

Electron driven processes in sulphur containing compounds CH_3SCH_3 and CH_3SSCH_3 ^{*}

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Abstract. Dissociative electron attachment to gas phase dimethyl sulphide (CH_3SCH_3) and dimethyl disulphide (CH_3SSCH_3) has been studied by means of a crossed beams apparatus. Cleavage of the C–S bond within CH_3SCH_3 and the S–S bond within CH_3SSCH_3 is observed within a resonance in the energy range below 2 eV and visible preferentially via the appearance of the fragment CH_2S^- . The striking finding is that the intensity of CH_2S^- generated from CH_3SSCH_3 is more than two orders of magnitude higher than the intensity of the respective anionic fragment generated from CH_3SCH_3 . Our results clearly demonstrate that the CH_3SSCH_3 molecule, which contains disulphide bridge is substantially more sensitive towards electron attachment resulting mainly in dissociation along the S–S bridge.

1 Introduction

The investigation of collisions between electrons and neutral molecules is of high importance for understanding and development of many naturally and technologically occurring processes [1]. Owing to many applications dissociative processes received a great deal of interest in recent years, among them dissociative electron attachment (DEA) processes, which are driven by low energy (<12 eV) electrons (LEEs). As demonstrated in a number of papers LEEs have a potential to break specific bonds at defined energy. Such processes can be both bond and site selective [2]. This selectivity is of high importance, e.g., in chemical lithography [3], nanofabrication [4,5] and for modification and functionalization of the surfaces [6,7]. Besides technological applications this specificity is relevant for radiation chemistry [8]. It has been shown recently that DEA to phosphoric acid esters [9] and nucleotide 2'-deoxycytidine-5-monophosphate [10] results in the ester linkage rupture that would lead to a single strand break in DNA.

Recent years have witnessed an increase of the interest in the studies of sulphur containing compounds. This has been mainly stimulated by the importance of these compounds in many biochemical processes. Indeed, it is well documented that such compounds can be implicated, e.g., in aging [11] or oxidative stress [12]. Besides, they can undergo reductive processes in case they are exposed to low energy electrons. Recent dissociative electron at-

tachment experiments on thiolated nucleobases, namely 2-thiothymine [13] and 2-thiouracil [14], have shown that the presence of the S atom within the molecular structure strongly influences the dissociation and hence the dominant fragments are generated from the sulphur site of the molecule.

In this contribution we will present the results from low energy electron driven reactions in dimethyl sulphide (CH_3SCH_3) and dimethyl disulphide (CH_3SSCH_3). These molecules may serve as model systems of sulphur containing peptides. In particular CH_3SSCH_3 is an interesting compound that contains a disulphide bridge hence can reflect the behaviour of the S–S bonds between the thiol groups of two cysteine amino acids, which are responsible for the stabilization of the tertiary structure and play an important role in the folding of proteins. In fact, a number of known enzymes and other proteins contain reducible disulphide bridges within peptide loops. Therefore it is desirable to understand how the sulphur-containing compounds can be altered by low energy electrons.

As will be demonstrated in the following, CH_3SSCH_3 captures electrons resulting in the formation of both shape and core excited resonances, which decompose into CH_2S^- , CH_3SS^- , HS^- , S^- and CH_3^- . The CH_3SCH_3 molecule preferentially forms core excited resonances in the energy range above 5 eV, which decay via formation of CH_2S^- , S^- and CH_3^- .

2 Experimental procedure

The experiments were performed with an electron/molecule crossed beams apparatus. It consists of an oven, a trochoidal electron monochromator (TEM)

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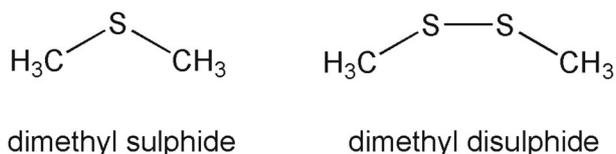


Fig. 1. Molecular structure of the investigated compounds.

and a quadrupole mass spectrometer (QMS). Briefly, an incident electron beam of well-defined energy (FWHM ≈ 200 meV, electron current ≈ 10 nA) generated from a TEM orthogonally intersects with an effusive molecular beam. The molecular beam emanates from a capillary, which is directly connected to the collision chamber. The samples of dimethyl sulphide and dimethyl disulphide are liquid under normal conditions and were introduced into the vacuum chamber via the inlet system both maintained at around 320 K in order to obtain sufficiently high vapour pressure and prevent the molecules from condensation at the surface of the electrodes. The pressure of the molecules in the gas phase measured by an ionisation gauge mounted at one of the flanges was in the range of 10^{-6} mbar.

The negative ions formed in the reaction zone are extracted from the reaction volume by a weak electric field (< 1 V/cm) towards a quadrupole mass analyser and detected by a single pulse counting technique. The intensity of the respective anions is recorded as a function of the incident electron energy. The electron energy scale was calibrated using SF_6 which forms SF_6^- near 0 eV. The samples of dimethyl sulphide and dimethyl disulphide were obtained from Sigma Aldrich with a stated purity of $\geq 99\%$. They were used after degassing in order to remove any remaining gases in the container.

3 Results and discussion

The ion yield curves of the fragment anions observed from electron attachment to dimethyl sulphide (CH_3SCH_3) and dimethyl disulphide (CH_3SSCH_3) (for the molecular structures see Fig. 1) are shown in Figures 2 and 3. It appears that dissociative electron attachment (DEA) to both compounds occurs in two energy regions below 2 eV and between 5–10 eV. The decomposition patterns in case of both molecules is similar, i.e., same fragment anions are generated for CH_3SCH_3 as for CH_3SSCH_3 , namely CH_2S^- (m/z 46), S^- (m/z 32) and CH_3^- (m/z 15). In addition, for CH_3SSCH_3 we observe two further anionic fragments, i.e., CH_3SS^- (m/z 79) and HS^- (m/z 33). A rough comparison of the anionic yields from both molecules at comparable experimental conditions shows that the dissociative attachment cross section of CH_3SCH_3 is around two orders of magnitude lower. In the following we will consider the fragmentation reactions of CH_3SCH_3 and discuss the results in the context of available literature results.

The reaction channel that is common for both investigated compounds is the formation of the CH_2S^- ion.

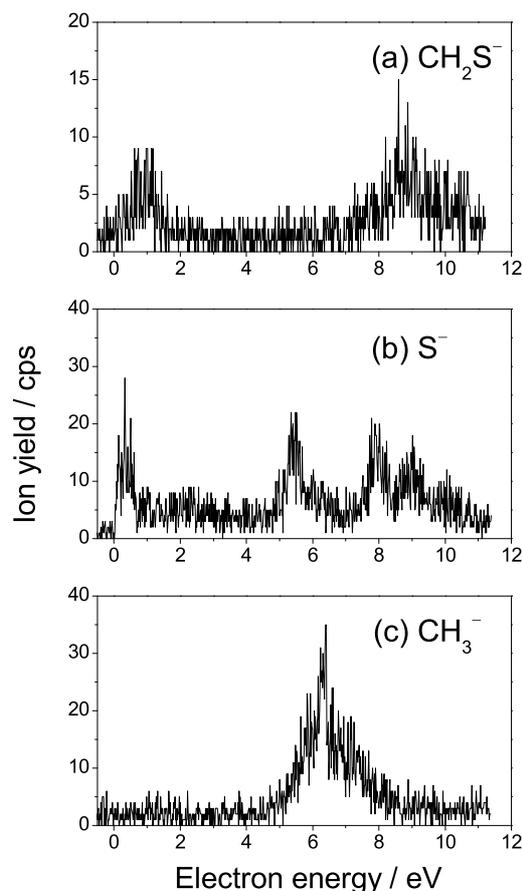
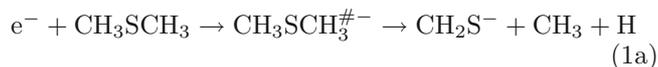


Fig. 2. Ion yield curves for the dissociative electron attachment to CH_3SCH_3 resulting in the formation of (a) CH_2S^- , (b) S^- and (c) CH_3^- .

The fragment anion can be attributed by stoichiometry to molecular anion of thioformaldehyde $\text{H}_2\text{C}=\text{S}$. In general, thioformaldehyde is unstable under normal laboratory conditions and hence forms a stable cyclic trimer $(\text{CH}_2\text{S})_3$. However, thioformaldehyde is characterized by positive electron affinity thus formed as a product of electron induced decomposition can form a stable negative ion. The reaction pathway in the case of CH_3SCH_3 that leads to the formation of CH_2S^- (Fig. 2) requires a cleavage of two bonds namely C–S and C–H, viz.:



with $\text{CH}_3\text{SCH}_3^{\#-}$ the transient negative ion, which is formed in the initial stage of electron capture. Based on the electron affinity of $\text{H}_2\text{C}=\text{S}$ (0.465 eV [15]) and the bond dissociation energies ($D(\text{C}-\text{S}) = 3.34$ eV and $D(\text{C}-\text{H}) \approx 1.8$ eV [16]), the thermodynamic threshold (expressed as the difference between the bond dissociation energy ($D(\text{R}-\text{X})$) and the electron affinity ($\text{EA}(\text{X})$) of the neutral fragment on which the excess electron is localized) for reaction (1a) is estimated to be 4.7 eV. The experimental appearance energy of the second, high energy

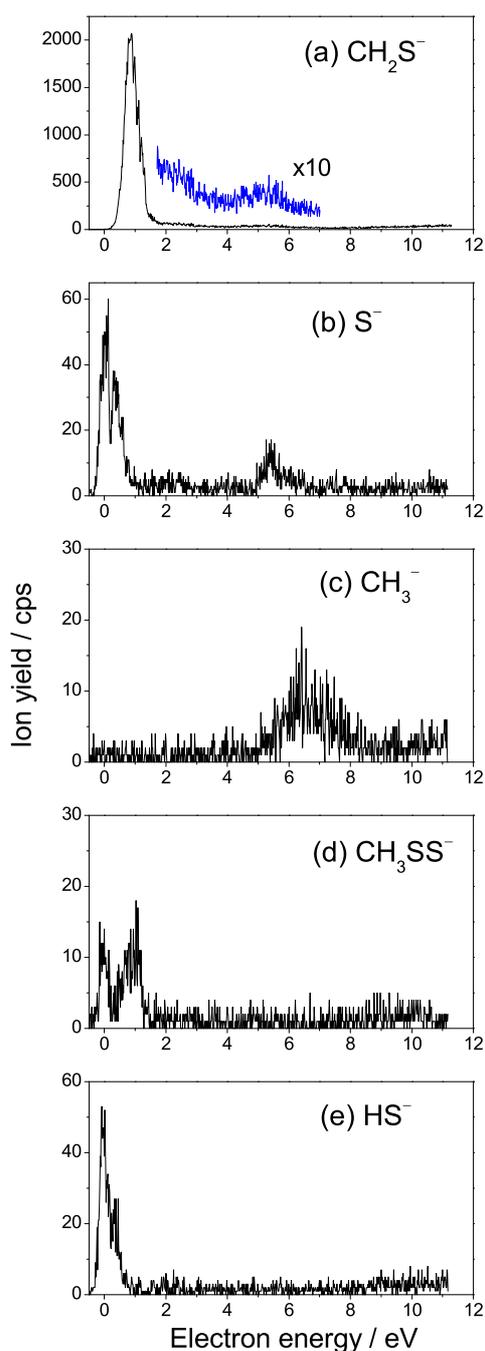
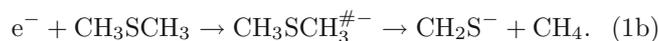


Fig. 3. Ion yield curves for the dissociative electron attachment to CH_3SSCH_3 resulting in the formation of (a) CH_2S^- , (b) S^- , (c) CH_3^- , (d) CH_3SS^- and (e) HS^- .

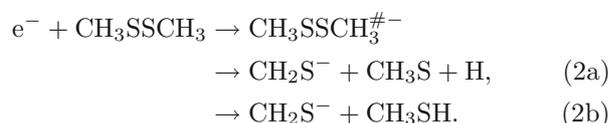
resonance is above the calculated threshold, therefore the structure can be generated via reaction (1a). However, within the ion yield curve further peak is visible with a maximum at around 0.9 eV thus considerably below the calculated threshold. The formation of this structure is only possible if the decomposition process is accompanied by the recombination of the two radicals CH_3 and H to

form CH_4 , viz.:



In this case the reaction can be driven by the gain of the energy from the formation of neutral stable molecule. Since the binding energy of the H- CH_3 bond is very high 4.5 eV [17] the thermodynamic threshold becomes as low as 0.2 eV and agrees well with the experimental findings. Indeed, such reactions are quite frequently observed for organic compounds. They have been recently reported for, e.g., acetamide and some of its derivatives [18], chlorodifluoroacetic acid methyl ester [19], pentafluoroaniline and pentafluorophenol [20].

For the CH_3SSCH_3 the dominant structure in the CH_2S^- ion yield is visible via a peak with a maximum at 0.9 eV followed by the weak contributions between 2–3 eV and 5–6 eV (Fig. 3). In this case the formation of the CH_2S^- ion requires rupture of the S-S bond and the C-H bond. Taking into account the above values of the electron affinity of CH_2S , the bond dissociation energy of C-H and the bond dissociation energy of S-S that is 3.2 eV [16] we arrive at the thermodynamic threshold of 4.54 eV. However, if one assumes the recombination of the radicals namely the CH_3S radical and the H radical to form CH_3SH ($D(\text{CH}_3\text{S-H}) = 3.99$ eV [16]) the threshold decreases to approximately 0.5 eV. We can hence postulate that the high energy peak between 5–6 eV can be generated according to reaction (2a) whilst the low energy peaks with a maximum at 0.9 eV and between 2–3 eV are most likely due to reaction (2b), viz.:



Since this most intense fragmentation channel is of importance in the context of low energy electron induced damage to proteins containing disulphide bridge it is therefore valuable to have an estimate value of the absolute cross section for the formation of CH_2S^- from CH_3SSCH_3 . This could be derived by using a calibration gas (SF_6) with a well established cross-section (2.4×10^{-18} m² at energy close to 0 eV [21]) and comparing the count rates of the DEA product ion with that of the calibrant (for the details see Ref. [22]). Assuming similar detection efficiencies for SF_6^- and CH_2S^- , the cross section is estimated to be $\approx 10^{-21}$ m² (with an accuracy of 1 order of magnitude) at the peak maximum of 0.9 eV (at temperature of 320 K, which is close to biological conditions). The estimated value is around one order of magnitude lower than that for the predominant ion $(\text{M-H})^-$ in the case of glycine [23], and around two orders of magnitude higher than that for $(\text{M-H})^-$ generated from dipeptides, i.e., glycyl-glycine, glycyl-alanine and alanyl-alanine [24].

Further anionic fragment, CH_3SS^- (Fig. 3), is exclusively generated from CH_3SSCH_3 due to the cleavage of the S- CH_3 bond. The intensity of this fragment is very low, i.e., the maximum count rate of CH_3SS^- is more than

two orders of magnitude lower than that of CH_2S^- . The position of the peak, with a maximum at 0.9 eV, matches well the position of the respective fragment from the previous experiment by Modelli et al. [25]. This is also true for the relative intensity between the CH_3SS^- and CH_2S^- fragments (see Tab. 1 in Ref. [25]).

Another, light fragment detected at m/z 32 can be attributed to the formation of S^- . The S^- ion in the case of CH_3SCH_3 is generated from several overlapping peaks in the energy range between 5–11 eV with additional low energy structure at around 0.4 eV (Fig. 2). The peaks in the high energy range can be easily attributed to core excited resonances (valence or Rydberg states) by comparison of their maxima with the high resolution VUV photo-absorption spectra [26]. The origin of the low energy peak is not obvious since, from electron transmission spectroscopy (ETS), the lowest shape resonance of σ_{SC}^* character has been observed at 3.25 eV [25] and theory predicts the resonance of B_2 symmetry at 2.6 eV [27].

The S^- yield from CH_3SSCH_3 is visible via three resonant features located at around 0 eV, 0.4 eV and 5.4 eV (Fig. 3). Taking into account the ETS data [28] we can ascribe the high energy feature to shape resonance involving S–S antibonding state. The low energy structures lie slightly below the theoretically (resonance of σ_{SS}^* character at 0.8 eV [27]) as well as experimentally (σ_{SS}^* resonance at 1.04 eV [28]) predicted resonances. On the other hand, assuming that formation of the S^- anion is accompanied by the release of the CH_3SCH_3 molecule as a neutral counterpart the thermodynamic threshold is 0.3 eV, which is in reasonable good agreement with the experimental data.

Figure 3 also presents the yield of the anionic fragment detected at m/z 33 from CH_3SSCH_3 . From stoichiometry, it can be attributed to the HS^- ion. The formation of HS^- would require a scission of two bonds namely S–S and C–S that has to be accompanied by the concomitant hydrogen transfer from the methyl group to the S atom. The energy required to cleave these bonds would be around 5.7 eV and this cannot be compensated by electron affinity of the HS radical, which is 2.31 eV [15]. Since this anionic fragment is visible via two low energy overlapping structures below 1 eV the only plausible reaction route would be through a formation of a stable neutral counterpart in order to gain the necessary energy.

Finally, the fragment at m/z 15 is attributed to the CH_3^- anion that is visible via a broad structure with a peak maximum at around 6.3 eV in the case of CH_3SCH_3 (Fig. 2) and around 6.6 eV in the case of CH_3SSCH_3 (Fig. 3). The CH_3^- anion, although not detected from a previous DEA experiments on gas phase CH_3SSCH_3 [25,29], has been recorded from electrons impact on CH_3SCH_3 condensed on D_2O films as a predominant species [30]. The anionic fragment is most likely generated via a core excited resonance with some contribution from a high lying shape resonance. Indeed, a VUV photo-absorption experiment on CH_3SCH_3 provides an evidence for the existence of the core excited resonance at 6.348 eV, which is a result of the excitation to an antibonding

orbital along the sulphur lone pair electrons ($n_{\text{S}} \rightarrow \sigma^*$) of the CH_3SCH_3 molecule [26]. Furthermore, recent theoretical calculations predict the existence of high lying shape resonances at energy around 5.8 eV for CH_3SCH_3 and around 7 eV for CH_3SSCH_3 [27]. The energy of these theoretically predicted resonances matches quite well the peaks maxima from our experiments. The formation of the CH_3^- anion requires the cleavage of the single S–CH₃ bond. Taking into account the available values for the bond dissociation energy of C–S ($D(\text{C–S}) = 3.34$ eV [16]) and the electron affinity of the CH_3 radical that is 0.08 eV [15] we arrive at an energy threshold of 3.3 eV, which is around 2 eV lower than the measured appearance energy.

4 Conclusions

Dissociative electron attachment to both dimethyl sulphide and dimethyl disulphide leads to the formation of a series of anionic fragments in the whole energy range ≈ 0 –12 eV. While CH_3SCH_3 preferentially decomposes in the high energy range above 5 eV the CH_3SSCH_3 molecule is mainly fragmented below 2 eV. Interestingly, besides the CH_3^- anion all other anionic fragments generated from both compounds contain sulphur atom within the structure. A simple comparison of the anionic yields from both molecules at comparable experimental conditions shows that the dissociative attachment cross section of CH_3SSCH_3 is around two orders of magnitude higher than the cross section of CH_3SCH_3 . Our estimates of the cross section for the formation of a predominant product CH_2S^- (at 0.9 eV and 320 K) from CH_3SSCH_3 shows that it is reasonable high ($\approx 10^{-21}$ m²). This suggests that the presence of the disulphide bridge within the molecular structure facilitates the decomposition of the molecule initiated by the capture of low energy electrons. This finding is of importance taking into account that the S–S bridge is responsible for the stabilisation of the tertiary structure and plays a role in the folding of proteins.

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