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The Gas-Phase Reactions of the Allenyl Anion with CS_2, COS and CO_2

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Abstract: The allenyl anion reacts readily in the gas phase with CS_2 and COS to form the thioketenyl anion. The reaction involves a complex series of cyclization and ring-opening reactions in which the central carbon of allene and the carbon of the neutral reagent become equivalent. Despite the complexity, the reaction with CS_2 is useful in determining the site of deprotonation of unsymmetrical allenes. The reaction of the allenyl anion with CO_2 produces only an adduct, because the cleavage reaction to the ketenyl anion and ketene is endothermic. However, the allenyl anion is produced if the reaction is carried out in the reverse direction. © 1997 Elsevier Science Ltd.

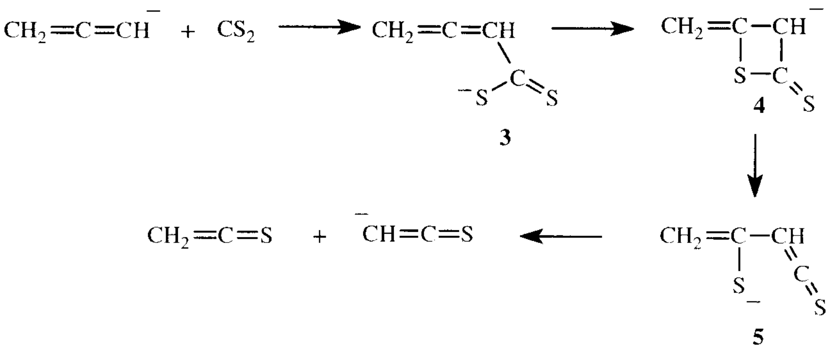
INTRODUCTION

In the gas phase the allenyl anion **1** is readily prepared by the reaction of a strong base (HO^-, NH_2^-) with allene, and when it is allowed to react with CS_2 it is rapidly cleaved to the thioketenyl anion **2** as shown in eq. 1.[1]

$$CH_2{=}C{=}CH_2 \xrightarrow{HO^-} \underset{\mathbf{1}}{CH_2{=}C{=}\overset{-}{C}H} \xrightarrow{CS_2} CH_2{=}C{=}S \; + \; \underset{\mathbf{2}}{\overset{-}{C}H{=}C{=}S} \qquad (1)$$

The neutral product formed, thioketene, is not detected but its structure is assigned on thermochemical and mechanistic grounds. To account for this reaction we postulated the mechanism shown in Scheme I. The ion **1** and CS_2 are attracted to one another by ion-induced dipole forces until they enter a long-lived ion-dipole complex within which chemical reactions occur. An adduct **3** is formed in an exothermic reaction; in the absence of solvent to dissipate this exothermicity, the energy remains within the adduct and can be used to fuel subsequent reactions. Cyclization to **4**, followed by ring opening to **5** produces an isomeric ion which can dissociate, by way of an intermediate ion-dipole complex, to the products. We estimate that overall this reaction is exothermic by 26 kcal/mol.[2]

Scheme I

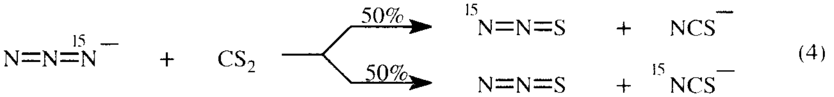


In subsequent work[3] we found that reactions of this type are general for anions which contain cumulative double bonds. Two examples are given in eq. 2 and 3.

$$\overset{-}{C}H{=}C{=}O \;+\; CS_2 \longrightarrow \overset{-}{C}H{=}C{=}S \;+\; COS \qquad (2)$$

$$\overset{-}{C}H{=}N{=}N \;+\; CS_2 \longrightarrow \overset{-}{C}H{=}C{=}S \;+\; N_2S \qquad (3)$$

Reactions in which ions are cleaved into two parts are extremely valuable in ion chemistry as an aid to the determination of ion structure. For example we used an analog of this reaction to determine the position of a label in azide ion (eq. 4,5).[4]



$$N{=}N{=}\overset{15}{N}^{-} \;+\; CS_2 \begin{cases} \xrightarrow{50\%} {}^{15}N{=}N{=}S \;+\; NCS^{-} \\ \xrightarrow{50\%} N{=}N{=}S \;+\; {}^{15}NCS^{-} \end{cases} \qquad (4)$$

$$\overset{15}{N}{=}N{=}N^{-} \;+\; CS_2 \longrightarrow \overset{15}{N}{=}N{=}S \;+\; NCS^{-} \qquad (5)$$

Recently we reported our detailed studies of the reactions of the ketenyl anion with CS_2 (eq. 2) in which we used ^{13}C-labeled ketenyl anion to trace the mechanism.[5] The results were in general accord with that proposed in Scheme I (with O replacing CH_2 in that Scheme), but also revealed some unexpected complexities. In this paper we report on our investigations, again using ^{13}C-labeling, of the mechanism of reactions of the allenyl anion with CS_2, COS and CO_2. We carried out this study because, if the mechanism is as straightforward as that depicted, it could be extremely useful as a probe for determining the site of deprotonation of substituted allenes. Consider, for example, deprotonation of methyl allene. Two allenic sites are available for deprotonation [6], and the resulting isomeric anions would generate product ions of different masses (eq. 6 and 7). By measuring the ratio of the m/z 57 and 71 peaks, the ratio of the two allenyl anions could be inferred.

$$CH_3{-}CH{=}C{=}CH^- + CS_2 \longrightarrow CH_3{-}CH{=}C{=}S + \underset{m/z\ 57}{\overset{-}{C}H{=}C{=}S} \qquad (6)$$

$$CH_3{-}\overset{-}{C}{=}C{=}CH_2 + CS_2 \longrightarrow CH_2{=}C{=}S + \underset{m/z\ 71}{CH_3{-}\overset{-}{C}{=}C{=}S} \qquad (7)$$

We therefore decided to carry out an investigation of the mechanism of this reaction using labeled allenyl anions in order to determine if it is suitable for structure determinations of these anions.

EXPERIMENTAL

The flowing afterglow-selected ion flow tube (FA-SIFT) which we used for these experiments has been described in detail elsewhere.[7] Briefly, it consists of two flow tubes separated by a quadrupole mass filter and terminated by a second quadrupole and an electron multiplier. In each tube a rapidly flowing stream of helium buffer gas is used to cool the ions to room temperature and to transport them down the flow tube. Ions are produced in the first flow tube by electron impact ionization and ion-molecule reactions. For example the allenyl anion is produced by introducing small amounts of N_2O and methane before the ionizer to produce hydroxide ion, which subsequently reacts with allene added downstream (eq. 8).

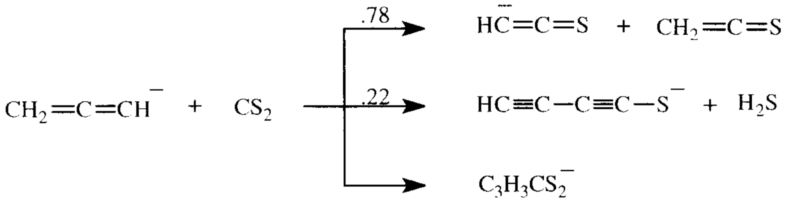
$$N_2O \xrightarrow{e^-} O^- \xrightarrow{CH_4} HO^- \xrightarrow{C_3H_4} C_3H_3^- \qquad (8)$$

At the end of the first flow tube the ions are sampled through an orifice into the first quadrupole where helium and the neutral precursors are removed by pumping and the ions of the desired mass-to-charge ratio are selected by the quadrupole and injected into the second flow tube. At the end of this tube they are again sampled, analyzed in the second quadrupole and detected by the electron multiplier. When a pure ion signal has been attained, vapor of the neutral reagent (e.g., CS_2) is introduced into the second flow tube and the ionic products of the reaction are determined. Reaction rate coefficients may readily be determined by measuring reactant ion intensities as a function of reaction distance at constant neutral flow, since in a flow system distance and time are linearly related. Product branching ratios were determined by plotting the fractional abundance of each product ion versus the extent of reaction. This plot was extrapolated to zero reaction distance to eliminate the effects of differential diffusive losses and possible secondary reactions.

Isotopically labeled allenyl anions were obtained by injecting the naturally occurring (3.3%) ^{13}C-containing ions of m/z 40. These ions are randomly labeled, with 1/3 of the isotope at each of the three carbons. The ketenyl anion was generated by allowing hydroxide ion to react with vinylene carbonate in the first flow tube.[8] Ketene was generated by pyrolysis.[9]

RESULTS AND DISCUSSION

The results of the reaction of the unlabeled allenyl anion with CS_2, COS and CO_2 are given in eq. 10-12. Reaction with CS_2 gives two products formed by bimolecular reactions, the thioketenyl anion **2** and an adduct which has lost a molecule of hydrogen sulfide. These two product ions are formed in a 78:22 ratio. An adduct, which is formed in a termolecular reaction involving collisions with the helium buffer gas and whose rate of formation is therefore dependent upon the helium pressure, comprises about 10% of the total ion signal at the 0.5 torr He pressure we used in our experiment.

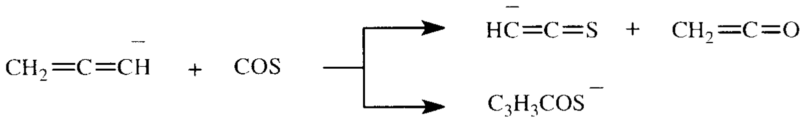


$$CH_2{=}C{=}\overset{-}{C}H + CS_2 \xrightarrow{.78} H\overset{-}{C}{=}C{=}S + CH_2{=}C{=}S$$

$$CH_2{=}C{=}\overset{-}{C}H + CS_2 \xrightarrow{.22} HC{\equiv}C{-}C{\equiv}C{-}S^- + H_2S \qquad (10)$$

$$CH_2{=}C{=}\overset{-}{C}H + CS_2 \longrightarrow C_3H_3CS_2^-$$

When the allenyl anion reacts with COS under the same reaction conditions (eq. 11), only a single bimolecular product ion is formed, the thioketenyl anion, together with about 50% of the adduct ion,



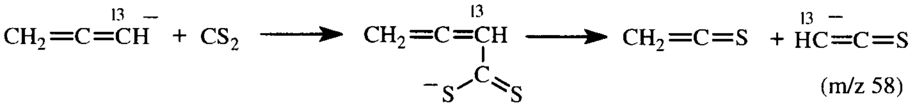
$$CH_2{=}C{=}\overset{-}{C}H + COS \longrightarrow H\overset{-}{C}{=}C{=}S + CH_2{=}C{=}O$$

$$CH_2{=}C{=}\overset{-}{C}H + COS \longrightarrow C_3H_3COS^- \qquad (11)$$

while reaction with CO_2 produces only adduct (eq. 12).

$$CH_2{=}C{=}\overset{-}{C}H + CO_2 \longrightarrow C_3H_3COO^- \qquad (12)$$

To gain more insight into the reaction we injected uniformly ^{13}C-labeled allenyl anions (m/z 40) and allowed them to react with CS_2. If the mechanism of the reaction is precisely that given in eq. 2 we would expect 33% of the resulting thioketenyl anions formed to be labeled with ^{13}C, those arising from allenyl anions in which the label is on the carbon bearing the negative charge (eq. 13). If the label is on either of the other two carbons it will be lost in the neutral product. We would therefore expect that the thioketenyl product ion will consist of 67% m/z 57 and 33% m/z 58.

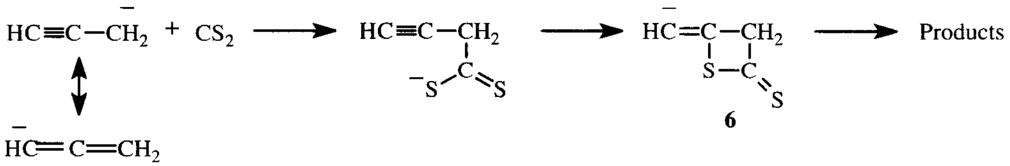


$$CH_2{=}C{=}\overset{13\ -}{C}H + CS_2 \longrightarrow CH_2{=}C{=}\overset{13}{C}H(-S-C{=}S) \longrightarrow CH_2{=}C{=}S + H\overset{13\ -}{C}{=}C{=}S \quad (13)$$

(m/z 58)

In fact, when the experiment is carried out <u>a mixture of exactly 50% labeled and 50% unlabeled ions is obtained</u>. Obviously the proposed mechanism is incorrect or incomplete.

We first considered whether the results could be accommodated by reaction through the other form of the anion, namely the propargyl anion, eq. 14.

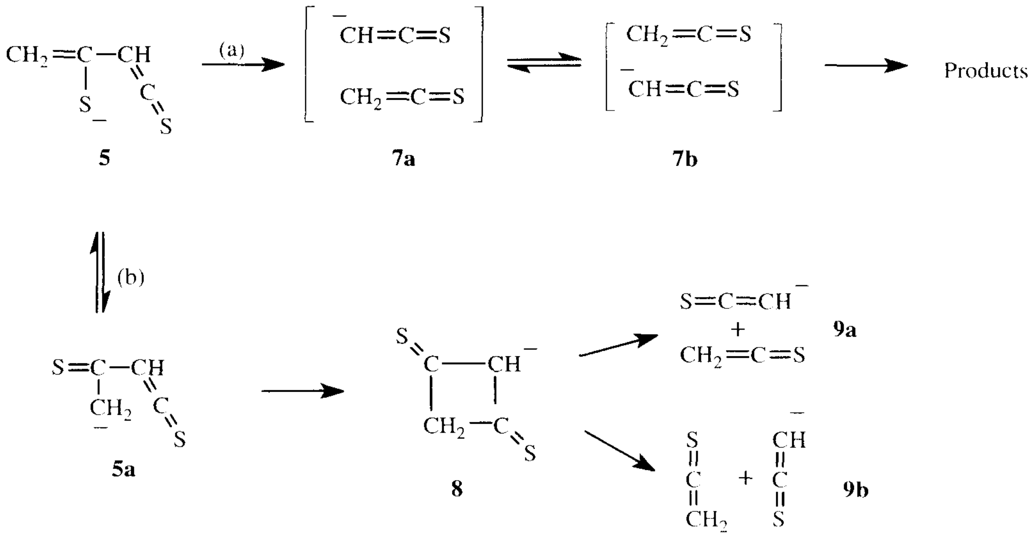


(14)

This process appears unlikely because the cyclization reaction to form 6 generates an unstabilized vinyl anion, which would be expected to be much higher in energy than the thioenolate anion of Scheme I. In addition, if this mechanism were to occur, 67% of the ions would be labeled, since the thioketenyl anion contains two carbons of allene, so that it cannot account for the 50% labeled ions observed. We sought a mechanism which would lead naturally to the observed ratio of products.

Two possible pathways came to mind, both originating from the rearranged ion **5** in Scheme I, and these are summarized in Scheme II. If the reaction follows path (a), **5** dissociates through an intermediate ion-dipole complex **7a** within which there is rapid proton transfer between the two components. Thus, since the proton transfer is thermoneutral, a 50:50 mixture of **7a** and **7b** will be formed before separating into products. Since in **7a** the thioketenyl anion contains one carbon originating in allene and in **7b** it contains two such carbons, the spectrum will contain equal amounts of m/z 57 and 58. This path has the drawback that thermoneutral proton transfer reactions between carbon atoms are usually slow in the gas phase, as they are in solution, so that the complex should dissociate before equilibration.

Scheme II

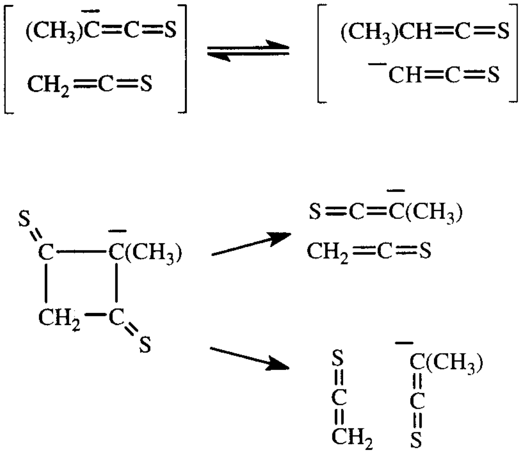


A second path is shown by (b) in which rotation about the carbon-carbon bond in **5** leads to the form shown in **5a**. This is followed by cyclization to the highly stabilized and symmetrical ion **8**. In this ion the CH and CH_2 groups retain their identity as being derived from the CH and CH_2 groups in the allenyl anion, but the central carbon of allene and the carbon of CS_2 become equivalent. Decomposition of **8** to the thioketenyl anion and thioketene can proceed in two equivalent ways, as shown in Scheme II, and would lead to the observed 50:50 mixture of labeled and unlabeled ions, as observed. Note that in (a) the CH and CH_2 groups of allene become equivalent by virtue of proton transfer reactions, while in (b) it is the central carbon of allene which loses its identity. Thus the two pathways can be distinguished by specifically labeling either the CH or CH_2 groups in the allenyl anion. This would be exceedingly difficult to accomplish with ^{13}C-labeling; however specific labeling of the CH group with methyl is simple, as shown in eq 15.

$$\mathrm{CH_3{-}C{\equiv}C{-}CH_3 \xrightarrow{H\bar{O}} \bar{C}H_2{-}C{\equiv}C{-}CH_3 \longleftrightarrow CH_2{=}C{=}\bar{C}{-}CH_3} \qquad (15)$$

The predicted results of the reaction of this 1-methyl allenyl anion by the two paths of Scheme II is shown in Scheme III. If path (a) is followed, the ion-dipole complex analogous to **7a** will be formed, and proton transfer reactions should generate a mixture of the ions, leading to the formation of both the thioketenyl anion and the methyl thioketenyl anion. However if path (b) is followed, the cyclic intermediate analogous to **8** will decompose exclusively to the methyl thioketenyl anion. When the reaction was carried out in the FA-SIFT, the methyl thioketenyl anion was formed in 95% yield, and the thioketenyl anion signal was less than 5%. In addition there was a small amount of the adduct with loss of hydrogen sulfide.

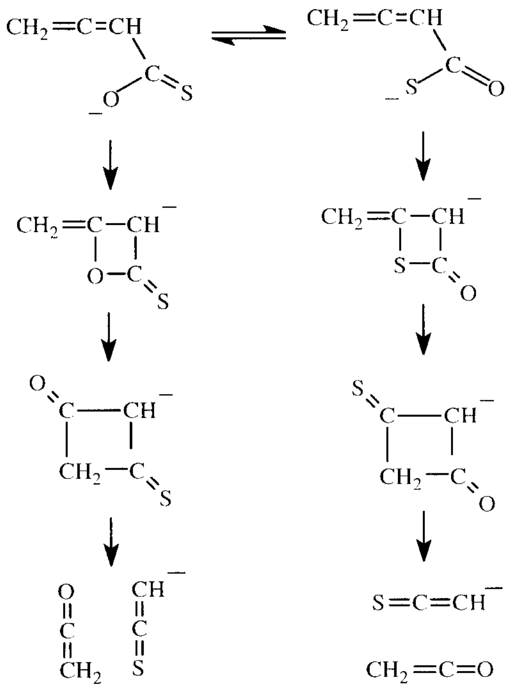
Scheme III



Thus this experiment strongly supports path (b), and also supports the proposal that this reaction can be used to determine the site of deprotonation of unsymmetrical allenes (eqs. 6,7). To test this we injected hydroxide ion and added methyl allene at the beginning of the second flow tube. An anion of m/z 53, corresponding to the methyl allenyl anion, was formed quantitatively. Downstream CS_2 was added and the ions of m/z 57 (thioketenyl anion) and m/z 71 (methyl thioketenyl anion) were formed in the ratio of 35:65, indicating that abstraction from the 3-carbon occurs more rapidly than that from the 1-carbon. If rapid proton transfer reactions occurred in the product ion-dipole complex, the same >95:5 ratio would be expected as found for the 2-butyne experiment.

We next examined the reaction of labeled allenyl anion with COS, in which the thioketenyl anion is the sole cleavage product ion (eq. 11). We estimate that reaction leading to the formation of the thioketenyl anion and neutral ketene is exothermic by 16 kcal/mol, while formation of the ketenyl anion and thioketene is thermoneutral at best, and perhaps slightly endothermic. When uniformly labeled allenyl anion is used in this reaction, 60% of the thioketenyl anion contains the label and 40% is unlabeled. The mechanism of this reaction is complicated by the fact that after initial addition of COS to the allenyl anion, cyclization can occur either through the oxygen or through the sulfur atom, as shown in Scheme IV.

Scheme IV



When we examined the analogous reaction of the ketenyl anion with COS we found that cyclization through sulfur occurs four times more readily than cyclization through oxygen.[5] Note in Scheme IV that when cyclization occurs through oxygen, the thioketenyl anion formed contains only the CH group of allenyl anion, while the other carbon arises from COS. Therefore this ion will contain 1/3 of the label. When cyclization occurs through sulfur, both carbons of the thioketenyl anion originate in the allenyl anion, and so this ion will contain 2/3 of the label. If 80% of the reaction occurs by sulfur cyclization and 20% occurs by oxygen cyclization, as found in the case of the ketenyl anion, than the resulting thioketenyl anion will be 60% labeled and 40% unlabeled, exactly as found experimentally. Thus our mechanism is in good accord with the observed experimental results. Note that by either path in Scheme IV a substituent attached to the carbon bearing the negative charge in the allenyl anion will be incorporated into the thioketenyl anion. This mechanism therefore predicts that the methyl allenyl anion produced by proton abstraction from 2-butyne (eq. 15) should react with COS, as it does with CS_2, to form the methyl thioketenyl anion exclusively, and it does produce the same 95% yield of this ion. It is not clear whether the small amount of the thioketenyl anion produced in both reactions (<5%) is due to the presence of an impurity in the acetylene or whether it arises by isomerization in the proton abstraction reaction or during injection.

Finally, let us consider the reaction of the allenyl anion with CO_2. Note (eq. 12) that only an adduct is formed, with no cleavage to the ketenyl anion and ketene. Indeed such a cleavage reaction is predicted to be endothermic by 10 kcal/mol, indicating that the reaction should occur in the opposite direction (eq. 16). We therefore generated the ketenyl anion in the first flow tube, injected it and added neutral ketene to the second flow tube. A peak at m/z 39, characteristic of the allenyl anion, appeared in the spectrum. Since the allenyl anion is a stronger base than the ketenyl anion, and ketene is present in large excess in the flow tube, the allenyl anion is neutralized by an exothermic proton transfer reaction, and soon reaches a steady state concentration of about 10% under the reaction conditions employed.

$$\mathrm{O{=}C{=}CH^{-} + CH_2{=}C{=}O \longrightarrow CH_2{=}C{=}CH^{-} + CO_2} \qquad (16)$$

These reactions occur rapidly in the gas phase. It would be interesting to see if analogous reactions occur in solution. If so, it might be feasible to use allenes as protecting groups during syntheses and then to remove them by using one of these cleavage reactions, thus replacing the allene by a highly reactive thioketene group. In any event, these processes promise to be useful tools for determining ion structure in the gas phase.

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