23**, 733 (1984).
 23. S. J. Yu, M. Gross and K. R. Fountain, *J. Am. Soc. Mass Spectrom.* **4**, 117 (1993).
 24. A. E. P. M. Sorriha, F. C. Gozzo, R. S. Pimpim and M. N. Eberlin, *J. Am. Soc. Mass Spectrom.* **7**, 1126 (1996).