Gas-phase Pyrolysis of Methyl Dimethylcarbamate and the Corresponding Mono- and Dithio Analogs[1]

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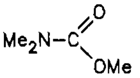
Gas-phase pyrolysis of methyl dimethylcarbamate (**1**), *O*-methyl dimethylthiocarbamate (**2**), *S*-methyl dimethylthiocarbamate (**3**), and methyl dimethyldithiocarbamate (**4**) has been carried out in the temperature range 1043 – 1404 K applying the gas-phase Curie-point pyrolysis technique. Real-time analyses of the pyrolyses were carried out by field ionization- and collision activation mass spectrometry. **1** and **4** were found to be thermally very stable even after pyrolysis at 1404 K. *N*-Methyl methanimine was found in moderate yield following pyrolysis of **2** and **3**. The possible isomerization of the ester functions were studied by application of collision activation mass spectrometry in combination with ^{18}O and ^{34}S labeling. The results are discussed considering available data on the simple acetic acid esters with special emphasis on the effect of increasing sulfur content.

Gasphasen-Pyrolyse von Methyl-dimethylcarbamat und den entsprechenden Mono- und Dithio-Analogen[1]

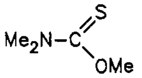
Die Gasphasen-Pyrolyse von Methyl-dimethylcarbamat (**1**), *O*-Methyl-dimethylthiocarbamat (**2**), *S*-Methyl-dimethylthiocarbamat (**3**) und Methyl-dimethyldithiocarbamat (**4**) wurde im Temperaturbereich 1043 – 1404 K mit Hilfe der Gasphasen-Curie-Punkt-Pyrolysetechnik untersucht. Echtzeit-Analysen der Pyrolysen wurden mit Feldionisierungs- und Stoßaktivierungs-Massenspektrometrie durchgeführt, **1** und **4** sind thermisch sehr stabil, sogar nach Pyrolyse bei 1404 K. Nach Pyrolyse von **2** und **3** wurde *N*-Methylmethanimin in kleinen Ausbeuten gefunden. Eine mögliche Isomerisierung der Esterfunktionen wurde durch Kombination von Stoßaktivierungs-Massenspektrometrie mit ^{18}O- und ^{34}S-Markierung untersucht. Die Ergebnisse werden unter Einbeziehung von Daten einfacher Essigsäureester diskutiert mit besonderer Betonung des Effektes des zunehmenden Schwefelgehaltes.

In contrast to carboxylic acid esters[2] gas-phase pyrolytic reactions of simple carbamates have been investigated only scarcely, the studies being limited to *N*-mono substituted and *N,N*-disubstituted systems exhibiting a β-hydrogen in the ester function[3]. In these cases the reaction pattern is dominated by the well-known β-elimination of an alkene[3c,d,e,g] and, when *N*-monosubstituted carbamates are studied, formation of isocyanates[3a,f].

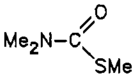
As a part of our continuing interest in the pyrolytically induced intramolecular rearrangements/isomerizations of simple carboxylic acid esters[4] and the corresponding mono-[5] and dithio[6] derivatives we here report on the unimolecular gas-phase pyrolyses of methyl dimethylcarbamate (**1**) and the corresponding mono- and dithio derivatives (**2** – **4**).


$Me_2N-C(=O)OMe$

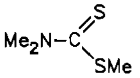
1


$Me_2N-C(=S)OMe$

2


$Me_2N-C(=O)SMe$

3


$Me_2N-C(=S)SMe$

4

The pyrolyses were carried out in the temperature range 1043 – 1404 K applying the gas-phase Curie-point pyrolysis technique described in detail in previous papers[7,8], using field ionization- and collission-activation mass spectrometry as detection technique.

Results and Discussion

Gas-phase pyrolysis of the carbamates **1** and **4** at 1043 K gave rise to only very minor decompositions of the compounds. In the case of **1** minor amounts of formaldehyde and methyl isocyanate was observed, whereas **4** gave rise to *N*-methyl methanimine and dimethyl sulfide. A somewhat higher thermal lability was observed for the monothiocarbamates **2** and **3**, which upon pyrolysis afforded significant amounts of *N*-methyl methanimine in addition to very minor amounts of methyl isocyanate, methyl isothiocyanate, and dimethyl sulfide. However, in all four cases the major fraction of the starting material apparently passed through the pyrolysis reactor without decomposition as demonstrated by the appearence of molecular ions of high intensity in the field ionization mass spectra recorded after pyrolysis ($M^{+\bullet}$ **1**: 103, **2**: 119, **3**: 119, and **4**: 135).

In order to elucidate the possible operation of pyrolytically induced isomerizations/rearrangements, i.e. to disclose the actual identity of the species giving rise to the molecular ions observed following pyrolysis, we studied the collision activation (CA) mass spectra of the electron impact-induced molecular ions of the carbamates **1** – **4** before and after pyrolysis.

In analogy to the isomerization/rearrangement of simple acetic acid esters[4,5] it was a priori expected that a methyl group migration between the two hetero atoms in the ester function could be provoked.

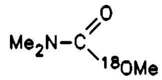

$Me_2N-C(=X)YMe \rightleftharpoons Me_2N-C(=XMe)Y$

A B

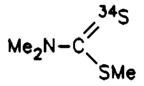
X/Y = O/O, S/O, O/S, S/S

Chem. Ber. **120**, 987 – 990 (1987) 0009 – 2940/87/0606 – 0987 $ 02.50/0

Obviously, a possible interconversion of the two monothiocarbamates **2** and **3** easily can be verified due to the different identity of the A and B systems. On the other hand, A will be identical to B in the cases of **1** (X = Y = O) and **4** (X = Y = S). However, in these cases an artificial difference between the A and B systems was introduced by isotopic labelling: **1′** (X = O, Y = ^{18}O), **4′** (X = ^{34}S, Y = S).

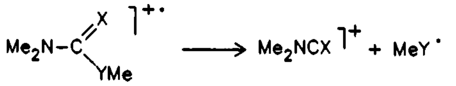


1′



4′

Hence, we were able to distinguish the A and B systems in all four cases based on the significant fragmentation observed in the CA mass spectrum.



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

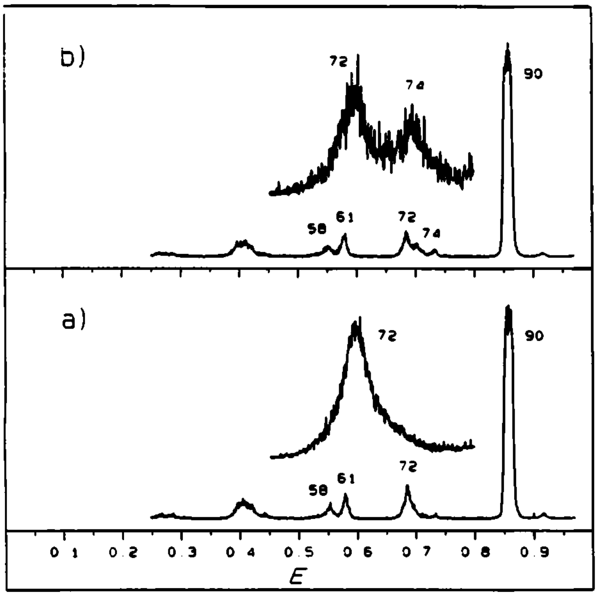
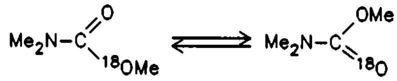


Figure 1. Collision-activation mass spectra of the electron-impact induced molecular ion *m/z* 105 a) before and b) after pyrolysis of ^{18}O-labelled methyl dimethylcarbamate (**1′**) at 1404 K (Co surface)

In Figure 1 the collision-activation mass spectra of the molecular ion *m/z* 105 of **1′** before and after pyrolysis at 1404 K are depicted. The CA analysis of the unpyrolysed carbamate disclosed the peak *m/z* 72 corresponding to Me_2NCO^+ (Fig. 1a) in accordance with the above fragmentation scheme. After pyrolysis the signal unambiguously turns up as a doublet exhibiting *m/z* values of 72 and 74 corresponding to Me_2NCO^+ and $Me_2NC^{18}O^+$, respectively. Hence, analogous to our previous results on methyl acetate pyrolysis[4], we conclude that pyrolytically induced isomerization of methyl dimethylcarbamate (**1**) occurs.



As in the case for simple monothioesters[5] the *S*-methyl thiocarbamate **3** is expected to be thermodynamically more stable than the corresponding *O*-methyl isomer **2**. This assumption is nicely verified by studying the gas-phase pyrolysis of the two monothiocarbamates **2** and **3**. In Figure 2 CA mass spectra of the electron impact-induced molecular ions of **2** (Fig. 2a) and **3** (Fig. 2c) are depicted together with that recorded of *m/z* 119 following pyrolysis of **2** at 1043 K (Fig. 2b).

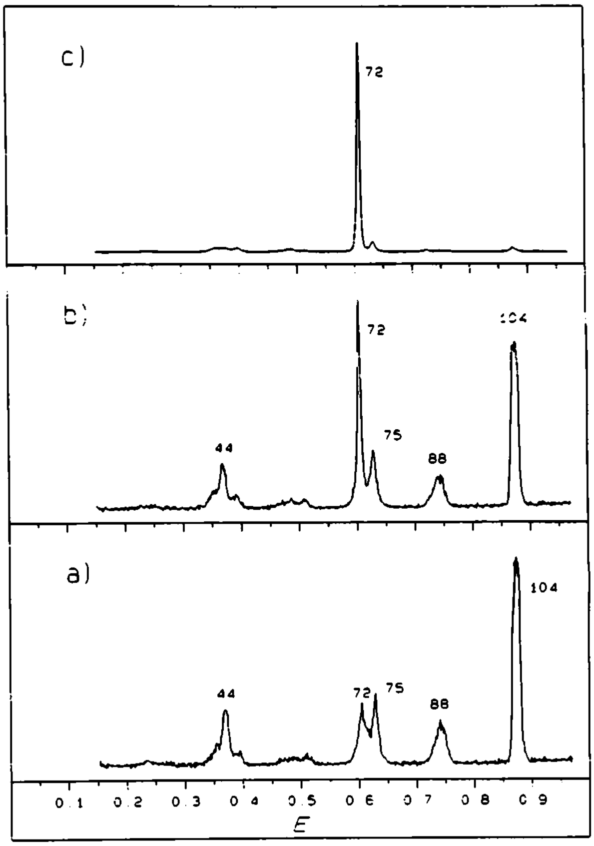
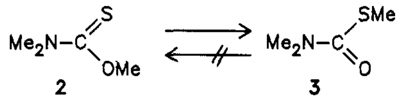


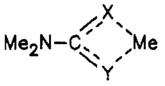
Figure 2. Collision-activation mass spectra of the electron impact-induced molecular ion *m/z* 119 a) before and b) after pyrolysis of *O*-methyl dimethylthiocarbamate (**2**) at 1043 K (Au surface) and of c) *S*-methyl dimethylthiocarbamate (**3**)

Obviously, the *O*-methylthiocarbamate **2** undergoes a rather high degree of rearrangement into the corresponding *S*-methyl isomer **3** upon pyrolysis, as unambigously demonstrated by the spectrum depicted in Fig. 2b), the appearance of which is rationalized as a superposition of the two CA spectra of the pure thiocarbamates **2** and **3**, respectively. In accordance with the assumed thermodynamical stability of **3** relative to **2**, pyrolysis of the *S*-methyl thiocarbamate **3** did not lead to any formation of **2**. Thus, the results are in close agreement with our previous studies on monothioacetic acid esters[5].



Due to the unimolecular nature of pyrolytic reactions studied by the gas-phase Curie-point pyrolysis technique[7a], the above studied rearrangements of the carbamates **1**, **2**, and **3** of necessity proceed via a four-membered transition state **C**, the latter being established by a "hand-to-hand" movement established by combination of $\sphericalangle$XCY and $\sphericalangle$CYC bends (cf. ref.[4]).

C



Remaining to be discussed is the pyrolytic behaviour of the dithiocarbamate **4**. Based on simple geometric considerations as well as semi-empirical MNDO calculations, the isomerization of methyl dithioacetate was predicted to be easily achieved, the activation energy being approximately 85 kJ/mol lower than that of methyl acetate[4,6,9]. Probably the same prevails in the case of **4**. The apparent lack of isomerization of methyl dithioacetate[6] could be explained by operation of an alternative rearrangement leading to an enethiolized structure blocking the S to S methyl group migration. However, disclosing the lack of isomerization in methyl dithioacetate as well as in methyl 2,2-dimethyldithiopropanoate[9] strongly indicated that the enethiolization apparently is not the complete explanation. In this context **4** constitutes an alternative approach by exhibiting a different substitution at the acid carbon. However, scrutiny of the CA mass spectrum of the molecular ion *m/z* 137 of the ^{34}S-labelled dithiocarbamate **4'** before and after pyrolysis at 1404 K (Fig. 3) unequivocally demonstrates the lack of isomerization, since the peak *m/z* 90 ($Me_2NC^{34}S^+$) in the case of isomerization would appear as a doublet *m/z* 90 ($Me_2NC^{34}S^+$) and *m/z* 88 (Me_2NCS^+) after pyrolysis, which appears not to be the case.

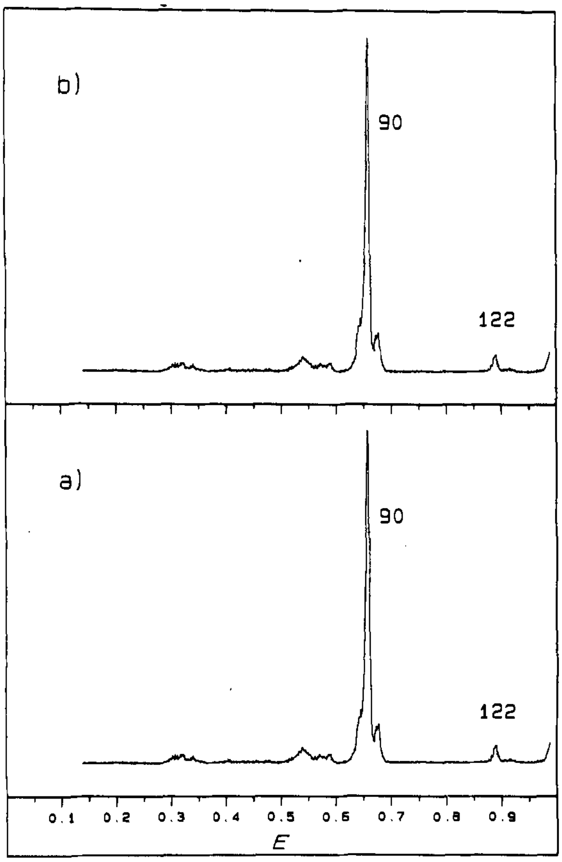
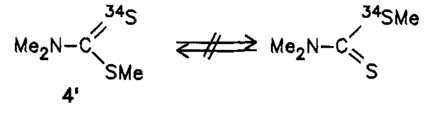


Figure 3. Collision-activation mass spectra of the electron impact-induced molecular ion *m/z* 137 a) before and b) after pyrolysis of ^{34}S-labelled methyl dimethyldithiocarbamate (**4'**) at 1404 K (Co surface)

Hence, we must conclude that the dithiocarbamate **4** does not isomerize under the conditions applied here.



The eventual answer to this question is still pending.

Experimental

Methyl dimethylcarbamate (**1**) was prepared from Me_2NCOCl and MeOH; the crude product was purified by distillation. The ^{18}O labelled carbamate (**1'**) was prepared analogously with $Me^{18}OH$. The latter was obtained from the Ag_2O-catalyzed hydrolysis of CH_3I and isolated by preparative GC (column: 2 m × 6 mm Porapak Q (50/80 mesh) at 150°C).

The sulfur containing carbamates **2**–**4** were prepared from Me_2NH and the corresponding methyl chloroformate. The *O*-methyl thiocarbamate **2** was isolated by preparative GC [column: 2 m × 6 mm, 10% Silar 10 C on Gas Chrom Q (100/120 mesh) at 160°C], whereas **3** and **4** were purified by distillation and crystallization, respectively.

The ^{34}S-labelled dithiocarbamate (**4'**) was prepared by the specific exchange of the thionosulfur of **4** with $^{34}S_8$ in an evacuated and sealed glass ampule (100°C, 16 h) (cf. ref.[6]).

The *flash vacuum pyrolysis experiments* were carried out by the techniques described in previous papers[7–10]. Product compositions were obtained by field-ionization mass spectrometry[7a]; possible isomerization reactions were studied by collision-activation mass spectrometry of the electron impact-induced molecular ions[7b].

CAS Registry Numbers

1: 7541-16-4 / **1'**: 107300-83-4 / **2**: 16703-45-0 / **3**: 3013-02-3 / **4**: 3735-92-0 / **4'**: 107300-84-5 / $MeN=CH_2$: 1761-67-7 / Me_2NCOCl: 79-44-7 / $Me^{18}OH$: 5770-05-8 / MeI: 74-88-4 / Me_2NH: 124-40-3 / ClC(S)OMe: 2812-72-8 / ClC(O)SMe: 18369-83-0 / $ClCS_2Me$: 16696-91-6

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