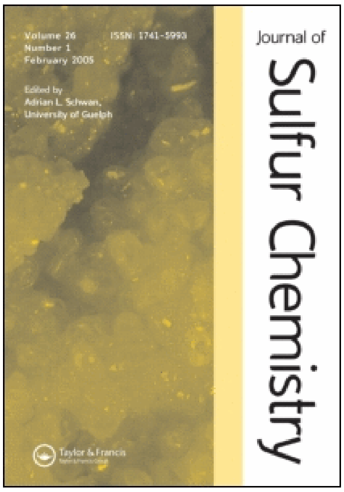

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NEUTRALIZATION-REIONIZATION MASS SPECTROMETRY OF SULFUR-CONTAINING COMPOUNDS

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This review covers the applications of collisional activation and neutralization-reionization mass spectrometries in the field of sulfur-containing reactive molecules.

Keywords: Collisional activation; neutralization-reionization; reactive intermediates

CONTENTS

1. INTRODUCTION

General aspects of the mass spectrometry of sulfur-containing organic compounds have been recently reviewed.[1] The present paper will therefore be restricted to a more specialized field of mass spectrometry, neutralization-reionization mass spectrometry (NRMS), which has proved in recent years to be a very efficient technique for the characterization of new reactive molecules in the gas phase.

When a beam of fast ions (4–10 keV regime) is focussed in a collision cell containing a neutral gaseous target, part of the translational energy of the ions will be converted into internal energy which may be high enough to modify the mass and/or the charge of the impinging ions. If the ions under consideration are singly charged positive ions, the most important processes observed are the fragmentation, the collisional (double) ionization and the neutralization of the ions (eqs. 1–3).

$$m_1^+ + N \rightarrow m_2^+ + m_3 + N \qquad (1)$$

$$m_1^+ + N \rightarrow m_1^{2+} + N + e \qquad (2)$$

$$m_1^+ + N \rightarrow m_1 + N^+ \qquad (3)$$

Fragmentation of the fast ions (also called collision induced dissociation, eq. 1) produces a set of fragment ions with relative abundancies and nature allowing quite frequently the structural identification of isomeric species.[2] Collisional (double) ionization is quantitatively less important than fragmentation due to the higher energy transfer required (eq. 2). Nevertheless, its usefulness in structural analysis of isomeric ions and in determination of double ionization energies has been reported.[3] The third process which may be of importance is the neutralization of the ions by charge exchange (eq. 3); this process produces a unidirectional beam of fast neutrals.[4] This reaction was considered for a long time as a nuisance as the neutrals are, of course, lost in the sectors of the mass spectrometer.

The nature of the collision gas has a very strong influence on the degree of competition between these processes. It is presently recognized that helium is the most efficient gas to induce fragmentations, oxygen favours the collisional (double) ionization process probably in an electron capture reaction, and polyatomic targets favour neutralization.

The neutralization reaction of fast ions has been rehabilitated owing to previous work of Gellene *et al.*[5] indicating that beams of fast neutrals can be reionized by collision with a gas. The potential of this method was thereafter rapidly recognized by McLafferty *et al.*[6] in the field of polyatomic organic intermediates. The method, presently named neutralization-reionization mass spectrometry (NRMS), has been reviewed on several occasions during the last ten years.[7]

In an NRMS experiment, a beam of mass-selected ions collides with a neutral target and a fraction of the ions are neutralized, thereby producing a beam of fast neutrals mixed with unreacted fast ions. A wide variety of gases has been used for this purpose: xenon, ammonia, organic targets, etc. A common feature of all these gases is that they are poor fragmenting agents. In a second step, the unreacted ions are removed electrostically by floating a deflector electrode or by floating a lens at a voltage higher than the accelerating voltage of the ions (Fig. 1). The neutral beam enters a second collision cell containing a second collision gas (usually oxygen) and some of the neutrals are collisionally reionized. This reionization process is also accompanied by fragmentations, and all the ions produced in this way and separated by a sector or a combination of sectors constitute the mass spectrum of the neutral molecules generated between the two cells, that is the NR spectrum. If the NR spectrum contains a signal corresponding to <<survivor ions>> (recovery signal), it is concluded that the neutral molecules isolated in the gas phase are stable with a life-time superior to the flight time between the two cells, typically a few microseconds. The non-occurrence of an isomerization process between the two collision cells can be demonstrated with a supplementary collisional activation step on the survivor ions provided sensitivity permits such experiments (practical examples will be discussed later).

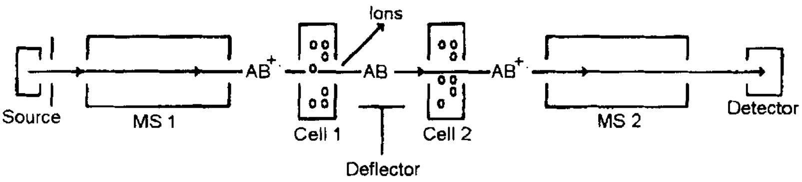


FIGURE 1 Schematic representation of an NRMS unit.

The absence of a recovery signal in the NR spectrum is indicative of the intrinsic instability of the neutral formed toward unimolecular fragmentation provided the geometries of the ion and the corresponding neutral are not too different. It is indeed accepted that the electron transfer processes correspond to vertical transitions so that excited states of the neutral may be populated in the neutralization step.

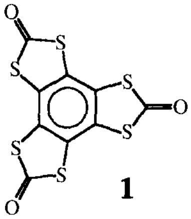
The NR methodology is not restricted to singly charged positive ions, and negative ions have also been involved in the electron transfer reactions. The notation used, $^{+/-}NR^{+/-}$, indicates what kind of charged species are involved; for example, $^{-}NR^{+}$ indicates that neutralization of an anion is followed by reionization into a cation. All these processes can be analyzed with a sector instrument presenting the reversed geometry B©©E (E stands for electric sector, B for magnetic sector and © for the collision cells), but multi-sector instruments present very important advantages in the preparation of a pure beam of precursor ions free of interference with isobaric ions.

2. HETEROCUMULENES

Small carbon clusters, $:C{=}(C)_n{=}C:$, are reactive molecules which have received considerable attention in recent years.[8] Addition of heteroatoms leads to heterocumulenes presenting a large variety of stability. This chapter is concerned with cumulenes of the type $S = (C)_n = X$ with X = O, S, NR or/and $n \geq 2$.

2.1. Polycarbon Dithiones, $S(C)_nS$

Contrary to the oxygenated analogue (ethenedione) which has never been produced and identified in the gas phase, ethenedithione has been characterized by NRMS.[9] Dissociative ionization of precursor **1** provides in fact a whole series of abundant $C_nS_2^{+\bullet}$ radical cations ($n = 2$–6). The connectivity of these cumulenes is clearly indicated by their CA spectra.[9] Their NR spectra indicate also in all the cases abundant recovery signals and fragmentation patterns closely related to those observed in the CA spectra. These combined informations strongly indicate that the polycarbon dithiones SC_nS and their radical cations are perfectly stable molecules in the gas phase.



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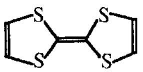

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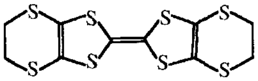

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Other compounds are also found to be excellent precursors of ethenedithione: the molecular ions of **2** readily lose two molecules of C_2H_2S giving $S{=}C{=}C{=}S^{+\bullet}$ ions,[10] and the same ions are produced in high yields from the tetrathiafulvene **3** after electron impact.[10] Typical spectra are collected in Figure 2: (a) the CA spectrum of the m/z 88 ions ($C_2S_2^{+\bullet}$) shows intense peaks for $CCS^{+\bullet}$, $CS^{+\bullet}$ and $S^{+\bullet}$ ions in agreement with the SCCS connectiv-

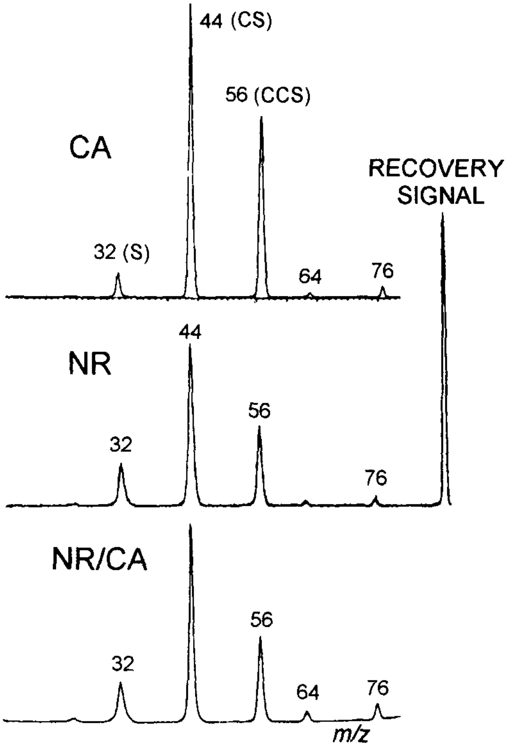
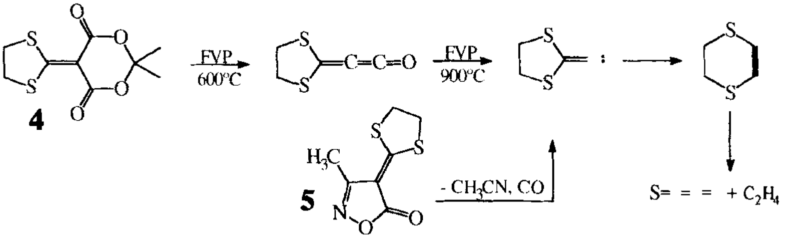


FIGURE 2 CA (**a**), NR (**b**) and NR/CA (**c**) spectra of $S{=}C{=}C{=}S^{+\bullet}$ ions (m/z 88).

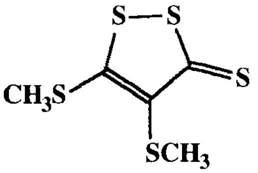
ity, (b) neutralization-reionization affords a very similar spectrum with an intense peak corresponding to survivor ions and (c) specific selection of these survivor ions, followed by collisional activation, generates again a very similar spectrum indicating the non-occurrence of isomerization between the neutralization and reionization cells. Experiment (c), termed NRMS/CA, is not always feasible for sensitivity reasons.

NRMS having indicated the stability of ethenedithione in the gas phase, flash-vacuum pyrolysis (FVP) has been applied to the precursors **4** and **5**. At high temperature, these heterocycles fragment as illustrated in Scheme 1, and by using an on-line coupling of FVP and MS/MS, the thermal production of ethenedithione was demonstrated, thereby stressing the complementarity of the techniques.[11] C_2S_2 was also identified by its matrix IR and UV spectra in FVP/matrix isolation experiments.[11]



Scheme 1

Heterocumulenes having an odd number of carbons are more stable than their analogues with an even number of carbons.[12] Thus, carbon subsulfide, SCCCS, is stable enough to allow isolation for a short time at room temperature. It is therefore not surprising that the NR spectrum of the corresponding radical cations presents a very intense recovery signal.[9,13] Dissociative ionization of 4,5-bis(methylthio)-1,2-dithiole-3-thione **6** has allowed the detection of a series of disulfides SC_nS together with their S-methylated forms, $CH_3SC_nS^+$ (n = 1–3). The CA spectra of these cations are characterized by a very



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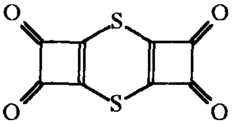
pronounced loss of $CH_3^•$ in agreement with calculated fragmentation energies.[13] Theory also predicts that the $CH_3SCCS^•$ radical is a stable species in the gas phase, with the most favourable dissociation products ($CH_3^•$ + SCCS) ca. 200 kJ/mol above the $CH_3SCCS^•$ radical. On the other hand, the radicals formed by methylation of the odd-carbon cumulenes C_nS_2 are predicted to be unstable toward unimolecular fragmentation (loss of $CH_3^•$). Indeed, NR experiments show a barely detectable recovery signal for $CH_3SCS^•$ and $CH_3SCCCS^•$ (Fig. 3). The base peaks of these spectra correspond to the reionization of S=C=S and S=C=C=C=S. In contrast, a significant recovery signal is observed in the NR mass spectrum of methylated ethenedithione, but this ion, too, decomposes in part to the SCCS neutral.

2.2. Polycarbon Oxide Sulfides, $S(C)_nO$

These <<non-symmetrical>> cumulenes have also been identified in NRMS experiments. The $C_2OS^{+•}$ radical cation is easily accessible by dissociative ionization of **7**. Its reduction into thioxoethenone, O=C=C=S, was confirmed by the CA and NR spectra.[14] Similarly, experimental evidence was also reported for the existence of higher homologues, OCCCS and OCCCCS, and their corresponding radical cations.[15]



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2.3. Iminoethenethiones, SCCNR and Iminopropadienethiones, SCCCNR

Iminoethenethione, HN=C=C=S, is also a stable molecule on the microsecond time scale of the NRMS experiment. The corresponding radical cations were generated by fragmentation of thiazolopyrimidinedione **8** molecular ions (Scheme 2). The NR mass spectrum clearly indicates a recovery signal and fragments in keeping with the HNCCS connectivity (Fig. 4a).[16] Iminoethenethione does not tautomerize to thioformyl cyanide, HC(=S)-CN, under the wall-less conditions of the NR experiment, but it does so under FVP conditions when generated from the isoxazolone **9**. The presence of a strong signal at *m/z* 45 in the NR spectrum (Fig. 4b) recorded after FVP of **9** confirms that tautomerization has taken place (also established by matrix IR

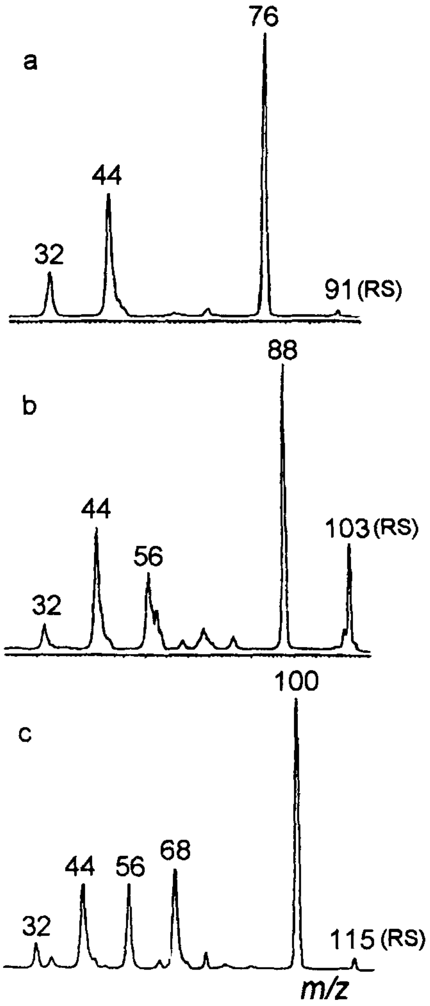
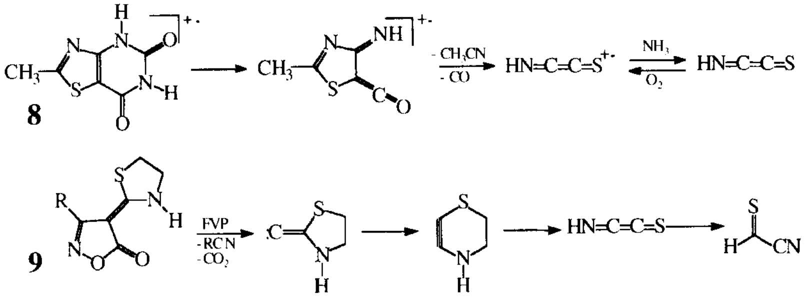


FIGURE 3 NR spectra of $CH_3S(C)_nS$ ions (a–c).

spectroscopy). Theory has supported these proposals (Fig. 5): indeed, the theory predicts that vertical neutralization[17] of ground-state $HNCCS^{+\bullet}$ ions should lead to neutral HNCCS (singlet) molecules with ca. 60 kJ/mol internal energy. Although this is a large value, due to a large change in geometry in going from the ion to the neutral, it is significantly less than the energy required (*ca.* 130 kJ/mol) for the dissociation into HNC + CS.



Scheme 2

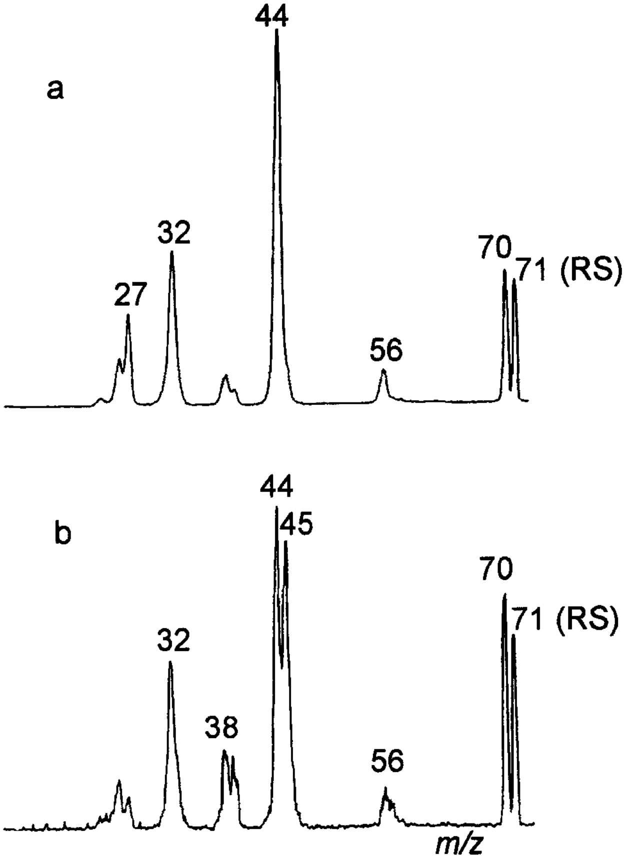
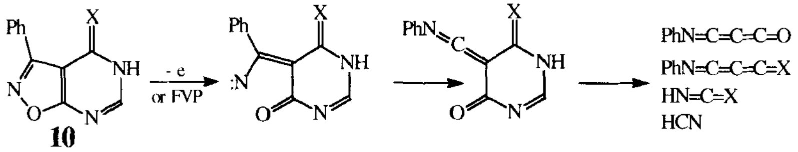


FIGURE 4 NR spectra of $C_2HNS^{+\cdot}$ ions: (**a**) HN=C=C=S$^{+\cdot}$ ions and (**b**) HC(=S)C ≡ N$^{+\cdot}$ ions.

This situation contrasts with the case of the oxygen analogue, HN=C=C=O, not observed during the NR experiment. Vertical neutralization of ground-state $HNCCO^{+\cdot}$ ions should lead to neutral molecules with *ca.* 100 kJ/mol internal energy, well above the energy required (*ca.* 14 kJ/mol) for the dissociation to HNC + CO (Fig. 5).[18]

The identification of monoimines derived from carbon suboxide, RNC_3O, was reported only recently by using a combination of techniques: NRMS, FVP/MS, FVP/IR and trapping experiments.[19] The first precursor used was the phenylisoxazolopyrimidinone **10** (X = O) which upon electron impact or pyrolysis undergoes similar fragmentations: cleavage of the isoxazole ring yielding a nitrene, rearrangement of this nitrene into a ketenimine which, in a retro Diels-Alder reaction, gives finally PhNCCCO (as ions in EI, or neutrals in FVP) + HCN + HNCO (Scheme 3, X = O).



Scheme 3

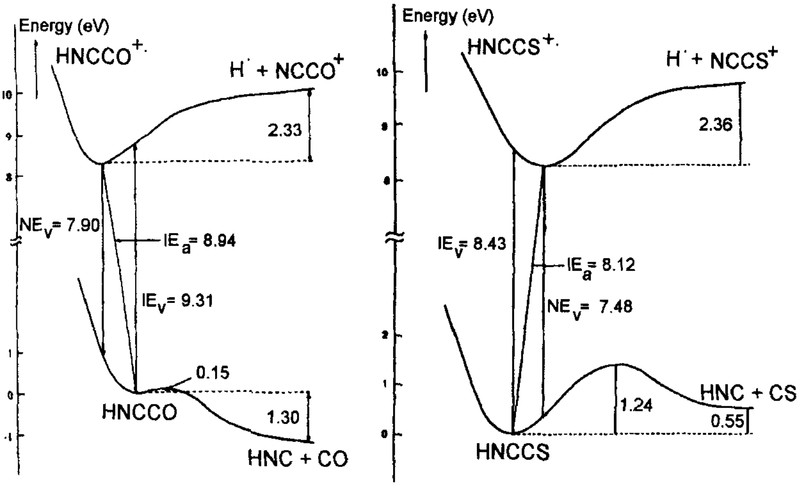
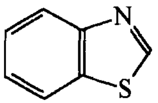


FIGURE 5 Schematic potential energy surfaces showing neutralization and reionization processes: (a) Fragmentation of HNCCS and $HNCCS^{+\cdot}$ and (b) Fragmentation of HNCCO and $HNCCO^{+\cdot}$ (NE_v = vertical neutralization energy, NE_a = adiabatic neutralization energy, IE_v = vertical ionization energy, and IE_a = adiabatic ionization energy).

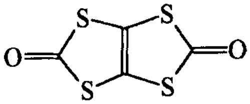
A similar approach has been used in the identification of phenyliminopropadienethione by CA and NR mass spectrometry using thione **10** (X = S) and other precursors.[20] Thermally, **10** (X = S) fragments into PhNCCCO, HNCS and HCN; evidence for the production of a very small amount of PhNCCCS has been found in an FVP/IR experiment (18 K, argon matrix). Other methods for the production of PhNCCCS in FVP reactions will be reported.

2.4. Polycarbon Monosulfides, :(C)nS

Dissociative ionization of benzothiazole **11** has allowed the detection of a series of polycarbon sulfide radical cations, $C_nS^{+\bullet}$ (n = 2–6) and also their corresponding HC_nS^+ ions.[21] The NR mass spectra of the $C_nS^{+\bullet}$ ions are characterized in all cases by significant recovery signals thus pointing to the stability of the isolated neutral vinylidenes, in agreement with theoretical considerations. The same is found for the corresponding polycarbon sulfide hydrides. The tetrathiapentalene-2,5-dione **12** has also allowed the identification of :C=C=S in the gas phase using CA/NR.[22a] This compound has also been found an excellent precursor of $S{=}C{=}C{=}S^{+\bullet}$ ions.[22b]



$\mathbf{11}^{+\bullet}$



$\mathbf{12}^{+\bullet}$

2.5. Various

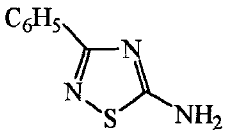
Recently, the new cumulenic ions, $SNCCO^+$, $SCNCO^+$, $SNCCS^+$, and $SCNCS^+$, have been generated by dissociative ionization.[23,24] The stabilities of the corresponding radicals $SNCCS^\bullet$, $SCNCS^\bullet$ and $SNCCO^\bullet$ have been evaluated by NR experiments and supported by theory. $SCNCO^\bullet$, on the contrary, is not accessible under NR conditions (no recovery signal).

The C_2NS system has been also briefly examined, but the corresponding ions from various precursors which were anticipated to differ in structure produced virtually identical CA spectra. Thus, no structure was assigned to the intense survivor signals in their NR spectra.[25]

3. NITRILE N-SULFIDES

3.1. Fragmentation of Heterocyclic Compounds

Nitrile *N*-sulfides, RCNS, are 1,3-dipoles of potential synthetic interest. However, in contrast to the well-known nitrile *N*-oxides, RCNO, the *N*-sulfides are short-lived intermediates that cannot usually be identified under ordinary conditions.[26] NRMS has also been of crucial importance in the identification of some of these dipoles. A quite general method for the production of α-distonic $R\text{-}C{\equiv}N^+\text{-}S^\bullet$ radical cations is based on the electron impact ionization of five-membered heterocycles incorporating at least one CNS linkage which frequently undergo retro 1,3-dipolar cycloaddition. For example, ionization of the phenylthiadiazole **13** produces $[C_6H_5,C,N,S]^{+\bullet}$ ions which are readily differentiated from their more conventional isomers (ionized phenyl isothiocyanate and phenyl thiocyanate) as their CA spectrum exhibits a very intense loss of sulfur.[27] Strong evidence that the reionized stable neutral is indeed benzonitrile *N*-sulfide comes also from the observation of this loss of sulfur in the NR spectrum and the occurrence of a significant recovery signal.



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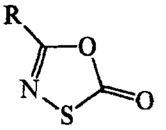
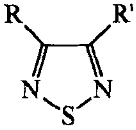


14 R = H, CH_3



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A similar approach has been used to identify thiofulminic acid, $H\text{-}C{\equiv}N{\rightarrow}S$, and acetonitrile *N*-sulfide, CH_3CNS, starting with the oxathiazolones **14**.[28]

More recently, it has been shown that the 1,2,5-thiadiazole system **15** constitutes an excellent precursor of $RCNS^{+\bullet}$ radical cations.[29] Figure 6 shows the CA/NR spectra of the *m/z* 84 ions produced by dissociative ionization of the dicyano compound **15** (R = R′ = CN). The *N*-sulfide connectivity is indicated by the fragments observed in the CA spectrum and confirmed by an MS/MS/MS experiment on the *m/z* 58 ions proving that they correspond to CNS^+ ions, not NCS^+ ions.[30] The high intensity of the recovery signal and the close analogy of the fragmentations in the NR/CA spectra confirm the stability of neutral cyanogen *N*-sulfide in the gas phase (Scheme 4).

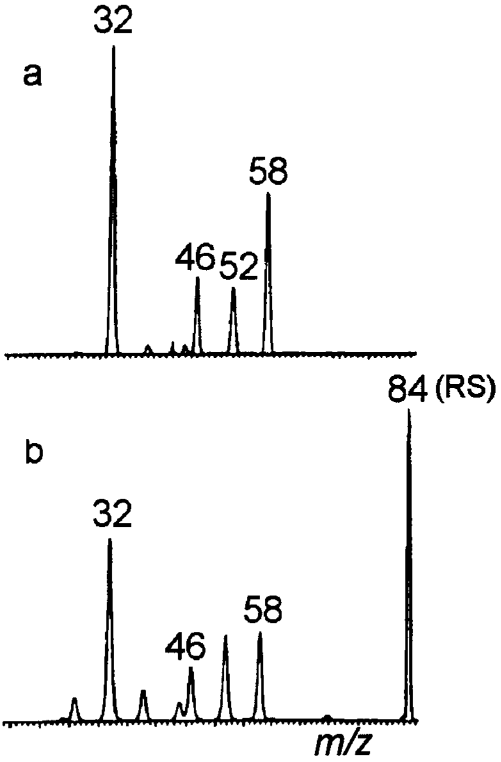
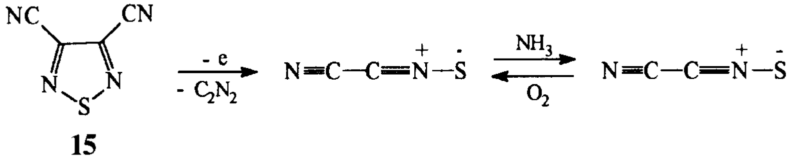


FIGURE 6 CA (**a**) and NR (**b**) spectra of the *m/z* 84 ions produced after dissociative ionization of the thiadiazole **15** (R = R′ = CN).



Scheme 4

Other *N*-sulfides have been generated in the same way: ClCNS, CH_3SCNS, NH_2CNS. In all these cases the recovery signals were found to be very intense in the NR spectra. This is in keeping with theoretical calculations indicating a geometrical similarity between the ions and the corresponding neutrals. For instance, vertical neutralization of ground-state $NH_2CNS^{+\bullet}$ ions should lead to neutral NH_2CNS molecules with just 8 kJ/mol internal energy.

3.2. Sulfuration of Nitriles

A more direct method for the production of nitrile *N*-sulfides as ions and neutrals in the gas phase has been described recently.[31] For instance, chemical ionization of acetonitrile with carbon disulfide as the reagent gas leads to the formation of *m/z* 73 ions of composition C_2H_3NS. Comparison with the molecular ions of methyl isothiocyanate and methyl thiocyanate leaves no doubt on their $CH_3\text{-}C{\equiv}N^+\text{-}S^\bullet$ connectivity. This is also indicated by the NR spectrum (Fig. 7) presenting structure-significant peaks at *m/z* 58, 46 and 32, the recovery signal pointing to the stability of the neutral dipole in the gas phase. The other molecules containing a nitrile group studied and characterized in the same way were HCNS, C_2H_5CNS, C_3H_7CNS, C_6H_5CNS, ICNS, BrCNS, ClCNS, NH_2CNS, $(CH_3)_2NCNS$ and *N*-cyanopyrrolidine *N*-sulfide.

4. THIAZYL AND THIONITROSYL COMPOUNDS

In contrast to nitroso compounds (RN=O) whose chemistry is well established, the existence of molecules containing the thionitroso moiety (RN=S) have been identified only very recently. In fact, sulfur-halogen-nitrogen species are known to exhibit sulfur-halogen (XS≡N) rather than nitrogen-halogen bonds.[32,33] Following earlier theoretical predictions,[34] the first experimental evidence for the existence of thionitrosyl hydride, H-N=S, was derived from NRMS experiments.[35] Following dissociative ionization of the oxathiazolone **14** (R=H), it was observed that [**14** – 2CO]$^{+\bullet}$ radical cations were generated in good yield. The connectivity of these ions is established by the signals at *m/z* 32 and 15 in the CA spectrum (Fig. 8a) ($S^{+\bullet}$ and NH^+, indicative of the $[H\text{-}N{=}S]^{+\bullet}$ structure). Conclusive evidence for the stability of the corresponding neutral in the gas phase is found in the NR spectrum (Fig. 8b) presenting an intense recovery signal and in the NR/CA spectrum of the survivor ions (Fig. 8c) which, given its identity with the previous spectra, indicates the absence of isomerization during the flight between the two cells.

As briefly explained above, thyazyl halides having sulfur in the central position (XSN) are well-known compounds. Thionitrosyl halide isomers have remained elusive molecules due to their higher energy content.[36] However, theoretical results revealed that the radical cation $[ClN{=}S]^{+\bullet}$ turned out to be significantly more stable than $ClSN^{+\bullet}$. Such a change in

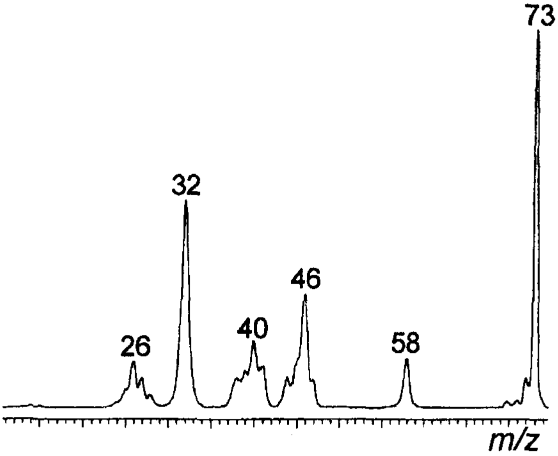


FIGURE 7 NR spectrum of acetonitrile *N*-sulfide radical cations (*m/z* 73).

relative energy ordering of isomers after ionization makes the ClNS system a suitable target for NRMS investigations. Thiazyl chloride trimer $(NSCl)_3$ was employed as the precursor.[37] Mild flash-vacuum pyrolysis, followed by ionization, produces quite abundant $[NSCl]^{+\bullet}$ ions; using a combination of CA/NR experiments and calculated energies of the vertically neutralized species (NE_V), it was suggested that the very weak recovery signal detected in the NR spectrum can be assigned to thionitrosyl chloride.

Theoretical considerations have predicted that thiazyl azide ($N_3S{\equiv}N$) is more stable towards nitrogen elimination than thionitrosyl azide ($N_3N{=}S$), the same holds for homolytic dissociations.[38] Reaction between NSCl and sodium azide has, however, not allowed the formation of this compound (unpublished MS results).[39]

It is quite interesting to note that the relative stability of the [R, N, S] isomers (thiazyl *vs* thionitrosyl) is highly dependent on the nature of the substituent R. If R=CN, theory agrees with experiment that thionitrosyl cyanide, S=N-CN, is clearly distinguishable from its less stable thiazyl cyanide (N≡S-CN) isomer and that the two are not interconverted by simple migration processes.[40] The CA, NR and NR/CA spectra of thionitrosyl cyanide ions (generated by dissociative ionization of the thiadiazolothiadiazole **16**, Scheme 5) (Fig. 9) are characterized by peaks in keeping with the SNCN connectivity, while the CA spectrum of thiazyl cyanide ions (gener-

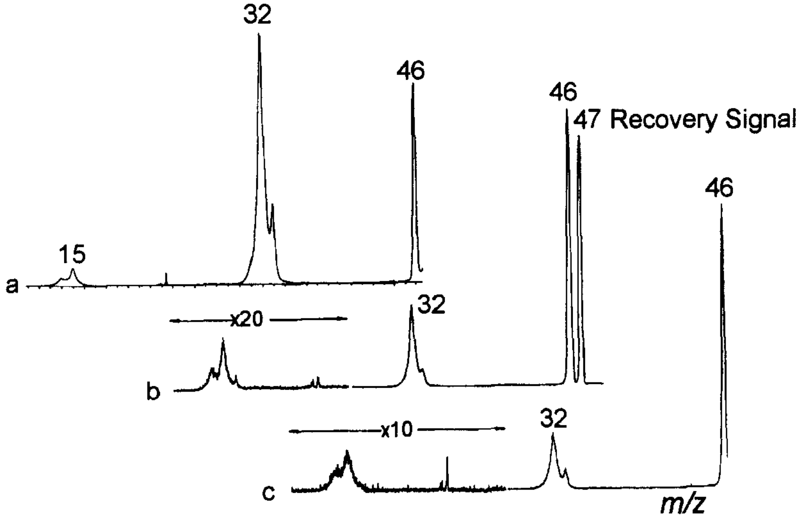
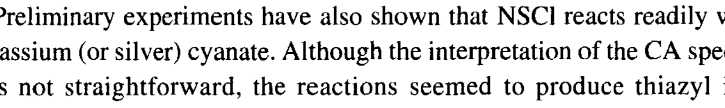


FIGURE 8 CA (**a**), NR (**b**) and NR/CA (**c**) spectra of the *m/z* 47 ions produced by dissociative ionization of the oxathiazolone **14** (R = H).

ated by reaction between NSCl and silver cyanide) features a very significant peak at *m/z* 44 ($CS^{+\bullet}$).



Scheme 5

Preliminary experiments have also shown that NSCl reacts readily with potassium (or silver) cyanate. Although the interpretation of the CA spectra was not straightforward, the reactions seemed to produce thiazyl isocyanate.[41] It is surprising that this isocyanate was not detected in a previous photoionization study.[42]

The thiadiazole **16** has also allowed the preparation of nitrogen disulfide radicals, SNS, in the mass spectrometer gas phase.[43] One of the fragmentation pathways of $\mathbf{16}^{+\bullet}$ produces $[N,S_2]^+$ ions of SNS connectivity readily discernable from their isomeric species NSS^+ generated when bombarding an N_2/COS gas mixture with high energy electrons and reversing the charge

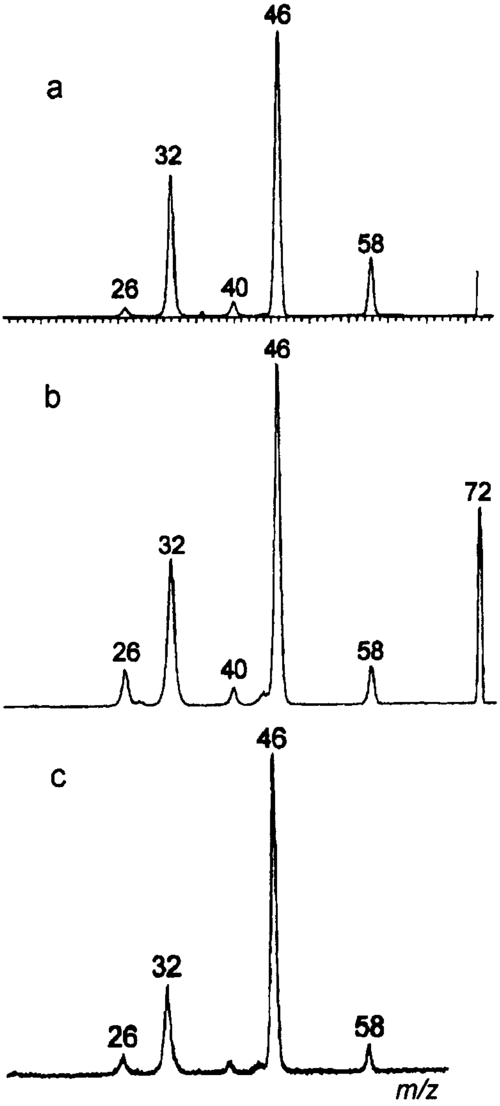


FIGURE 9 CA (**a**), NR (**b**) and NR/CA (**c**) spectra of thionitrosyl cyanide ions produced by dissociative ionization of a thiadiazolothiadiazole **16**.

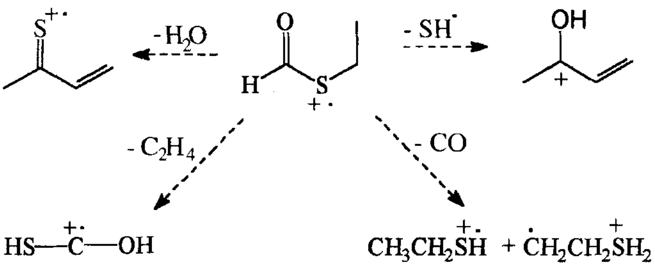
of the so-produced NSS^- anions.[44] Reduction of the SNS^+ cations or oxidation of the NSS^- anions produce distinct radical species identified by reionization (distinct NR spectra).

H_2NS^+ and the corresponding neutral radical have been detected experimentally by using a combination of CA and NR spectra. Thiourea $H_2NC(=S)NH_2$ has been used as a precursor following electron impact ionization.[45]

5. ION STRUCTURES AND REACTION MECHANISMS

In spite of its lower thermodynamic stability relative to the cyclic trimethylene sulfide ion *c*-$CH_2CH_2CH_2S$, the distonic ring-opened isomer, $^{\bullet}CH_2CH_2SCH_2^+$, does not spontaneously ring-close and thus represents a distinct, stable C_3H_6S species in the gas phase.[46] These distonic ions were prepared by dissociative ionization of 1,4-dithiane by loss of thioformaldehyde.

A series of S-alkyl thioformates, HC(=O)SR, has been studied in search of new distonic ions, isomers of methyl thioformates.[47] The unimolecular chemistry of the molecular ions of these compounds appeared to be quite complex, the loss of water and $SH^{\bullet}$ being prominent processes (if R > CH_3) yielding thioacroleine ions (or isomeric cyclic thiete ions and hydroxycarbenium ions, respectively. Hydroxythiirane ions were suggested to be key intermediates in these fragmentations.[47a,b] The loss of ethene from the molecular ions of S-ethyl thioformate does not proceed *via* the McLafferty rearrangement as shown by CA/NR spectra and ion-molecule reactions indicating the formation of carbene ions, HS-$C^{+\bullet}$-OH.[47c] (Scheme 6). Finally, mixtures of conventional thiol radical cations and β-distonic isomers were formed in the decarbonylation process of *S*-alkyl thioformates involving a sulfurane intermediate, $RS^+(H)$-$C^{\bullet}$=O and/or a hydrogen bridged ion molecule complex, O=C···H^+···SH(R-H)$^{\bullet}$.[47d]

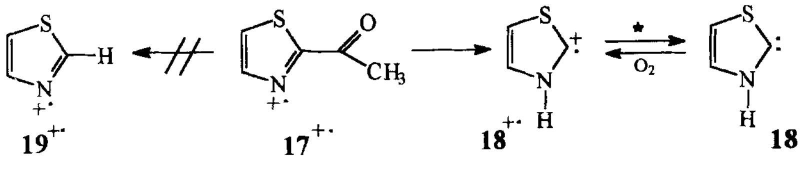


Scheme 6

The chemistry of dimethyl sulfoxide molecular ions, $CH_3S(=O)CH_3^{+\bullet}$, has also received some attention. It illustrates a situation where molecular ions dissociating in the ion source or in a field-free region eliminate neutral fragments possessing the same composition (CH_3 in the present case) with the production of isomeric ions. Using again a combination of CA, NR and CA/NR spectra, it has been clearly shown that the fragmenting metastable DMSO ions undergo a 1,3-H shift before losing $CH_3^\bullet$, thus forming $H_2C{=}S{=}OH^+$ ions. Molecular ions with a higher energy content (fragmenting in the ion source) undergo the classical α-cleavage with the formation of isomeric CH_3-$S{=}O^+$ ions.[48]

$^+NR^+$ clearly distinguished the methylthiomethyl cation, $CH_3SCH_2^+$, from isomeric protonated thioacetaldehyde, $CH_3CH{=}SH^+$, and protonated thiirane, *c*-$CH_2CH_2SH^+$.[49] It is worth noting that these experiments were performed on an original tandem quadrupole acceleration-deceleration mass spectrometer in contrast with all other experiments described here, which were carried out on (multi)sector instruments.[50] The tandem quadrupole instrumentation also allows variable-time neutralization-reionization mass spectrometry to be performed. Using this particular methodology, it has been shown that metastable $H_3S^\bullet$ hypervalent radicals of lifetimes up to 2.8 μsec are formed by vertical neutralization of vibrationally excited cations.[51]

Very recently,[52] dissociative ionization of 2-acetylthiazole **17** has enabled the generation of 3*H*-thiazole-2-ylidene **18** after reduction of the corresponding ions $\mathbf{18}^{+\bullet}$ (Scheme 7). The ions $\mathbf{18}^{+\bullet}$ are readily differentiated from the conventional thiazole molecular ions $\mathbf{19}^{+\bullet}$ by collisional activation. Although the spectra were found to be quite similar, a very significant peak at *m/z* 59, corresponding to $HNCS^{+\bullet}$ ions (confirmed by MS/MS/MS experiment), is seen only in the former case. The observation of recovery peak in the NR spectrum (Fig. 10) together with the tell-tale peak at *m/z* 59 is consistent with the stability of thiazol-2-ylidene **18** in the gas phase.



Scheme 7 (* *N,N*-dimethylaniline)

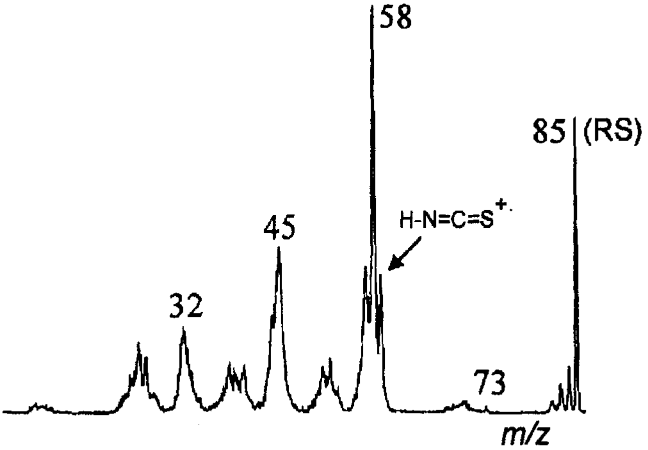
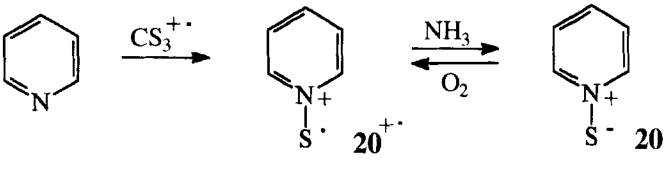


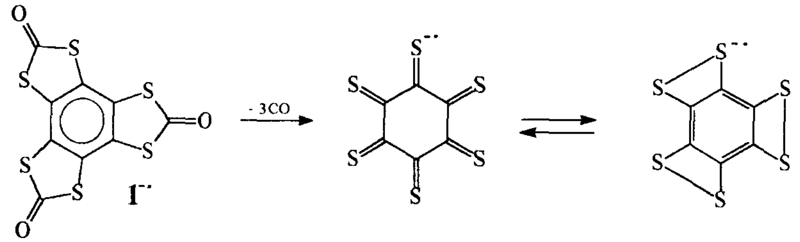
FIGURE 10 NR spectrum of the *m/z* 85 ions produced by dissociative ionization (loss of ketene) of 2-acetylthiazole **17**.

Chemical ionization of pyridine using carbon disulfide as the reagent gas has led to the formation of a new distonic ion, pyridine *N*-sulfide radical cation **20**$^{+\bullet}$.[53] Using a hybrid spectrometer of sectors-quadrupole-sectors configuration,[54] it has been established that the ions originate mainly by reaction between neutral pyridine and $CS_3^{+\bullet}$ radical cations. The structure was established by CA (intense loss of sulfur not observed for the isomeric pyridinethiones) and by ion-molecule reactions, for instance the transfer of a sulfur atom of **20**$^{+\bullet}$ to pyridine-d_5. The NR spectrum also indicates the stability of the neutral dipole in the gas phase (Scheme 8).



Scheme 8

The radical anions $C_6S_6^{-\bullet}$ have been generated in high abundance by electron impact ionization of **1** in the negative ion mode and successfully oxidized into the neutral molecule C_6S_6 (Scheme 9).[55]



Scheme 9

Radicals having a phosphorus-sulfur bond, $P_xS_y^{\bullet}$, have also been characterized in NRMS experiments.[56–58]

6. ATMOSPHERICALLY IMPORTANT SULFUR CONTAINING MOLECULES

The chemistry of atmospheric sulfur compounds is of great environmental importance. Several publications have appeared concerning the evaluation of the relative stabilities of various isomers suspected to play a role in the atmospheric sulfur cycle.

A combination of charge reversal (CR, collisional transformation of anions to cations and positively charged fragment ions) and $^-NR^+$ indicated that $HSO^{\bullet}$ and $SOH^{\bullet}$ are viable, clearly distinguishable molecules in the gas phase.[59] Hydroxysulfinyl, $HO\text{-}S{=}O^{\bullet}$, and sulfinic acid, $S(OH)_2$, were also found to be thermodynamically stable species in the gas phase. Hydroxysulfinyl radical was predicted to undergo exothermic reaction with ($^3\Sigma$) O_2 to yield SO_2. Sulfinic acid can be depleted by photoinduced reactions with ($^1\Delta$) O_2 or hydroxy radicals.[60] Experiments were reported on the successful gas phase generation of hydrogen thioperoxide, HSOH, and thiooxonium ylid, SOH_2.[61] These peculiar species were prepared in a chemical ionization (CI) ion source from mixtures of H_2S/N_2O and CS_2/H_2O, respectively.

Dissociative ionization of diisopropoxy disulfide gives rise to $H_2S_2O_2^{+\bullet}$ ions whose CA spectrum is in keeping with the $HOSSOH^{+\bullet}$ connectivity. The NR experiment confirms that neutral dihydroxy disulfide resides in a potential minimum deep enough to prevent isomerization during the time of its observation (~10 μsec).[62]

The stability and dissociations of dimethylhydroxysulfuranyl radical, $(CH_3)_2S^{\bullet}\text{-}OH$, a key intermediate in the atmospheric oxidation of dimethyl sulfide, have been investigated by NRMS. The corresponding ions were prepared by protonation of dimethyl sulfoxide and the hypervalent radical produced by reduction dissociates completely within 4.5 μsec by loss of $CH_3^{\bullet}$ and $OH^{\bullet}$.[63]

7. CONCLUDING REMARKS

The development of neutralization-reionization mass spectrometry has been of major importance in the field of identification of new reactive molecules in the gas phase. Its application requires the use of modern mass spectrometers, preferably multi-sector instruments, and the experimental results require also frequently the assistance of theoretical chemistry. The predictive value of NMRS is an invaluable help for further studies having a more preparative finality, like flash-vacuum pyrolysis.

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