3-Mercaptopropanal

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Gaseous 3-mercaptopropanal, generated by thermal decomposition of the corresponding oligomer, has been characterized by i.r. and photoelectron spectroscopy, and mass spectrometry. The possibility of a 3-mercaptopropanal–thietan-2-ol equilibrium is discussed, as is the mechanism of unimolecular thermal decomposition.

In a series of recent papers [1—3] we reported on the intermediacy of 3-mercaptopropanal (1) in the thermally induced decomposition of 1,2-oxathiolane, the eventual products being acrylaldehyde (2) [1—3] and allyl alcohol (3).[1,2] However, a detailed study of the aldehyde (1) was left for future consideration. In the present paper we report the characterization of gaseous 3-mercaptopropanal, and discuss the mechanism of decomposition.

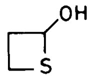
The monomeric species (1) has not been reported previously. Attempts to synthesize the compound by addition of hydrogen sulphide to acrylaldehyde at low temperature afforded an oligomeric microcrystalline compound $(C_3H_6OS)_n$ (4), described by one group as a ' 3-mercaptopropanal-oligomer '.[4] A second group,[5] isolating the product as a waxy substance, formulated it as the isomeric thietan-2-ol (5). I.r. spectroscopy (KBr) revealed, however, that the two products were identical [the latter was generously supplied by the Givaudan group (*cf.* ref. 5)]. The i.r. spectrum of (4) revealed a striking resemblance to that of mercaptoacetaldehyde dimer (known to possess the 2,5-dihydroxy-1,4-dithiane structure [6]), suggesting structural similarities.

Heating compound (4) *in vacuo* to around 375 K caused smooth decomposition. By field-ionization mass spectrometry (FI) we found that only one species, with molecular weight 90, was formed. *A priori* both isomers (1) and (5) were possible candidates; however, gas-phase i.r. spectroscopy unequivocally identified the product as 3-mercaptopropanal. The spectrum was dominated by intense absorptions at 2 712 and 2 810 (aldehyde CH) and 1 750 cm^{-1} (C=O); bands of lower intensities were observed in the 2 900—3 000 cm^{-1} region and around 1 400 cm^{-1}, both ascribed to CH_2 vibrations. Not unexpectedly, no SH vibrations were observed, as these absorptions generally are weak.[7] Of major diagnostic importance was the absence of absorption bands in the OH region (3 200—3 600 cm^{-1}).

In agreement with the foregoing conclusion, calculation of the heats of formation of (1) and (5), by applying the principle of group additivity formulated by Benson,[8] revealed a 12.6 kcal mol^{-1} stabilization of (1) relative to (5) [$\Delta H_f°(1)$ −35.1; $\Delta H_f°(5)$ −22.5 kcal mol^{-1}].† Similarly, by applying the Benson method,[8] the reaction entropy for the conversion (1) $\longrightarrow$ (5) [$\Delta S_r°(1 \longrightarrow 5)$] was calculated to be −9.3 cal mol^{-1} K^{-1}. Hence, we must conclude that at ambient temperature (5) is essentially absent. Even at high temperatures (>1 000 K) only very minor amounts of (5), if any, will be present.

$HSCH_2CH_2CHO$ (1) $CH_2{=}CHCHO$ (2)

$CH_2{=}CHCH_2OH$ (3) $(C_3H_6OS)_n$ (4)


(5)

In the following we provide further characterization of compound (1) based on photoelectron (p.e.) spectroscopic and mass spectrometric studies.

Photoelectron Spectroscopy.—The p.e. spectrum of (1), part of which is depicted in Figure 1, exhibits two well resolved low energy peaks at 9.45 and 10.28 eV, respectively, above the σ-onset at about 11.8 eV. Additionally, a minor peak at 8.9 eV is observed, apparently originating from a minor constituent.

It seems straightforward to assign the two low energy ionizations to the lone pairs at sulphur and oxygen, respectively. However, a more detailed analysis may shed some light on the actual conformational state of (1).

Figure 2 shows a correlation diagram for the 3-mercaptopropanal system. As suitable basis values for the sulphur 3*p* lone pair (n_S) in thiols and the oxygen lone pair ($n_{C=O}$) in carbonyl compounds, we have chosen the ionization energies of ethanethiol (9.29 eV) [9] and propanal (9.99 eV),[10] respectively. In the case of (1) we have to consider two different effects for stabilization/destabilization of the single energy levels. These are the inductive stabilization caused by introduction of a second heteroatom, and the influence of a possible intramolecular hydrogen bond, respectively. The effect on the oxygen lone pair by introduction of a mercapto group β to the aldehyde group in propanal can most probably be neglected, whereas it appears reasonable, to expect a 0.2—0.3 eV stabilization of the n_S lone pair by introduction of an aldehyde moiety β to the mercapto function in ethanethiol, owing to the inductive effect of the carbonyl group.[11] However, inductive effects alone do not account for the observed ionizations in (1), which are (*cf.* Figure 2) a 0.29 eV stabilization of $n_{C=O}$ and a 0.16 eV stabilization of n_S. On the other hand, by taking an intramolecular hydrogen bond into account, we are able to rationalize the observed ionizations, since it has been reported that hydrogen bonding generally leads to stabilization of the

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† Values of $\Delta H_f°$ and $\Delta S°$ for the C–(H)(C)(O)(S) group are not available. The values used (−4.92 kcal mol^{-1} and −16.11 cal mol^{-1} K^{-1}) are taken as averages of the corresponding values for C–(H)$(C)_2$(O) and C–(H)$(C)_2$(S) [8] (S. W. Benson, personal communication).

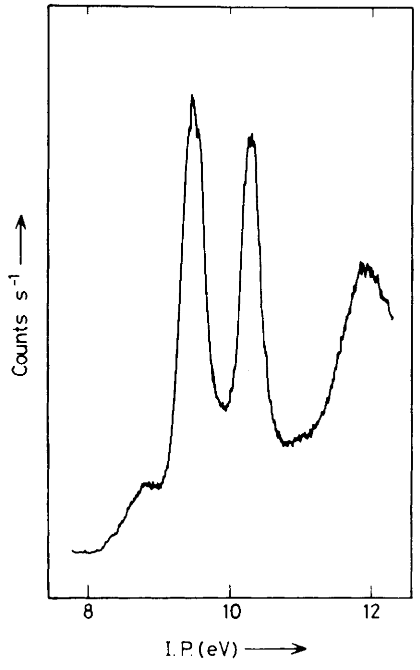


Figure 1. Photoelectron spectrum of 3-mercaptopropanal (1)

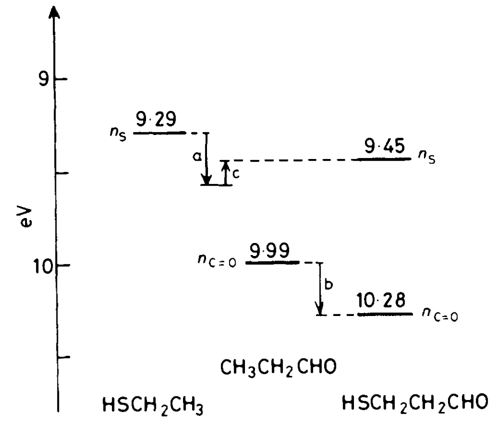
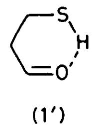


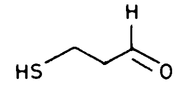
Figure 2. Correlation diagram for 3-mercaptopropanal (1) based on observed ionization energies. The letters a, b, and c refer to the inductive stabilization of n_S, the stabilization of the electron donor ($n_{C=O}$), and destabilization of the electron acceptor (n_S), respectively (see text for further details)

electron donor, and destabilization of the electron acceptor.[12] From a literature survey, it seems reasonable to adopt values for the stabilization of the electron donor ($n_{C=O}$) of 0.3—0.4 eV and destabilization of the electron acceptor (n_S) of 0.1—0.2 eV on hydrogen bonding.[12] Combining this with the aforementioned inductive stabilization of n_S by 0.2—0.3 eV reveals a picture which mimics that observed for (1) almost completely (Figure 2). Hence, we conclude that (1) in the gas phase most probably exists in a hydrogen-bonded form (1′), and not in the non-chelated form (1″), although this is not at first sight compatible with the observed relatively high lying carbonyl stretching mode (1 750 cm^{-1}). However, the SH · · · O hydrogen bond apparently is relatively weak.[13]

Remaining to be discussed is the minor constituent, apparently giving rise to the low lying ionization at 8.9 eV.



(1′)



(1″)

One possible candidate would be the aforementioned isomeric thietan-2-ol (5), as cyclic sulphides exhibit n_S ionizations around 8.3—8.5 eV,[14] which, however, are expected to be inductively stabilized by 0.3—0.4 eV by the hydroxy group in the α position.[11]

As mentioned in the introduction, structural similarities between 2,5-dihydroxy-1,4-dithiane and the '3-mercaptopropanal-oligomer' (4) are indicated; thus (4) probably contains a sulphide moiety with an α-hydroxy group, presumably incorporated in a ring system. Hence the 8.9 eV ionization may well be assigned to a n_S lone pair in the precursor of (1), *i.e.* the oligomer (4). For completeness, however, we have to consider further C_3H_6OS isomers as possible candidates. One possibility would be 3-hydroxypropanethial, which, however, is not expected to exhibit an ionization energy as low as 8.9 eV.* On this basis and in view of the previous exclusion of thietan-2-ol, we suggest, taking the experimental conditions into account, that the 8.9 eV ionization should be ascribed to the oligomer (4).

Mass Spectrometry.—As mentioned in the introduction, field ionization mass spectrometric analysis of the gaseous product formed by thermal decomposition of the oligomer (4) disclosed a single compound only, with molecular weight 90.

Impact of 70 eV electrons generates a variety of fragment ions (Figure 3). Monitoring the unimolecular (DADI) and the collision-induced (CAMS) decompositions of the molecular ion reveals three primary reaction paths: expulsion of CO, loss of ·SH, and elimination of H_2O (Figure 4); these reactions will now be discussed in detail.

Skeletal rearrangements caused by expulsion of CO are commonly observed in the mass spectra of carbonyl compounds.[18] The simple extrusion of CO would lead to ionized ethanethiol. However, analysing the *m*/*z* 62 ion by CAMS revealed significant differences between the spectrum of *m*/*z* 62 originating from (1) and that of ionized ethanethiol (Figure 5).

Recently, ion–dipole complexes have been recognised as a new class of stable radical cations in the gas phase.[19] In the present case $C_2H_6S^{+\cdot}$ may be described as $H_2S \rightarrow (CH_2{=}CH_2)^{+\cdot}$ (6), the complex formation involving electron donation from the sulphur lone pair to the partly filled π-bonding orbital in the ethylene radical cation.[20] An experimental verification that the *m*/*z* 62 ion is the ion–dipole complex was obtained by studying the CAMS spectrum of the *m*/*z* 62 ion originating from 3-mercaptopropan-1-ol (7), analogously to the experiments described in ref. 19. The two spectra were identical.

On this basis we suggest that the *m*/*z* 62 ion obtained from (1) is formed by transfer of the aldehydic hydrogen to the sulphur atom, with simultaneous elimination of CO.

The direct loss of HS· from thiol functions appears atypical, and indeed in the case of $DS[CH_2]_2CHO$ this reaction sur-

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* By choosing propanol [15] and ethanethial [14] as well as prop-2-enethiol [16] and ethenol [17] as models for the frontier orbitals in 3-hydroxypropanethial and 3-mercaptoprop-1-enol, respectively, and making corrections for inductive stabilization and hydrogen bonding, we estimate the lowest ionization energies to be ≥9.3 and *ca.* 8.8 eV for the two C_3H_6OS isomers, respectively. The latter, however, can be dismissed in the light of the lack of OH absorptions in the i.r. spectrum.

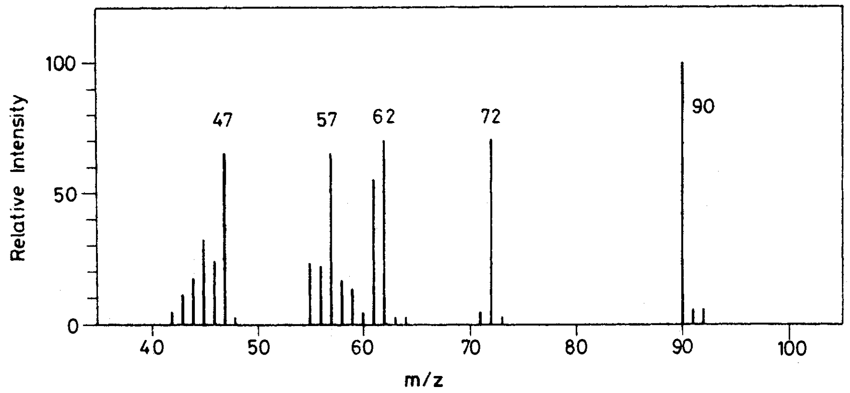


Figure 3. Electron impact ionization mass spectrum (70 eV) of 3-mercaptopropanal

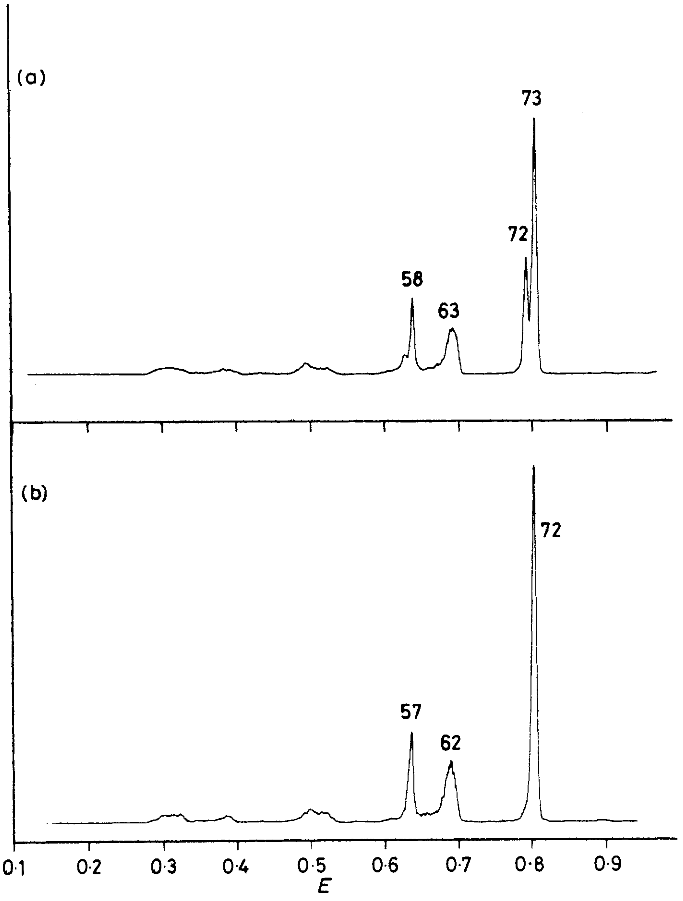


Figure 4. Collision activation mass spectra of the EI-induced molecular ions of the 3-mercaptopropanal (1) ($M^{+\bullet}$) (b) and 3-[^{2}H]mercaptopropanal ($M^{+\bullet}$) (a)

prisingly becomes an $^{\bullet}SH$, and not $^{\bullet}SD$, loss exclusively (Figure 4). Hence, the reaction obviously involves specific hydrogen shifts. The product ion (*m/z* 57), investigated by DADI and CAMS, resembles the $C_3H_5O^+$ ion from allyl alcohol (3) and butanal closely. In the latter case the ion is known to possess $CH_2{=}CH{-}CH{=}OH^+$ structure (8).[21] Hence, the formation of *m/z* 57 from (1) is tentatively considered to proceed by transfer of the mercapto hydrogen to the aldehyde oxygen, with subsequent loss of $^{\bullet}SH$. However, an elimination *via* a rearranged molecular ion such as (9) cannot be excluded.

The elimination of H_2O is by far the most important low-energy process of ionized (1) (DADI: $[M - H_2O]^{+\bullet}$; 97%). A CAMS analysis of the $[M - H_2O]^{+\bullet}$ (*m/z* 72) ion reveals abundant (*m/z* 71) and *m/z* 45 (CHS^+) ions together with minor signals at *m/z* 39 ($C_3H_3^+$) and *m/z* 57 (C_2HS^+). These fragmentations are in accord with those expected for the $CH_2{=}CH{-}CH{=}S^{+\bullet}/CH_2{=}C{=}CH{-}SH^{+\bullet}$ system. In the case of $DS[CH_2]_2CHO$ H_2O is still lost preferentially (DADI: $[M - H_2O]^{+\bullet}$; 75%) relative to HDO. The CAMS analysis of the deuterium-labelled $[M - H_2O]^{+\bullet}$ (*m/z* 73) ion discloses that the loss of $H^{\bullet}$ and the ions C_2HS^+ and CHS^+ are unaffected by the label, whereas the $C_3H_3^+$ ion becomes $C_3H_2D^+$.

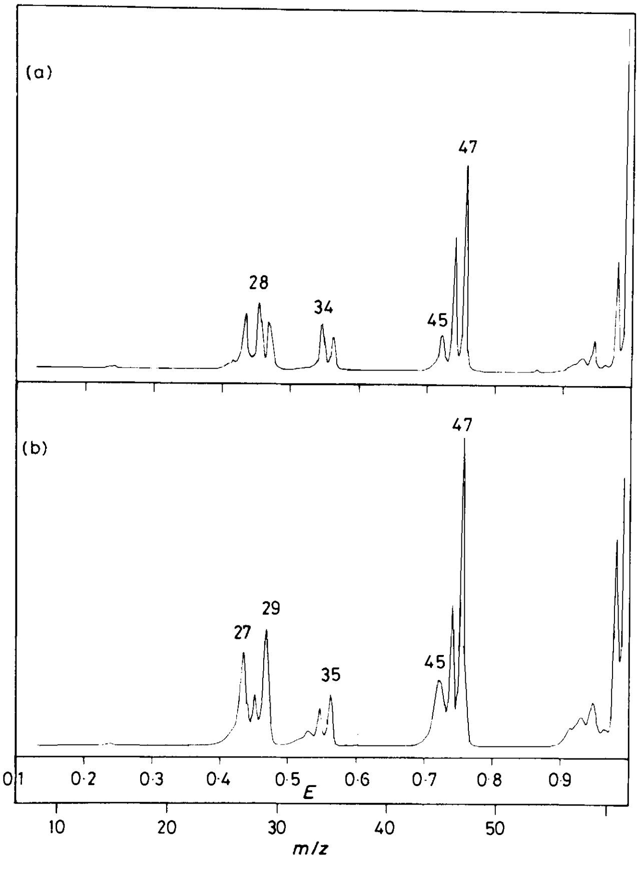
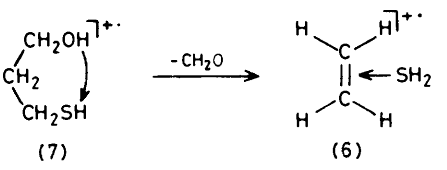
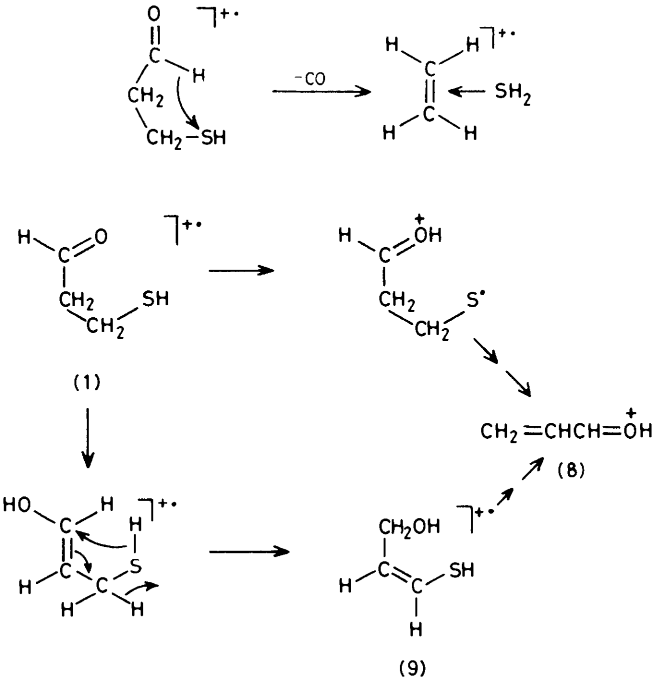


Figure 5. Collision activation mass spectra of the ions *m/z* 62 from 3-mercaptopropanal (a) and the molecular ion of ethanethiol (b)



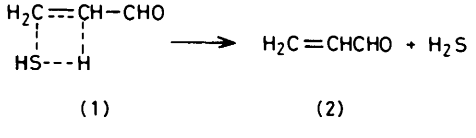
These results are consistent with the ions $CHD{=}CH{-}CH{=}S^{+\cdot}$/$CHD{=}C{=}CH{-}SH^{+\cdot}$ (*m/z* 73). Furthermore, the ions $[M - H_2O]^{+\cdot}$ and $[M - HDO]^{+\cdot}$ decompose by common reaction paths, *i.e.* they possess identical CAMS/DADI spectra, apart from the mass shift already mentioned.

The elimination of H_2O presumably requires rearrangement of the molecular ion prior to fragmentation.* The fact that the enol is the thermodynamically favoured form in the case of radical cationic enol/keto species [23] implicates the enethiol structure (9) as well as the ionized thietan-2-ol as plausible candidates.* The latter accounts easily for the appearance of $[M - HDO]^{+\cdot}$, the product ion being a strained cyclic structure, which, however, by analogy to the elimination of H_2O through an intermediary ionized 2-methyl-2-hydroxyoxetane,[24–26] is assumed to fragment *via* ionized thioacrylaldehyde. The latter ion structure may in addition be formed directly by a six-centred elimination from the structure (9).



Thermolysis.—Finally, we discuss the stability of 3-mercaptopropanol (1). Thermally induced decompositions have previously been reported to some extent in connection with work on the thermal lability of 1,2-oxathiolane.[1–3,27]

The elimination of hydrogen sulphide, leading to acrylaldehyde (2), is the predominant reaction in the temperature range investigated (400—1 400 K). At low temperatures (400—500 K), acrylaldehyde (2) was the only product observed.[3] Deuterium labelling experiments [3] indicated, not unexpectedly, that loss of hydrogen sulphide took place as a simple 1,2-elimination. On the other hand, we previously [1,27] tentatively suggested that propenol formation proceeded *via* the cyclic isomer, thietan-2-ol (5). However, the present work forces us to review the mechanism for propenol formation, the latter product being observed in minor amounts under pyrolytic conditions only, *i.e.* >1 000 K. On the basis of reports of the pyrolysis of various C_3H_6O isomers, we conclude that (5) is formed directly from (1) and not consecutively *via* another C_3H_6O isomer, *e.g.* oxetane, which does not give (3) upon pyrolysis.[28]



Taking the hydrogen-bonded structure (1′) into account, we conclude that the loss of elemental sulphur from (1) is accompanied by a transfer of the mercapto hydrogen to the oxygen atom, the propenol eventually produced being a result either of a rearrangement of the possible 1,3-diradical or a concerted hydrogen migration. Isotopic labelling by deuterium in this case would be of no value, as the hydrogen atoms in ionized (3) randomize completely.[29]

Conclusion.—As a whole the foregoing data reveal the presence of 3-mercaptopropanal as a monomeric species in

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* Elimination of water from aldehydes has been reported previously to proceed *via* ionized cyclobutanols, involving a specific transfer of a γ hydrogen.[22]

the gas phase, and rule out the existence of *e.g.* ring-closed isomers such as thietan-2-ol.

The existence of (1) in the gas phase as a monomeric species is limited to relatively low partial pressures; oligomerization apparently takes place with considerable speed at partial pressures above 0.1 Torr.

Experimental

I.r. spectra (4 000—400 cm^{-1}) were recorded with a Perkin-Elmer 580 grating spectrometer, using a 1 m multireflection gas cell with KBr windows. Vapour from decomposition of compound (4) *in vacuo* was led directly into the gas cell. Decreases in the intensity of the spectra were observed with time, giving rise to a deposit on the windows, ascribed to the starting material (4).

The p.e. spectra were recorded with a Perkin-Elmer PS-18 spectrometer (He^I source) and calibrated with a mixture of argon and xenon introduced into the target chamber simultaneously with the sample. The oligomer (4) was placed directly in a heatable inlet for solid samples, the temperature being increased to 52—55 °C. The spectrum depicted in Figure 1 could be maintained in principle for several hours. However, a slight increase in the 8.9 eV ionization with time was observed. The experimental resolution was 35 meV and the reported ionization energies are average values of four determinations.

The mass spectrometric investigations were carried out using a Varian MAT CH 5D double-focusing spectrometer equipped with a combined EI/FI/FD ion source. The EI spectra were measured at 70 eV (100 μA) with a resolution of *ca.* 1 000; the ion source temperature was *ca.* 200 °C. The FI spectra were obtained using a 10 μm tungsten wire, activated in benzonitrile vapour, as emitter. Metastable ions were detected in the second field-free region by the DADI technique. Collision activation was carried out by introduction of He as target-gas *via* a needle valve into the second field-free region as previously described.[27] The CA-spectra are uncorrected for unimolecular fragmentation processes.

Acknowledgements

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