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On the Isomerization of Dimethyl Carbonate and Its Mono-, Di-, and Trithio Analogs

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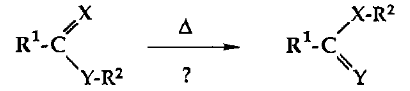
Gas-phase pyrolysis of dimethyl carbonate and its mono-, di-, and trithio analogs has been performed in the temperature range from 1253 to 1404 K applying the gas phase Curie-point pyrolysis technique. Real-time analyses have been carried out by means of mass-spectrometric techniques. The possible isomerizations of the ester functions have been studied by collisional activation mass spectrometry in combination with appropriate D, ^{18}O, and ^{34}S labeling. It is demonstrated that methyl group migrations can be induced pyrolytically in cases where oxygen-to-oxygen or oxygen-to-sulfur isomerizations are involved; in contrast, sulfur-to-oxygen as well as sulfur-to-sulfur isomerizations apparently do not take place.

In recent papers[2)-7)] we have reported on investigations of pyrolytically induced reactions of simple acetic acid esters and carbamic acid esters, as well as of the corresponding mono- and dithio analogs, in the dilute gas phase. Particular attention has been paid to the elucidation of the mechanism involved in 1,3-alkyl shifts in the ester function (eq. 1).

(1)



$R^1 = CH_3, (CH_3)_2N$; $R^2 = CH_3, C_2H_5$;

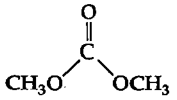
X/Y = O/O , O/S , S/O , S/S

In the case of esters with $R^2 = C_2H_5$ it should be noted that the well-established elimination of ethene, leading to the corresponding acid[8)], has been found to be the predominant reaction[3,4)].

Methyl acetate[2)] as well as methyl *N,N*-dimethyl carbamate[7)] undergo 1,3-methyl group migration. Analogously, rearrangements of the corresponding thiono esters to the thiolo esters have been observed, whereas the reverse rearrangement, i.e. thiolo-to-thiono conversion, has not been detected, in accordance with the approx. 20 kcal/mol stabilization of the thiolo esters relative to the corresponding thiono species[3,7)].

Surprisingly, however, we have not been able to induce 1,3-methyl group migration in dithioesters[6,7,9)], the compounds studied comprising, in addition to the above mentioned, methyl dithiobenzoate and methyl 3,3-dimethylbutanedithioate. The apparent lack of a 1,3-methyl group migration seems nevertheless, from a thermodynamical as well as a geometrical point of view, unexpected and is furthermore in contradiction to the results of semiempirical MO studies[10)].

In order to further elucidate the possible rearrangement reactions of the ester function, we here report on studies of the gas-phase pyrolysis of dimethyl carbonate (**1**) and the corresponding mono-, di-, and trithio analogs **2**–**6**.



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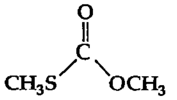

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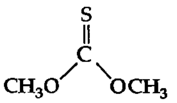

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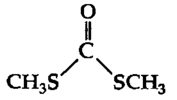

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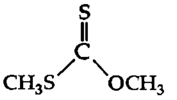

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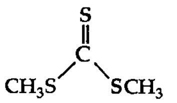

6

The pyrolyses have been carried out in the temperature range 1253–1404 K by applying the gas-phase Curie-point pyrolysis technique as described in detail in previous papers[11)-13)], using mass-spectrometric techniques (MS and MS/MS)[14,15)] in combination with specific ^2H, ^{18}O and ^{34}S labeling.

Results and Discussion

Dimethyl carbonate and the corresponding mono-, di-, and trithio analogs have been assumed to be thermally relatively stable, and gas-phase pyrolysis in the temperature

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range 1253–1404 K indeed leaves a significant amount of the intact ester which might be used for isomerization studies. However, pyrolysis leads to some decomposition of the carbonates, which, on the other hand, does not afford well-characterized organic molecules. Thus, the decomposition reactions have not been studied further.

To elucidate the possible pyrolytically induced isomerizations of the carbonates we have applied collisional activation mass spectrometry (CAMS)[16,17] on the electron-impact-induced molecular ions of the unlabeled compounds **1**–**6** as well as to appropriate isotopomers as a sensitive analytical technique[2,3,7,12]. Observed changes in the CA mass spectra of the molecular ions of apparently undecomposed starting material subsequent to pyrolysis can in general unambiguously be associated with a thermally induced intramolecular isomerization.

Dimethyl Carbonate (1)

The CA mass spectrum of the molecular ion of **1** (m/z = 90, $M^{+\bullet}$) exhibits two dominant peaks at m/z = 61 and 31, corresponding to $[M - HCO^{\bullet}]^+$ and CH_3O^+, respectively, the latter most probably exhibiting a CH_2OH^+ structure[18,19] (Figure 1a). Obviously, as the molecule contains three identical hetero atoms, an oxygen-to-oxygen methyl group migration would be detectable only if one of the oxygen atoms were labeled appropriately. Thus, we have specifically labeled one of the methoxy groups with ^{18}O. The CA mass spectrum of the resulting species **1'** (m/z = 92, $M^{+\bullet}$) reveals the expected splitting of the fragment ion peaks, i.e. m/z = 63/61 and m/z = 33/31 corresponding to $[M - HC^{16}O^{\bullet}/HC^{18}O^{\bullet}]^+$ and $CH_3{}^{18}O^+/CH_3{}^{16}O^+$, respectively (Figure 1b).

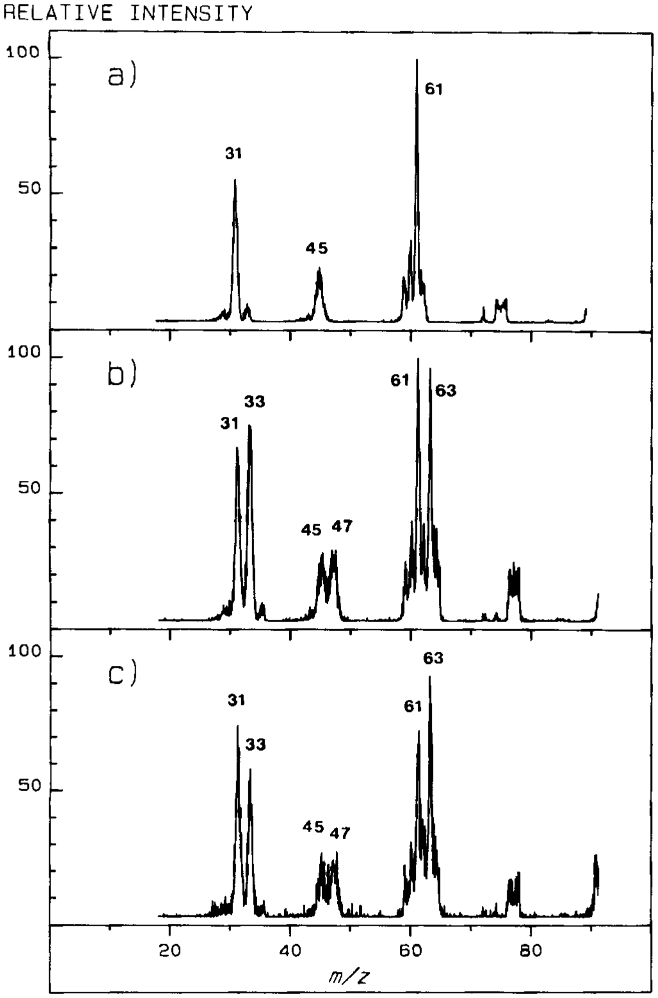


Figure 1. Collisional activation mass spectra of the molecular ions of a) **1**, b) **1'**, and c) **1'** after pyrolysis at 1404 K

After pyrolysis of **1'** at 1404 K, the CA mass spectrum of the species with m/z = 92 has changed significantly (Figure 1c). It is immediately seen that the original nearly 1:1 ratios of the peaks at m/z = 63/61 and m/z = 33/31 have now changed in favor of the peaks at m/z = 63 and m/z = 31 at the expense of those at m/z = 61 and m/z = 33, respectively.

Obviously the shift observed in the ratios of the peaks at m/z = 63/61 and m/z = 33/31 after pyrolysis can be rationalized in terms of an increased content of "$CH_3{}^{16}O$" relative to "$CH_3{}^{18}O$" in pyrolyzed **1'**. Consequently, we conclude that dimethyl carbonate is to some extent subject to a pyrolytically induced oxygen-to-oxygen methyl group migration. From Figure 1c is estimated that 38% of **1'** undergo a degenerate methyl group migration (eq. 2).

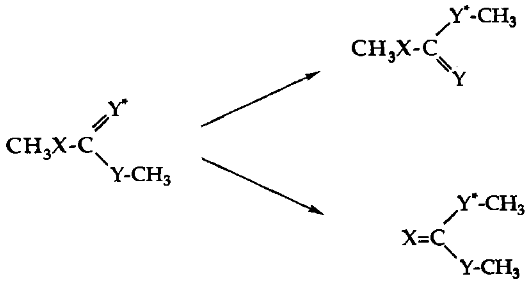
(2)


$$\mathrm{CH_3O\text{-}C(=O)\text{-}{}^{18}O\text{-}CH_3} \xrightarrow{\Delta} \mathrm{CH_3O\text{-}C(\text{-}O\text{-}CH_3)(={}^{18}O)}$$

1'

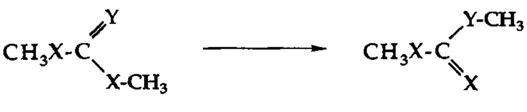
The apparent low conversion in the case of dimethyl carbonate is in accordance with the isomerization behavior found for methyl acetate[2].

In contrast to the simple acetic acid esters[3], the unsymmetrical mono- and dithio carbonates a priori may undergo two different isomerizations (eq. 3).

(3)


$$\mathrm{CH_3X\text{-}C(=Y^{*})\text{-}Y\text{-}CH_3} \longrightarrow \mathrm{CH_3X\text{-}C(\text{-}Y^{*}\text{-}CH_3)(=Y)}$$
$$\mathrm{CH_3X\text{-}C(=Y^{*})\text{-}Y\text{-}CH_3} \longrightarrow \mathrm{X{=}C(\text{-}Y^{*}\text{-}CH_3)(\text{-}Y\text{-}CH_3)}$$

On the other hand, on symmetrical grounds only one isomerization is possible in the case of the corresponding symmetrical carbonates (eq. 4).

(4)


$$\mathrm{CH_3X\text{-}C(=Y)\text{-}X\text{-}CH_3} \longrightarrow \mathrm{CH_3X\text{-}C(\text{-}Y\text{-}CH_3)(=X)}$$

Dimethyl Monothiocarbonates 2, 3

In the case of dimethyl monothiolocarbonate (**2**) a priori two possible isomerizations have to be looked for, i.e. a degenerate oxygen-to-oxygen and a sulfur-to-oxygen methyl group migration (**2** → **3**).

The CA mass spectrum (Fig. 2a) of **2** (m/z = 106, $M^{+\bullet}$) shows three dominant peaks at m/z = 75, 59, and 47 corresponding to $[M - CH_3O^\bullet]^+$, $[M - CH_3S^\bullet]^+$, and CH_3S^+, respectively. This spectrum has been found to be unambiguously distinguishable from that of the isomeric dimethyl monothionocarbonate (**3**), the latter (Figure 2b) exhibiting two signals at m/z = 76 and m/z = 61 corresponding to $[M - CH_2O]^{+\bullet}$ and $[M - CHS^\bullet]^+$, respectively.

In order to elucidate a possible oxygen-to-oxygen methyl group migration in **2**, we have studied the corresponding $^{18}OCH_3$-labeled isotopomer **2'**. As expected, the CA mass spectrum of **2'** (Figure 3a) shows three dominant peaks at m/z = 75, 61, and 47 corresponding to $[M - CH_3{}^{18}O^\bullet]^+$, $[M - CH_3S^\bullet]^+$, and CH_3S^+, respectively. After pyrolysis of **2'** at 1404 K the CA mass spectrum of the corresponding molecular ion peak at m/z = 108 reveals, in addition to the three above-mentioned peaks, originating from **2'**, a weak peak at m/z = 77 (Figure 3b), the latter being due to the loss of $CH_3{}^{16}O^\bullet$ from the rearranged isotopomer $CH_3SC(^{18}O)OCH^{+\bullet}$. Unfortunately, the quite poor signal-to-noise ratio of the relevant region at m/z = 75/77 of Figure 3b does not permit to quantify the extent of isomerization. The apparent absence, on the other hand, of peaks at m/z = 78, 76, and 63 in the spectrum of the pyrolyzate unambiguously rules out a possible thiolo → thiono rearrangement (**2** → **3**); this is in agreement with our previous studies on simple thiono and thiolo esters (eq. 5)[3,7].

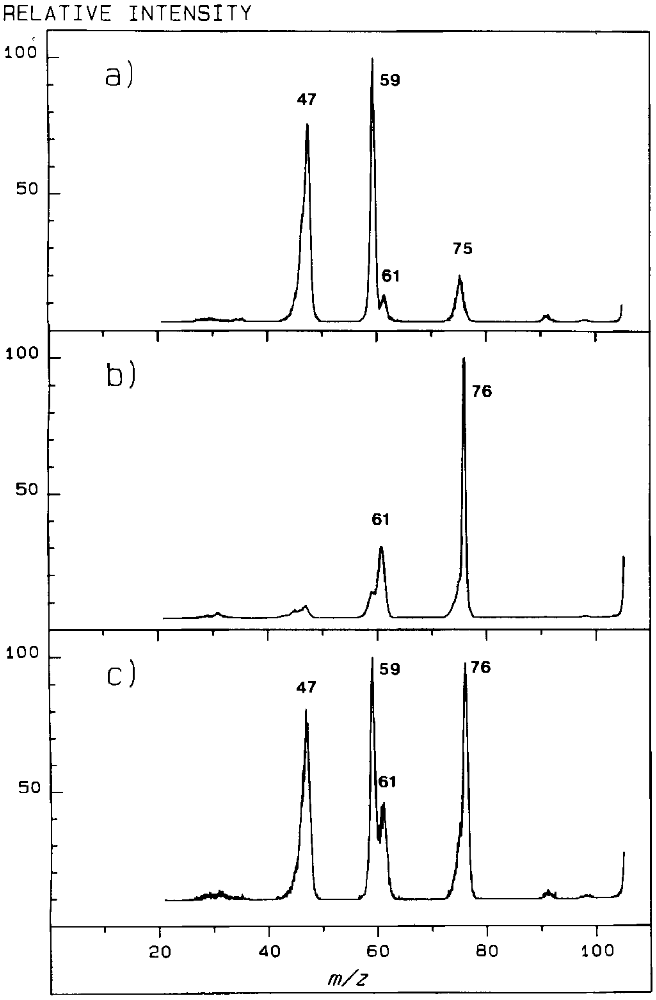
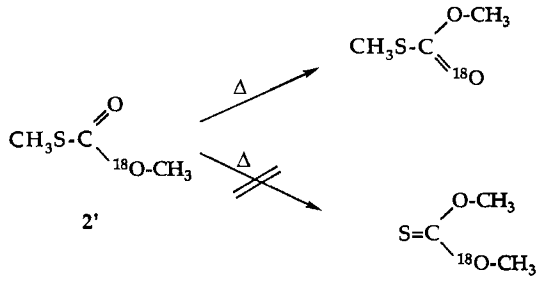


Figure 2. Collisional activation mass spectra of the molecular ions of a) **2**, b) **3**, and c) **3** after pyrolysis at 1253 K

(5)



2'

3'

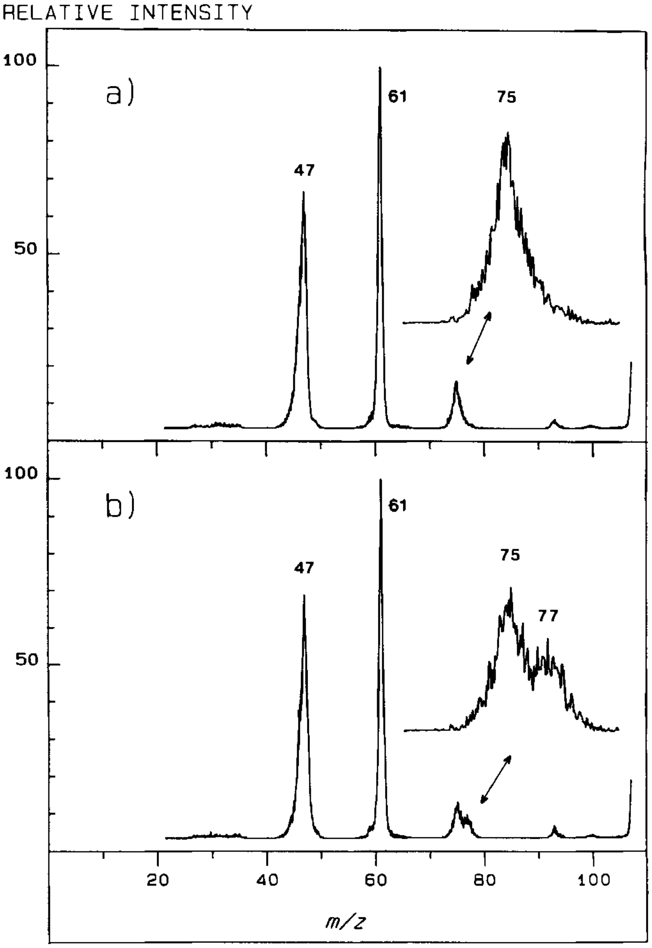
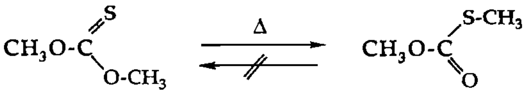


Figure 3. Collisional activation mass spectra of the molecular ions of a) **2'** and b) **2'** after pyrolysis at 1404 K

Returning to dimethyl monothionocarbonate (**3**) it has been, by analogy to methyl thionoacetate[3], to be expected that a thiono → thiolo rearrangement, i.e. **3** → **2**, prevails. An inspection of the CA mass spectrum (Figure 2c) of the species at m/z = 106 after pyrolysis of **3** at 1253 K reveals the presence of dominant peaks at m/z = 76, 75, 61, 59, and 47. The peaks are best explained in terms of a mixture of **3** (m/z = 76, 61) and **2** (m/z = 75, 59, 47). These findings together with the above described data for **2** clearly point to an irreversible operation of the reaction **3** → **2** (eq. 6).

(6)



3 **2**

Dimethyl Dithiocarbonates 4, 5

Based on our previous studies[3,7] as well as on the above-mentioned findings concerning the lack of evidence for a thiolo → thiono isomerization, we have not expected to observe a **4** → **5** isomerization. In fact, the CA mass spectrum (Figure 4a) of the molecular ion of **4** (m/z = 122, $M^{+\bullet}$) exhibits three dominant peaks at m/z = 94 ($[M - CO]^{+\bullet}$), m/z = 75 ($[M - CH_3S^{\bullet}]^+$), and m/z = 47 (CH_3S^+) in accordance with previously reported 70-eV mass spectra[20].

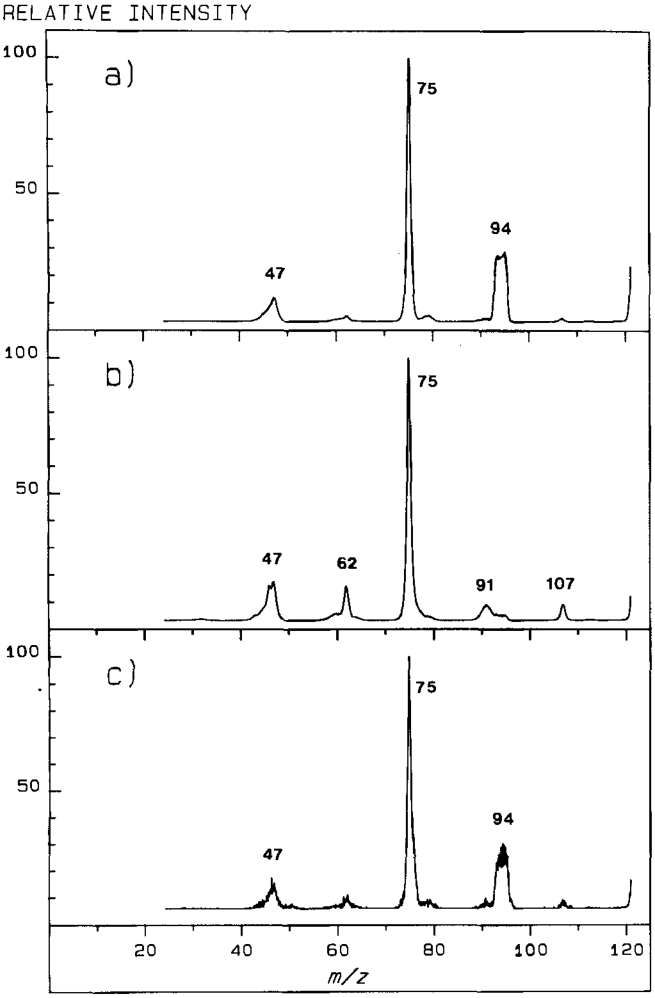


Figure 4. Collisional activation mass spectra of the molecular ions of a) **4**, b) **5** recorded before pyrolysis, and c) **5** after pyrolysis at 1253 K

No changes have been observed subsequent to pyrolysis, thus demonstrating the lack of isomerization of **4**.

Turning to the unsymmetrical dimethyl thiolothionocarbonate (**5**) we have again faced the possibility of two different isomerizations, i.e. an oxygen-to-sulfur and a degenerate sulfur-to-sulfur methyl group migration, the former leading to **4**.

The CA mass spectrum of the molecular ion of **5** (m/z = 122, $M^{+\bullet}$) exhibits two significant signals at m/z = 75 and m/z = 47 corresponding to $[M - CH_3S^{\bullet}]^+$ and CH_3S^+, respectively (Figure 4b). In addition, ion peaks at m/z = 107 and 62 resulting from the loss of $CH_3^{\bullet}$ and elimination of COS, respectively, are observed. The latter skeletal rearrangement has been discussed previously[20]. After pyrolysis at 1253 K the CA mass spectrum of the resulting ion with peak at m/z = 122 reveals an increase in intensity of the signal at m/z = 94 (Figure 4c). Thus, it seems obvious that an oxygen-to-sulfur methyl group migration had been induced leading to a mixture of **4** and **5** in the pyrolyzate. However, due to the identity of the two sulfur atoms a possible sulfur-to-sulfur migration must remain undetected.

Even the study of the $^{34}S{=}C$-labeled species **5'** has remained inconclusive (Figure 5). The CA mass spectrum of **5'** (m/z = 124, $M^{+\bullet}$) (Figure 5a) displays peaks at m/z = 77/75 ($[M - CH_3{}^{32}S^{\bullet}/CH_3{}^{34}S^{\bullet}]^+$) and 49/47 ($CH_3{}^{32}S^+/$

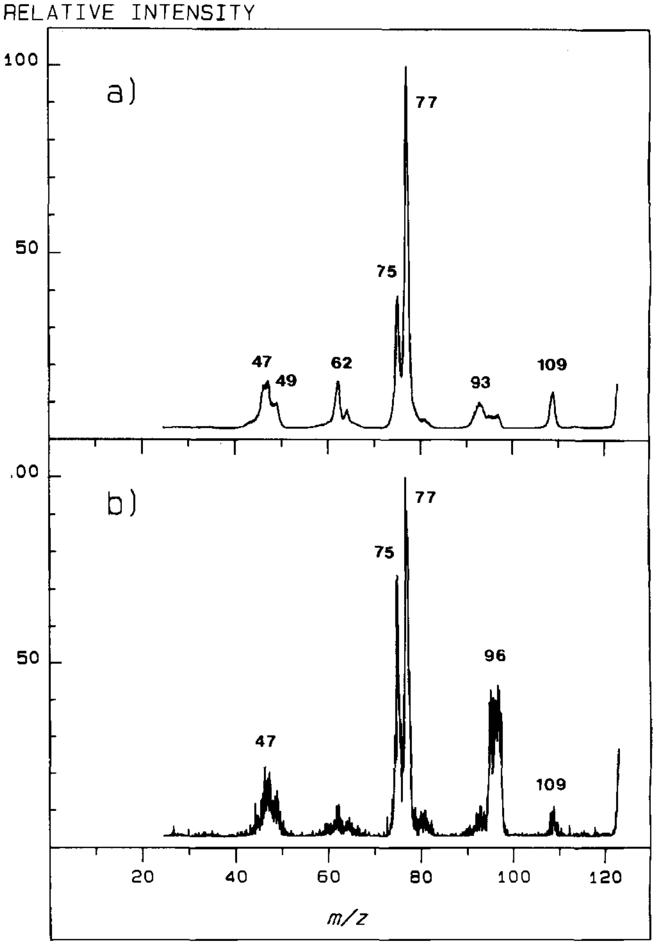


Figure 5. Collisional activation mass spectra of the molecular ions of **5'** recorded a) before and b) after pyrolysis at 1253 K

$CH_3{}^{34}S^+$), respectively. The measured intensity ratio (3:1) of the peaks at $m/z = 77/75$ reflects the actual labeling of the thiocarbonyl group, which amounts to ca. 50%. Thus, it can be concluded that randomization of the sulfur atoms in the ionized state takes place to a negligible extent only, in contrast to the thiono-to-thiolo rearrangement apparently observed for aryl-substituted carbonates[21]. An equivalent splitting is observed for the peaks at $m/z = 47/49$ and 62/64. Upon pyrolysis (1253 K) the spectrum of the ion with peak at $m/z = 124$ is changed as depicted in Figure 5b. The expected peak at $m/z = 96$ ($[M - CO]^{+\bullet}$) develops simultaneously with a relative increase of the ion peak at $m/z = 75$ ($[M - CH_3{}^{34}S^\bullet]^+$).

Further evidence for the thermally induced oxygen-to-sulfur methyl group migration is obtained by studying the OCD_3 isotopomer **5″**. The corresponding CA mass spectrum of the molecular ion ($m/z = 125$, $M^{+\bullet}$), shown in Figure 6a, exhibits the dominant peak at $m/z = 78$ ($[M - CH_3{}^{32}S^\bullet]^+$) in addition to ion peaks corresponding to loss of $CH_3^\bullet$ ($m/z = 110$) and COS ($m/z = 65$). It should be noted that the loss of methyl originates exclusively from the thiomethyl group. The CH_3S^+ ion peak appears as a doublet ($m/z = 47/50$), the two signals exhibiting distinctly different peak shapes indicating individual pathways for the formation of CH_3S^+ and CD_3S^+. After pyrolysis (1253 K) the characteristic peak at $m/z = 97$ ($[M - CO]^{+\bullet}$) in addition to the appearance of that at $m/z = 75$ is observed; the latter signal corresponds to $[M - CD_3S^\bullet]^+$ (Figure 6b). It should be noted that no splitting of the ion peaks at $m/z = 110$ and 65 is observed after pyrolysis, which is in full agreement with the fragmentation pattern of **4** (Figure 4a). Thus, the ion peaks at $m/z = 110$ and 65 observed after pyrolysis originate exclusively from unpyrolyzed **5″**. No information can be obtained from the CH_3S^+/CD_3S^+ doublet, due to the presence of equivalent signals ($m/z = 47$ and 50) before pyrolysis.

The final answer as to whether a concurrent sulfur-to-sulfur methyl group migration occurs as well is obtained by studying the $^{34}S{=}C/OCD_3$ doubly labeled isotopomer **5‴**. Prior to pyrolysis the CA mass spectrum of the molecular ion of **5‴** ($m/z = 127$, $M^{+\bullet}$) exhibits the peaks at $m/z = 80/78$ corresponding to $[M - CH_3{}^{32}S^\bullet/CH_3{}^{34}S^\bullet]^+$, the presence of the ion peak at $m/z = 78$ again reflecting the actual ^{34}S labeling of the thiocarbonyl group of ca. 50% (vide supra) (Figure 7a). The formation of the ions with peak at $m/z = 112$, 65/67, and 47–52 is due to the loss of methyl and COS, respectively, and CH_3S^+, as discussed above. After pyrolysis (1253 K) the spectrum of the ion with peak at

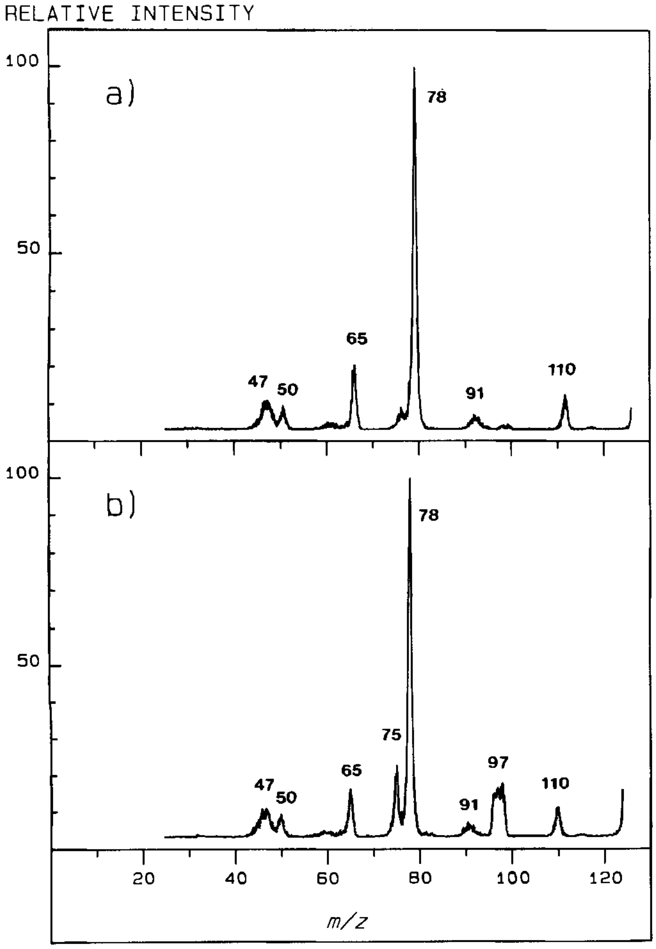


Figure 6. Collisional activation mass spectra of the molecular ions of **5″** recorded a) before and b) after pyrolysis at 1253 K

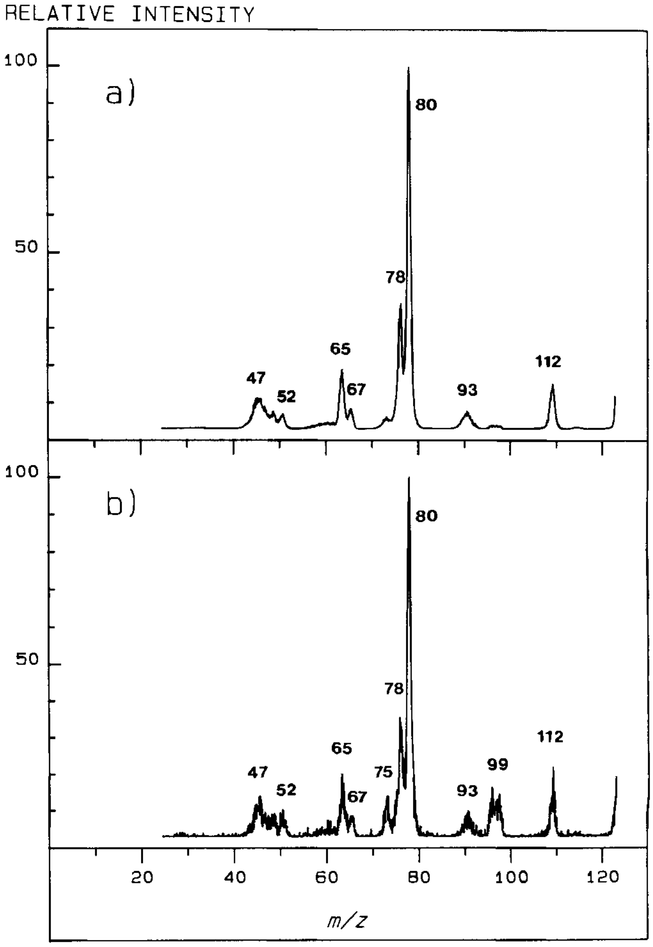
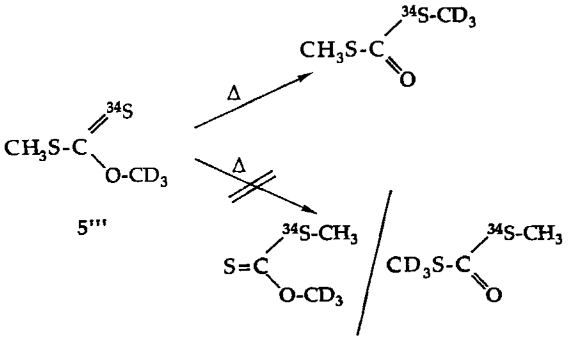


Figure 7. Collisional activation mass spectra of the molecular ions of **5‴** recorded a) before and b) after pyrolysis at 1253 K

$m/z = 127$ exhibits, in addition to the characteristic ion peak at $m/z = 99$ ($[M - CO]^{+\bullet}$), a peak at $m/z = 80/78/75$, the latter being attributed to the loss of $CH_3{}^{32}S^\bullet/CH_3{}^{34}S^\bullet/CD_3{}^{34}S^\bullet$ (Figure 7b).

Since a possible sulfur-to-sulfur methyl group migration would lead to an increase in the intensity of the peak at $m/z = 78$ relative to that of the peak at $m/z = 80$ (which is *not* observed), we conclude that only an oxygen-to-sulfur methyl group migration prevails (eq. 7).

(7)

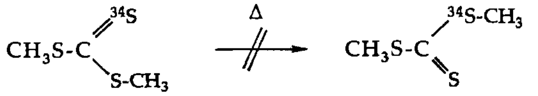


5'''

Dimethyl Trithiocarbonate (6)

An apparent lack of isomerization of simple dithioesters[6,7,9] has been expected to prevail in the case of dimethyl trithiocarbonate as well. The CA mass spectrum of the molecular ion of the carbonate **6** ($m/z = 138$, $M^{+\bullet}$) reveals a single dominant peak at $m/z = 91$ corresponding to $[M - CH_3S^\bullet]^+$. In order to elucidate whether a sulfur-to-sulfur methyl group migration takes place, we have studied the $^{34}S{=}C$-labeled isotopomer **6'** ($m/z = 140$, $M^{+\bullet}$). The corresponding CA mass spectrum of the molecular ion displays peaks at $m/z = 93$ and 91 corresponding to $[M - CH_3S^\bullet]^+$ and $[M - CH_3{}^{34}S^\bullet]^+$, respectively, the intensity of the latter being due to the abundance of ^{34}S in the CH_3S group. An inspection of the CA mass spectrum of the ion with peak at $m/z = 140$, after pyrolysis, does not disclose any relative increase of the ion peak at $m/z = 91$, which would indicate a sulfur-to-sulfur migration. Hence, we conclude that also in the case of dimethyl trithiocarbonate, a thermally induced sulfur-to-sulfur methyl group migration is not operative (eq. 8).

(8)



6'

The final answer to the question concerning the origin of the effects reported in the present study is still pending.

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Experimental

The carbonates **1**–**5** were prepared from the appropriate chloroformate and methanol. Compound **4** was isolated in moderate yield as a by-product from the synthesis of **2**. The trithiocarbonate **6** was kindly supplied by Dr. *L. Henriksen*, Department of General and Organic Chemistry, H. C. Ørsted Institute, University of Copenhagen.

The CD_3- and ^{18}O-labeled compounds were prepared analogously by application of CD_3OD and $CH_3{}^{18}OH$, respectively. The latter was obtained from the Ag_2O-catalyzed hydrolysis ($H_2{}^{18}O$) of CH_3I[7].

The ^{34}S-labeled thiocarbonates were prepared by specific exchange of the thiono sulfur atom with $^{34}S_8$ in an evacuated and sealed glass ampoule (100°C, 16 h)[6,7].

All compounds were purified by preparative GC (2 m × 6 mm 10% Silar 10CP on Gas Chrom Q, 100/120 mesh).

The mass-spectrometric investigations were carried out by using a Varian MAT CH 5D double-focussing spectrometer equipped with a combined EI/FI/FD ion source.

Collision activation was carried out on 70-eV electron-impact-induced molecular ions in the second field-free region by introducing He as target gas[11,12]. The CA spectra were not corrected for unimolecular processes.

Low-pressure pyrolysis was carried out by using the gas-phase Curie-point technique as described previously in detail[11,12]. Gold-plated filaments[13] were applied to suppress possible surface-promoted reactions.

All data were obtained with an HP3497A data acquisition/control unit and an HP3956A digital voltmeter and processed by an HP9836 computer. Signal averaging and digital filtering were applied in order to study weak signals.

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