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Gas-phase Reactions of Isomeric Carbene and Distonic Radical Anions Derived from Methylthioacetone with Dimethyl Disulfide

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The gas-phase ion/molecule reactions of the $\text{CH}_3\text{S}^-\text{CDCN}$, $\text{CH}_3\text{S}^-\text{CCN}$ and $^-\text{CH}_2\text{S}^-\text{CDCN}$ ions formed in the reaction of the O^{--} ion with $\text{CH}_3\text{SCD}_2\text{CN}$ have been studied with the use of Fourier-transform ion cyclotron resonance (FTICR). In the reaction of the $\text{CH}_3\text{S}^-\text{CDCN}$ carbanion with the model substrate, dimethyl disulfide, a CH_3SD molecule is expelled from the collision complex with the indicated formation of a $(\text{CH}_3\text{S})_2\text{CCN}$ ion. In the reactions of the carbene radical anion, $\text{CH}_3\text{S}^-\text{CCN}$, loss of a $\text{CH}_3\text{S}^{\cdot}$ radical occurs and the formation of an ion with a $(\text{CH}_3\text{S})_2\text{CCN}$ structure is again indicated. A distinct reactivity is observed for the distonic radical anion, $^-\text{CH}_2\text{S}^-\text{CDCN}$, which reacts with dimethyl disulfide by the competing losses of CH_3SH and $\text{CH}_3\text{S}^{\cdot}$ from the collision complex. It is proposed that the loss of CH_3SH yields a $\text{CH}_3\text{SCHS}^-\text{CDCN}$ or $\text{CH}_3\text{SCHS}^-\text{CDCN}$ radical anion, whereas the loss of $\text{CH}_3\text{S}^{\cdot}$ is proposed to lead to a $\text{CH}_3\text{SCH}_2\text{S}^-\text{CDCN}$ carbanion. The formation of these species in the reactions of the $^-\text{CH}_2\text{S}^-\text{CDCN}$ ion is discussed as involving an initial radical or nucleophilic attack on one of the sulfur atoms in dimethyl disulfide followed by cleavage of the sulfur–sulfur bond prior to the loss of a CH_3SH molecule and/or a $\text{CH}_3\text{S}^{\cdot}$ radical.

The structure, stability and unimolecular dissociations of distonic ions have been studied extensively,^{1–5} whereas insight into the gas-phase bimolecular chemistry of such ions is somewhat more limited.^{6,7} The interest in the bimolecular chemistry of distonic ions, however, may be considered to be of general significance, since the formal separation of the radical and charge sites offers the possibility of examining reactions which involve primarily only one of these centers. With respect to distonic radical cations, a number of studies indicate that these species can react differently from the isomeric conventional radical cations and/or the related cations. Notably, a distonic radical cation may react by hydrogen atom abstraction or a formal transfer of a functional group originating from the substrate, whereas the conventional radical cations often prefer to react by charge exchange if this process is exothermic.^{6,7} For example, the distonic radical cation, $^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}$ reacts with CH_3SSCH_3 by a $\text{CH}_3\text{S}^{\cdot}$ radical abstraction, whereas a related conventional radical cation, i.e. ionized cyclopentanone, reacts only by electron transfer.⁸ A similar reactivity difference has been reported for the sulfur-containing distonic ion, $(\text{CH}_3)_2\text{SCH}_2^+$,^{9,10} and the isomeric molecular ion of ethyl methyl sulfide.^{8,11,12} Dimethyl disulfide has also been used as a substrate to probe the reactivity of some of the few distonic radical anions that have been generated as stable species in the gas phase.^{13–17} In particular, the $^-\text{CH}_2\text{CO}_2^-$ ion is reported to be able to react by $\text{CH}_3\text{S}^{\cdot}$ abstraction with the suggested formation of a $\text{CH}_3\text{SCH}_2\text{CO}_2^-$ ion,¹⁷ whereas a preliminary study indicated that a simple $\text{CH}_3\text{S}^{\cdot}$ transfer does not occur in the reactions of the distonic radical anion of tetramethyleneethane with dimethyl disulfide.¹⁶

In a previous study we reported that a stable sulfur-containing distonic radical anion, $^-\text{CH}_2\text{S}^-\text{CDCN}$, is formed in the reactions of the O^{--} ion with deuterium-labelled methylthioacetone, $\text{CH}_3\text{SCD}_2\text{CN}$.¹⁵ This ion was structurally distinguished from the isomeric carbene radical anion, $\text{CH}_3\text{S}^-\text{CCN}$, on the basis of high-kinetic-energy

collision-induced charge-reversal experiments. The distinct structure of these two radical anions, in combination with reports which indicate that dimethyl disulfide is a suitable substrate for probing the reactivity of distonic ions in the gas phase, prompted us to examine the ion-molecule chemistry of the $^-\text{CH}_2\text{S}^-\text{CDCN}$ and $\text{CH}_3\text{S}^-\text{CCN}$ species with this disulfide.

EXPERIMENTAL

The results were obtained using a single cell Fourier-transform ion cyclotron resonance (FTICR)^{18–20} mass spectrometer designed and constructed at the University of Amsterdam.²¹ The experimental operating procedure for this instrument has been described previously.^{22,23} The O^{--} ions were generated from N_2O by dissociative capture of electrons with an energy of 1.0–1.5 eV. Unwanted ions were ejected from the FTICR cell by applying appropriate radio-frequency (RF) pulses to the excitation plates of the cell.²⁴ The experiments were performed by first examining the reactions of a selected ion with the parent compound, methylthioacetone, and then studying the formation of the product ions formed with CH_3SSCH_3 , also admitted to the cell. These two series of experiments were performed directly after each other, in order to maintain similar experimental conditions. The occurrence of subsequent reactions of certain product ions with the neutral species present in the cell was prevented by continuous ejection of these product ions (see also Results). This was achieved by applying an appropriate low-amplitude RF pulse to the excitation plates of the cell during the entire reaction period. Attachment of low-energy electrons to the neutral species present in the cell during the reaction time was avoided by ejection of these electrons from the FTICR cell following a procedure described previously.²⁵

The total pressure of N_2O , methylthioacetone and dimethyl disulfide was $(8–10) \times 10^{-5}$ Pa as measured with an uncalibrated ionization gauge placed in a side arm of the main pumping line. The ratio between the partial pressures of the compounds in all experiments was 1:1:1. The

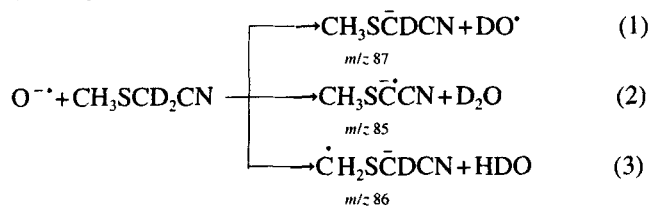
* Author for correspondence.

temperature of the trapping plate situated opposite the filament was measured to be ≈ 330 K, whereas the inlet systems, the leak valves, and the vacuum vessel of the instrument were all at room temperature.

All samples were commercially available with the exception of $\text{CH}_3\text{SCD}_2\text{CN}$ ($\geq 95\%$ d_2), which was prepared from the unlabelled compound as described previously.¹⁵

RESULTS

Gas-phase ion/molecule reactions are currently being studied by a number of different instrumental methods including high pressure techniques, such as flowing after-glow (FA)²⁶ or selected-ion flow tube (SIFT),²⁶ as well as the low pressure FTICR method.²⁰ The latter method has proven to be very useful in mechanistic studies of ion/molecule reactions in the gas phase,²⁷⁻²⁹ owing, in part, to its versatility for the determination of the relationships between reactant and product ions by appropriate ion-ejection procedures.^{28, 30} This feature of the FTICR method is, in particular, useful if a single cell instrument is used, since the neutral precursors of the various ions are inevitably present in the cell together with the selected substrate. With respect to the present study, it should be emphasized that the (radical) anions of interest are formed in the reactions of $\text{O}^{\cdot -}$ with $\text{CH}_3\text{SCD}_2\text{CN}$ as indicated in Reactions (1)–(3) and described in a previous report.¹⁵ In other words, in the experiments concerned with the reactivity of the (radical) anions towards dimethyl disulfide, the other neutral compounds N_2O and $\text{CH}_3\text{SCD}_2\text{CN}$, are also present in the cell of the single cell FTICR instrument used (see experimental). Thus, it proved necessary to perform two series of independent experiments. The first series of experiments is concerned with the reactivity of a selected ion with the parent species while the second series of experiments investigates the reactions of the same ion with dimethyl disulfide added to the cell. In the second series of experiments, the origin of the product ions was confirmed by continuous ejection, from the cell, of one of the product ions of the reactions with the parent compound (*vide infra*).



Carbanion

The carbanion of methylthioacetone nitrile displays no observable reactivity towards either N_2O or the parent compound under our experimental conditions. With dimethyl disulfide added to the cell, product ions with an m/z ratio of 132 are formed (Reaction (4)). These ions can be ascribed to the loss of CH_3SD from the collision complex in a relatively slow process, as indicated by the observation that the conversion into products is only 5% after a reaction time of 0.5 s (Fig. 1). A rate constant was not estimated for this reaction, owing mainly to the fact that the pressure of the substrate is measured only approximately with the ionization gauge of the instrument. A similar consideration applies to the other overall processes described in this report, which is concerned mainly with the pathways open in the reactions of the different (radical) anions with dimethyl disulfide.

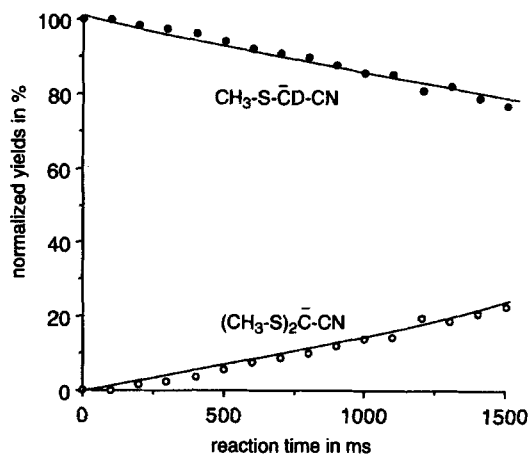
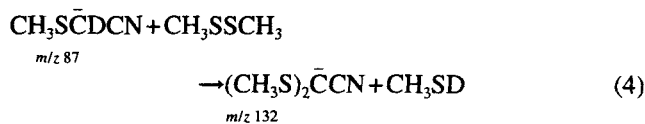


Figure 1. Variation in the normalized ion abundances with time in the reaction of the CH_3SCDCN carbanion with CH_3SSCH_3 . The pressure of the neutral species present in the FTICR cell were: $p(\text{N}_2\text{O})=3 \times 10^{-5}$ Pa, $p(\text{CH}_3\text{SCD}_2\text{CN})=3 \times 10^{-5}$ Pa and $p(\text{CH}_3\text{SSCH}_3)=3 \times 10^{-5}$ Pa (see text).



Carbene radical anion

The carbene radical anion of methylthioacetone nitrile is unreactive towards N_2O whereas it reacts with the parent compound to afford the related CH_3SCDCN carbanion. This reaction appears to be relatively facile since 45% of the carbene radical anions are seen to be converted into the carbanion after a reaction time of 0.5 s. If dimethyl disulfide is admitted to the cell, an additional product ion with an m/z value of 132 is generated in a reaction which involves the loss of a $\text{CH}_3\text{S}^{\cdot}$ radical from the collision complex (see Reaction (5)). This process can be considered to be relatively slow, in keeping with the observation that the conversion into product ions is changed only from 45% to 65% at a reaction time of 0.5 s if dimethyl disulfide is added to the cell (Fig. 2).

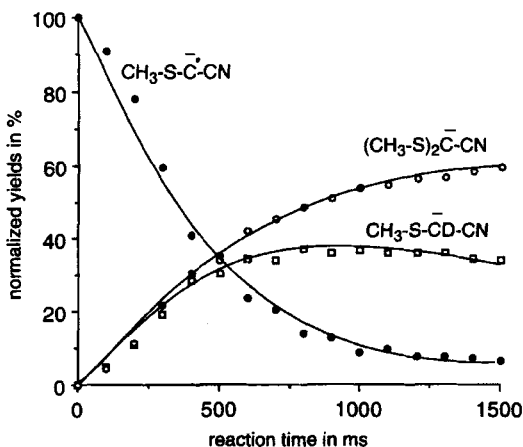
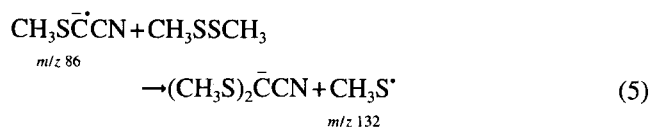


Figure 2. Variation in the normalized ion abundances with time in the reaction of the CH_3SCCN carbene radical anion with CH_3SSCH_3 . The pressure of the neutral species present in the FTICR cell were: $p(\text{N}_2\text{O})=3 \times 10^{-5}$ Pa, $p(\text{CH}_3\text{SCD}_2\text{CN})=3 \times 10^{-5}$ Pa and $p(\text{CH}_3\text{SSCH}_3)=3 \times 10^{-5}$ Pa (see text).



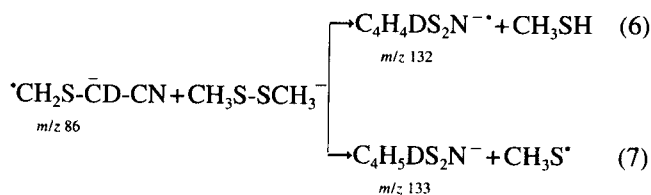
To verify that the product ion with an m/z ratio of 132 is formed in the reaction of the carbene radical anion with dimethyl disulfide and not in a subsequent reaction of the CH_3SCDCN carbanion generated in the reaction with the parent compound, an additional experiment was performed. In this experiment, the CH_3SCDCN ion was ejected continuously from the cell during the entire reaction time (see experimental). However, the product ion with m/z 132 was generated persistently under these experimental conditions also, thus confirming that the carbene radical anion reacts with CH_3SSCH_3 as shown in (Reaction (5)).

Distonic radical anion

The distonic radical anion too, does not display any observable reactivity towards N_2O but reacts with the parent compound with the formation of two product ions. Thus the carbanion, CH_3SCDCN , and an ion of m/z 88 are generated. The latter species has been assigned a CH_2DSCDCN structure and it is suggested that it is formed by D^{\cdot} abstraction from the methylene group of neutral $\text{CH}_3\text{SCD}_2\text{CN}$.¹⁵ The overall reaction of the distonic radical anion with the parent compound proceeds with a conversion into products of 25% after a reaction time of 0.5 s. In the presence of the substrate CH_3SSCH_3 , the conversion into products is only slightly more than 25% after a reaction time of 0.5 s in line with the observation that the two additional product ions with m/z values of 132 and 133 are formed only in relatively low yields as shown in Fig. 3.

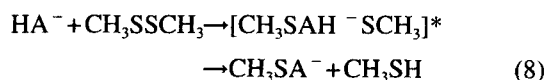
To complement the procedure described for the carbene radical anion, an experiment was performed in which the ions of m/z 87 were ejected continuously from the cell. This experiment revealed that the product ion with an m/z ratio of 132 is also formed in the direct reaction of the distonic radical anion with CH_3SSCH_3 . In addition, a similar ion ejection experiment confirmed that the product ion of m/z 133 arises as a result of a direct reaction of the distonic radical anion and not, for example, in a possible subsequent reaction of the m/z 88 ion with dimethyl disulfide. In conclusion, the distonic radical anion is indicated to react

with dimethyl disulfide as shown in Reactions (6) and (7).



DISCUSSION

Relatively simple anions and also some radical anions are reported to react with dimethyl disulfide in the gas phase by an elimination reaction across a carbon-sulfur bond and/or a displacement process involving initial attack on a sulfur atom.^{31,32} The elimination pathway suggested involves an initial formation of an ion-molecule complex containing a $\text{CH}_2=\text{S}$ molecule and a $\text{CH}_3\text{S}^{\cdot-}$ ion which either dissociates to give the observed $\text{CH}_3\text{S}^{\cdot-}$ ion or undergoes an addition reaction to form a stable $\text{CH}_3\text{SCH}_2\text{S}^{\cdot-}$ species.³¹ It was concluded that the elimination pathway dominates in the reactions of charge-localized anions, e.g. NH_2^- and CH_3O^- , derived from molecules with a gas-phase acidity, ΔH_{acid}^0 , larger than or equal to 1592 kJ mol^{-1} . A different behaviour was reported for the charge-delocalized carbanions, such as $\text{CH}_3\text{COCH}_2^-$, $^-\text{CH}_2\text{CN}$ and $^-\text{CH}_2\text{NO}_2$. It was concluded that these ions react mainly by attack on a sulfur atom followed by loss of CH_3SH from the collision complex as generalized Reaction in (8) for an HA^- anion. In addition, it was reported that anions derived from molecules with a gas-phase acidity lower than 1470 kJ mol^{-1} display no, or only a marginal, reactivity towards dimethyl disulfide in the gas phase.³¹



In line with these findings, the present charge-delocalized carbanion, CH_3SCDCN , reacts relatively slowly with dimethyl disulfide by loss of CH_3SD from the collision complex (Fig. 1). The slow nature of the overall reaction may be considered to be in line with the gas-phase acidity of the methylene group in methylthioacetone which is reported to be $1494 \pm 8\text{ kJ mol}^{-1}$ and thus not very different from the apparently critical value of about 1470 kJ mol^{-1} .³³ For the radical, CH_3SCHCN the gas-phase acidity can be placed at a value of $1505 \pm 10\text{ kJ mol}^{-1}$, thus revealing that the carbene radical anion, $\text{CH}_3\overset{\cdot}{\text{C}}\text{CN}$, is only slightly more basic than the related carbanion.³⁴ The relatively minor difference in gas-phase acidity between the radical and the parent compound could be considered to be in line with the observation that the carbene radical anion does not appear to react much more easily with dimethyl disulfide than does the carbanion (see results and Figs 1 and 2). It should be emphasized, however, that the carbene radical anion reacts with dimethyl disulfide by the loss of a $\text{CH}_3\text{S}^{\cdot}$ radical from the collision complex (Reaction (5)) and that this process, in a formal sense, may involve either an initial radical attack or a nucleophilic attack on one of the sulfur atoms in dimethyl disulfide.³²

Initial radical or nucleophilic attack may also be thought to occur in the reactions of the distonic radical anion. This ion may be represented, in principle, not only by the CH_2SCDCN formulation shown in Reactions (6) and (7) but also with the radical and charge centres interchanged; i.e. as CH_2SCDCN . If the former representation is

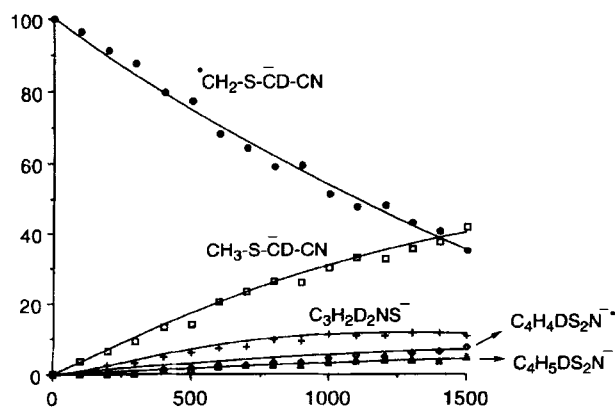
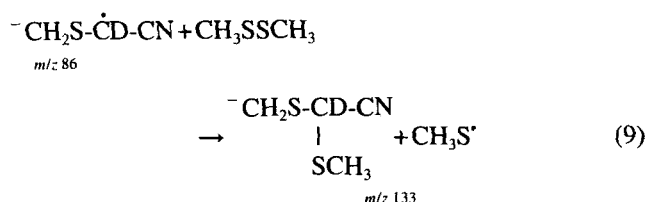


Figure 3. Variation in the normalized ion abundances with time in the reaction of the distonic radical anion CH_2SCDCN , with CH_3SSCH_3 . The CH_3SCDCN and $\text{C}_3\text{H}_2\text{D}_2\text{NS}^-$ ions arise in the reaction of the distonic radical anion with the parent compound, whereas the $\text{C}_4\text{H}_4\text{DS}_2\text{N}^{\cdot-}$ and $\text{C}_4\text{H}_5\text{DS}_2\text{N}^{\cdot-}$ species are formed in the reactions with CH_3SSCH_3 . The pressure of the neutral species present in the FTICR cell were: $p(\text{N}_2\text{O}) = 3 \times 10^{-5}\text{ Pa}$, $p(\text{CH}_3\text{SCD}_2\text{CN}) = 3 \times 10^{-5}\text{ Pa}$ and $p(\text{CH}_3\text{SSCH}_3) = 3 \times 10^{-5}\text{ Pa}$ (see text).

considered to be the most adequate, the losses of $\text{CH}_3\text{S}^\bullet$ and CH_3SH from the collision complex formed in the reaction with dimethyl disulfide may be visualized as in Scheme 1. In this Scheme, the initial step is proposed to be a radical attack on a sulfur atom leading to a complex composed of a $\text{CH}_3\text{S}-\text{CH}_2-\dot{\text{C}}\text{D}-\text{CN}$ ion and a $\text{CH}_3\text{S}^\bullet$ radical. This complex may dissociate by the loss of $\text{CH}_3\text{S}^\bullet$ or react further by a hydrogen-atom abstraction from the methylene group of the $\text{CH}_3\text{S}-\text{CH}_2\dot{\text{C}}\text{D}-\text{CN}$ ion. The selective occurrence of this hydrogen-atom abstraction by the $\text{CH}_3\text{S}^\bullet$ radical requires, of course, that the methylene C—H bond dissociation energy be considerably lower than the dissociation energy of the C—H bond of the CH_3 group or the C—D bond in the $\text{CH}_3\text{S}-\text{CH}_2-\text{S}-\dot{\text{C}}\text{D}-\text{CN}$ ion.

With the assumption that the $\dot{\text{C}}\text{H}_2\text{S}\dot{\text{C}}\text{DCN}$ ion reacts by nucleophilic attack on a sulfur atom, a complex of a $\dot{\text{C}}\text{H}_2\text{SCD}(\text{SCH}_3)\text{CN}$ radical and a CH_3S^- ion will be formed (see Scheme 1). This complex would be expected, however, to react further by deuterium abstraction with the formation of a $\dot{\text{C}}\text{H}_2\text{SC}(\text{SCH}_3)\text{CN}$ ion of m/z 131. Irrespective of the fact that a product ion with an m/z ratio of 131 is not formed in the reactions of the distonic radical anion (see Reactions (6) and (7)), a clear conclusion concerning the initial step in the reaction sequence can not be reached. This becomes even more apparent if the reactant distonic ion is formulated as $\dot{\text{C}}\text{H}_2\text{S}\dot{\text{C}}\text{DCN}$. Radical attack on a sulfur atom in dimethyl disulfide would lead, in this instance, to the primary carbanion shown in Reaction (9). The formation of such a product ion can not be excluded, of course, even though it may be considered unlikely since such a carbanion is anticipated to be less stable than, for example, the charge-delocalized $\text{CH}_3\text{S}-\text{CH}_2-\text{S}-\dot{\text{C}}\text{D}-\text{CN}$ species shown in Scheme 1.



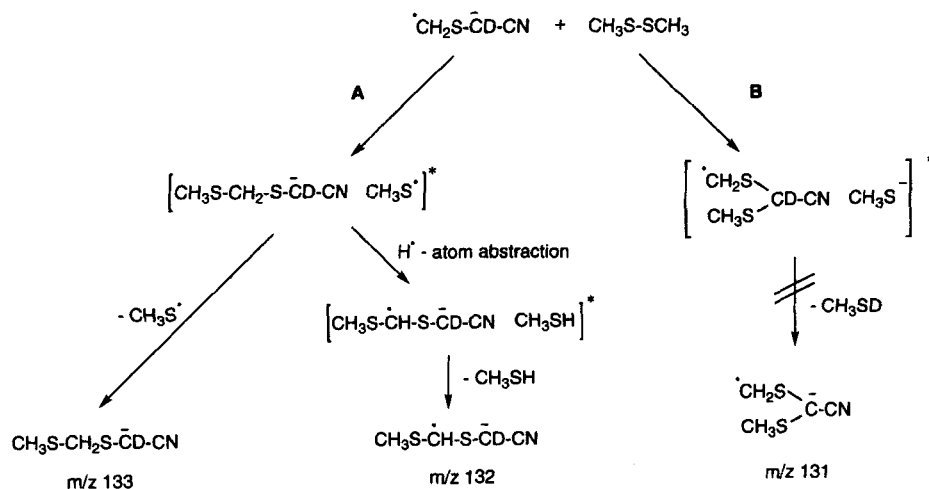
In addition, the $\dot{\text{C}}\text{H}_2\text{S}$ site in the $\dot{\text{C}}\text{H}_2\text{S}\dot{\text{C}}\text{DCN}$ ion may attack a sulfur atom in dimethyl disulfide thus forming the complex $[\text{CH}_3\text{SCH}_2\text{S}\dot{\text{C}}\text{DCN} \text{ } ^-\text{SCH}_3]^*$ shown in Scheme 2.

A possible subsequent reaction would then be deuterium abstraction by the CH_3S^- ion with formation of an ion with an m/z ratio of 131 in contrast to the experimental observations (*vide supra*). The loss of CH_3SH from the complex involves, of course, a proton abstraction, whereas the loss of a $\text{CH}_3\text{S}^\bullet$ radical more probably involves an electron transfer within the postulated $[\text{CH}_3\text{SCH}_2\text{S}\dot{\text{C}}\text{DCN} \text{ } ^-\text{SCH}_3]^*$ complex (see Scheme 2).

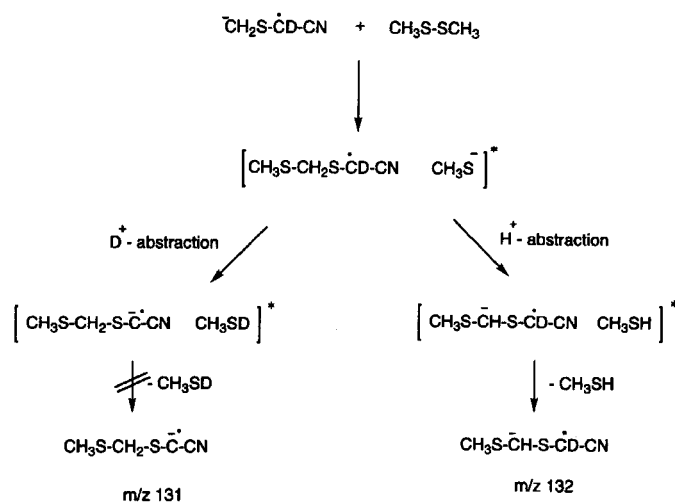
The sole occurrence of proton abstraction in the $[\text{CH}_3\text{SCH}_2\text{S}\dot{\text{C}}\text{DCN} \text{ } ^-\text{SCH}_3]^*$ complex would require that the -CD- position between the CN group and a sulfur atom is significantly less acidic than the methylene group in between the two sulfur atoms. This seems to be at odds with the fact that a CN group enhances the acidity of an adjacent radical position much more than a sulfur atom increases the acidity of an adjoining group, as shown by the finding that the $\dot{\text{C}}\text{H}_2\text{CN}$ radical is about 85 kJ mol^{-1} more acidic than CH_3SCH_3 in the gas phase.^{32,35} In combination with the absence of a product ion corresponding to the loss of CH_3SD from the collision complex, these considerations suggest that the most likely mechanistic scheme involves the indicated initial radical attack on a sulfur atom by the distonic ion formulated as $\dot{\text{C}}\text{H}_2\text{S}\dot{\text{C}}\text{DCN}$ (see Scheme 1). It should be mentioned, however, that an electronic coupling through the sulfur atom is possible in either representation of the distonic radical anion. As a result, the mechanistic considerations with respect to the occurrence of an initial radical or nucleophilic attack on a sulfur atom do not allow any real insight to be obtained into the radical and charge distributions in the reactant distonic ion.

CONCLUSIONS

The (radical) ions formed in the reactions of O^- with methylthioacetone nitrile react differently with dimethyl disulfide. The carbanion, $\text{CH}_3\text{S}\dot{\text{C}}\text{DCN}$, and carbene radical anion, $\text{CH}_3\text{S}\dot{\text{C}}\text{CN}$, both react with the formation of a $(\text{CH}_3\text{S})_2\dot{\text{C}}\text{CN}$ ion, although via different pathways. The carbanion is likely to react by an initial nucleophilic attack on one of the sulfur atoms of dimethyl disulfide followed by deuterium transfer and loss of CH_3SD , whereas the reaction of the carbene radical anion can be formulated as a $\text{CH}_3\text{S}^\bullet$ radical abstraction. Only the distonic radical anion, $\dot{\text{C}}\text{H}_2\text{S}\dot{\text{C}}\text{DCN}$, reacts with dimethyl disulfide by the



Scheme 1. Proposed pathways for the reaction of the distonic radical anion formulated as $\dot{\text{C}}\text{H}_2\text{S}\dot{\text{C}}\text{DCN}$ with dimethyl disulfide. Pathway A involves initial radical attack on a sulfur atom followed by the loss of $\text{CH}_3\text{S}^\bullet$ or a subsequent hydrogen atom transfer prior to the elimination of CH_3SH . Pathway B involves a nucleophilic attack on a sulfur atom and is indicated to lead to the loss of CH_3SD (see also text).



Scheme 2. Suggested pathways for the reaction of the distonic radical anion formulated as $\text{CH}_2\text{S}^{\cdot-}\text{C}\dot{\text{D}}\text{CN}$ with dimethyl disulfide. The initial step in the sequence is proposed as a nucleophilic attack on a sulfur atom (see also text).

competing losses of $\text{CH}_3\text{S}^{\cdot+}$ and CH_3SH from the collision complex in a process which is likely to involve initial radical attack on one of the sulfur atoms. The occurrence of the loss of $\text{CH}_3\text{S}^{\cdot+}$ as well as CH_3SH allows the distonic radical anion to be distinguished from the isomeric carbene radical anion species by its bimolecular chemistry with dimethyl disulfide.

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