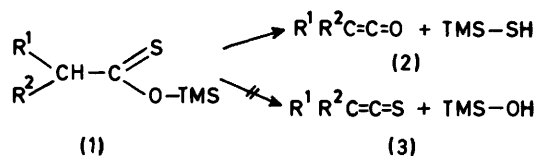


Gas-phase Thermolyses. Part 8.¹ Gas-phase Thermolysis of Methyl and Ethyl Monothioacetates ²

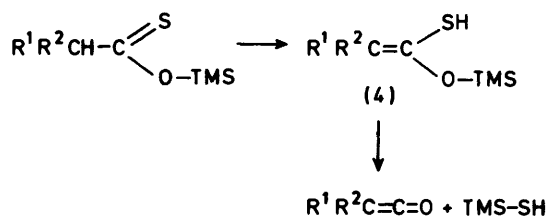
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The unimolecular gas-phase thermolyses of the four methyl and ethyl monothioacetates (5)–(8) have been studied by the flash vacuum thermolysis–field ionization mass spectrometry technique in the temperature range 883–1 404 K. The types of reactions verified were keten formation, thiono–thiolo rearrangement, and, in the case of the ethyl esters, ethylene elimination. The possible mechanisms for keten formation are discussed, and it is concluded that the thiono–carboxylates eliminates the mercaptan *via* an enethiolized structure, whereas the decomposition of the thio–esters apparently proceeds *via* direct 1,2–elimination of the thiols.

RECENTLY, we investigated the unimolecular gas phase thermolytic decomposition of a series of trimethylsilyl thionocarboxylates (1) in an attempt to study the possible application to thioketen synthesis.³ However, the conclusion was rather surprising, as we found the major products to be the corresponding ketens (2), whereas only very minor amounts of the thioketens (3) were generated. A possible explanation of this reaction,

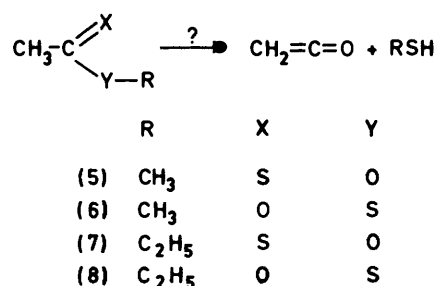


involving a primary rearrangement to the corresponding thio–ester, followed by an immediate, and quantitative rethermolysis, was ruled out, partly based on an estimate of the thermodynamics of the former reaction. Assuming $\Delta H_r \approx \Delta G_r \approx -62 \text{ kJ mol}^{-1}$ (*i.e.* $\Delta S_r \approx 0$)⁴ for the thio–thiono rearrangement, the equilibrium constant for the thiono–thiolo system can, according to the van't Hoff equation, be calculated to be $\log_e K(293 \text{ K}) \approx 25$ and $\log_e K(1 043 \text{ K}) \approx 7$, respectively, *i.e.* even at very elevated temperatures the thiono–esters will be the thermodynamically more favourable isomers. On this background we concluded that the ketens most probably were generated directly from the thiono–carboxylates. The mechanism was tentatively formulated to involve an enethiolized intermediary structure (4).



Although the gas-phase thermolyses of some thiono– and thio–esters have been reported previously,^{5,6} we here report, initiated by the above study, on the pure unimolecular gas-phase thermolyses of the simple methyl

and ethyl monothioacetates (5)–(8), focusing on possible keten formation.



EXPERIMENTAL

The esters (6) and (8) were synthesized by alkylation of thioacetic acid by methyl and ethyl iodide, respectively. Compound (6) had b.p. 97–98 °C (lit.,⁷ 98 °C) and (8) b.p. 115–116 °C (lit.,⁷ 116.4 °C). Compounds (5)⁸ and (7)⁹ were synthesized according to previously described methods.

Flash Vacuum Thermolysis.—The thermolyses were carried out using the flash vacuum thermolysis–field ionization mass spectrometry (*f.v.t.–f.i.m.s.*) technique, which has been described in detail previously.¹⁰ The method is based on a direct combination of a thermolysis unit fulfilling the requirements for a Knudsen reactor, with a Varian MAT CH 5D double focusing mass spectrometer equipped with a combined electron impact ionization–field ionization–field desorption (*e.i.–f.i.–f.d.*) ion source. The *f.i.* spectra after thermolysis were recorded with a scan rate of 50–100 a.u. s⁻¹ (signal-to-noise >1 000).

Collision activation mass spectra¹¹ were obtained by introducing helium as the collision gas *via* a needle valve into the second field-free region of the mass spectrometer. The collision gas is admitted as a molecular gas beam focused on the ion beam just behind the intermediate focus slit. The *c.a.* spectra of the single ions were obtained by scanning the electrostatic field.

The *c.a.m.s.* analyses of the thermolysate mixtures are generally carried out on the single field ionized molecules.¹⁰ However, the compound exhibiting the highest molecular weight in the reaction mixture, *i.e.* in the present case the undecomposed esters, may advantageously be analysed by *c.a.m.s.* of the molecular ion in the electron impact induced mass spectrum, as this ion evidently is not a result of *e.i.* induced fragmentation. The sensitivity of the *c.a.m.s.* analysis is hereby enhanced strongly. The *c.a.m.s.* spectra

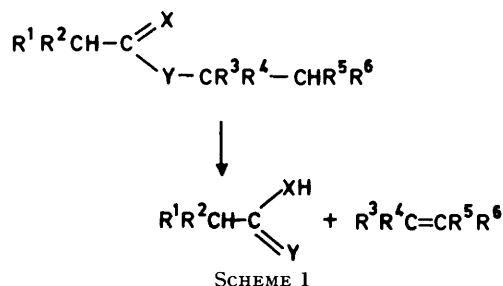
of the single ions are recorded within 5 s [signal-to-noise *ca.* 50 (f.i.-c.a.m.s.), >1 000 (e.i.-c.a.m.s.)].

The relative e.i.-c.a.m.s. and f.i. sensitivities of the single compounds available were determined using the gas inlet system of the mass spectrometer. The relative ester f.i. sensitivities were found to be: thiono/thiolo 1.7; the sensitivity of ethylene was calculated to be 0.07 relative to ethyl thionoacetate. Additionally, it should be mentioned that the thiono- and thiolo-esters exhibit equal e.i.-c.a.m.s. sensitivities.

In the present work the thermolysis unit was slightly modified compared to the original version¹⁰ as the injection block was substituted by a 100 ml glass bulb connected to the reactor *via* a glass capillary leak, the leak rate being equal to *ca.* 5×10^{-3} Torr l s⁻¹. Samples of *ca.* 10 μ l of the single esters were introduced into the evacuated bulb. This set-up is advantageous for recording c.a. spectra, as it allows a continuous flow of thermolysis products into the ion source; it is, however, only suitable for compounds with rather high vapour pressures.

RESULTS AND DISCUSSION

During the past decades the gas-phase thermolyses of alkyl carboxylates, as well as the corresponding monothio derivatives, have been studied intensively.^{5,6,12} However, the investigations have almost exclusively been limited to compounds possessing a β -hydrogen atom in the ester alkyl group, in order to elucidate the elimination of alkenes from these esters to yield the corresponding acids (Scheme 1). In contrast to this, methyl esters



have only been studied rarely,^{5,13,14} apparently due to their lack of ability to undergo a similar reaction. In no cases thermolyses under pure molecular conditions have been reported. From a very recent study on the unimolecular gas-phase thermolysis of methyl acetate in the temperature range 1 043–1 404 K we concluded that the predominant reaction is an oxygen–oxygen methyl group migration accompanied by very minor amounts of keten formation only.¹⁵

Thermolysing (5) and (6) at 1 043 K resulted in the development of nearly identical spectra (Figure 1). In both cases the major products are keten (9) (*M* 42) and methanethiol (10) (*M* 48). The low intensity peak at *m/z* 58, which *a priori* could be explained as a minor amount of thioketen, was, upon high resolution, surprisingly found to be a C₃H₆O isomer, the unimolecular

* A possible candidate is acetone; however, owing to the very minor amounts of C₃H₆O formed, we were unable to obtain satisfactory c.a. spectra to elucidate the actual structure (*cf.* ref. 11b).

formation of this compound, however, at the present being unclear.*

It is observed (Figure 1) that considerable amounts of the esters (*M* 90) are recovered. In this connection it should be noted that Figure 1 is only a representation of the relative product distributions following thermolyses

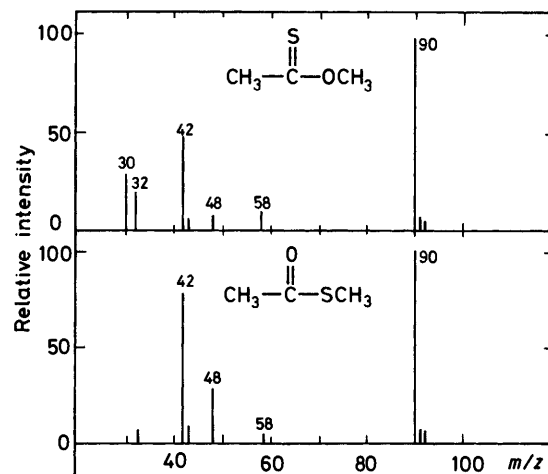
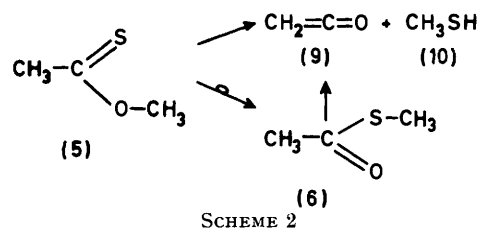


FIGURE 1 Field-ionization mass spectra of methyl thionoacetate and methyl thioloacetate following thermolysis at 1 043 K

of the respective esters, whereas a mutual comparison of the individual yields is not possible.¹⁰

It has been reported previously that thiono-esters may be rearranged thermally into the corresponding thermodynamically more favourable thiolo-compounds.^{5,6,16} On this background, in combination with the above-mentioned product distribution, it is conceivable that besides direct keten formation from the single esters, one should, in the case of (5), take a reaction involving primary thiono–thiolo rearrangement followed by methanethiol elimination from (6) into account (*cf.* Scheme 2). Hence, it is obvious that a detailed examination of the peak with *m/z* 90 (*cf.* Figure 1) corresponding to the so-called unreacted ester is appropriate. For this purpose we studied the c.a. spectra of the peak with *m/z* 90 after thermolysis of the two esters.



In Figures 2a and e the c.a. spectra of the molecular ion (*m/z* 90) of unthermolysed (5) and (6) are shown, respectively. Additionally, the c.a. spectra of the peak with *m/z* 90 after thermolysis of (5) at 883, 1 043, and 1 404 K are depicted in Figures 2b, c, and d, respectively. By elevating the thermolysis temperature a progressive relative increase in the intensity of the peak of *m/z*

43,* corresponding to a thermally induced intramolecular thiono-thiolo [(5) \rightarrow (6)] rearrangement, is seen. The (5):(6) ratios are, based on the spectra depicted in Figure 2, calculated to be 9, 1.0, and <0.05 following thermolysis at 1 043, 1 253 (not shown), and 1 404 K, respectively. The reverse reaction, *i.e.* a possible (6) \rightarrow (5) rearrangement, is not observed, in agreement with the much higher energy of activation for the latter reac-

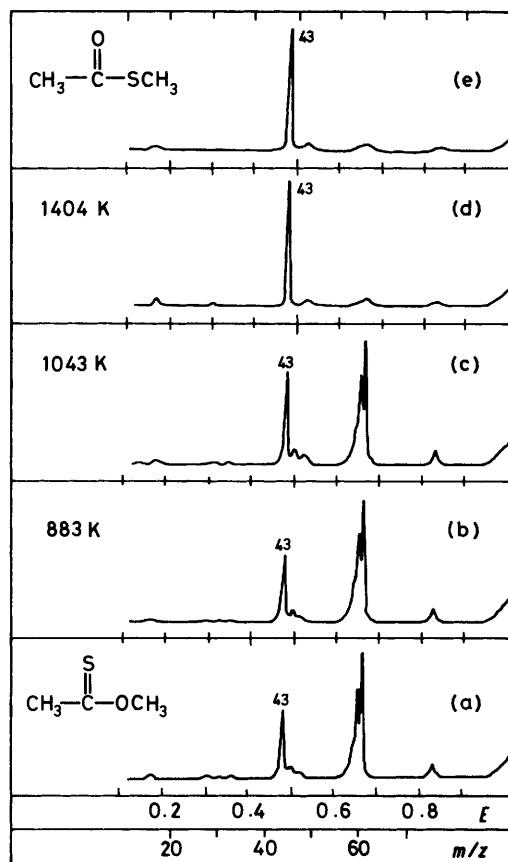


FIGURE 2 Collision activation mass spectra of the electron impact-induced molecular ions of methyl thionoacetate without thermolysis (a), following thermolysis at 883 K (b), 1 043 K (c), and 1 404 K (d), respectively, and unthermolysed methyl thioacetate (e)

tion, due to the thermodynamic stabilization of (6) by *ca.* 80 kJ mol⁻¹ relative to (5).⁵

To elucidate the relative importance of the possible mechanistic pathways for keten formation outlined above, the keten:methyl thioacetate ratio [(9):(6)] seems to be crucial. Taking the above calculated (5):(6) ratio as well as the relative thiono-thiolo f.i. sensitivities (1.7, see Experimental section) into account, the (9):(6) ratios after thermolysis of (5) and (6) at 1 043 K were calculated to be 8.8 and 0.8, respectively (*cf.* Figure 1). Thus, by thermolysis of (5) no more than *ca.* 10% of the

* The presence of an *m/z* 43 ion (CH₃C≡O⁺) in the c.a. spectra of thionoacetates reflects the thiono-thiolo isomerization in the ionized state (A. Ohno, T. Koizumi, Y. Ohnishi, and G. Tsuchihashi, *Org. Mass Spectrom.*, 1970, **3**, 261).

keten formed can be generated *via* a pathway involving primary rearrangement into (6) followed by quantitative rethermolysis of the latter. However, in general the f.v.t. method used only causes very low degrees of rethermolyses, owing to the very short contact times applied (*ca.* 300 μs).¹⁰ On this background we conclude that the major fraction of the keten formed originates directly from the single esters (5) and (6), respectively. Finally, it should be mentioned that the absolute yield of keten is *ca.* 1.5 times higher after thermolysis of (6) than of (5) at 1043 K.

In Figure 3 the f.i. spectra recorded after thermolysis of the ethyl monothioacetates (7) and (8) at 1 404 K are shown. It is immediately seen that the ethyl case, not unexpectedly, is much more complicated than the above methyl case.

Four thermally generated fragments dominate the picture. These are ethylene (11) (*M* 28), keten (9) (*M* 42), acetaldehyde (12) (*M* 44), and ethanethiol (13) (*M* 62). In addition considerable amounts of so-called unreacted ester (*M* 104) are observed. As in the methyl case the low intensity peaks at *m/z* 58 were identified as 'C₃H₆O'. In the following we shall first turn to a discussion of the actual composition of the ester peak at *m/z* 104 based on a c.a.m.s. analysis.

The c.a.m.s. spectra of unthermolysed (7) and (8) are depicted in Figures 4a and e, respectively. In Figures 4b-d the c.a. spectra of (7) after thermolysis at 883, 1 043, and 1 404 K, respectively, are shown. Similar to the methyl ester case a smooth progressive conversion

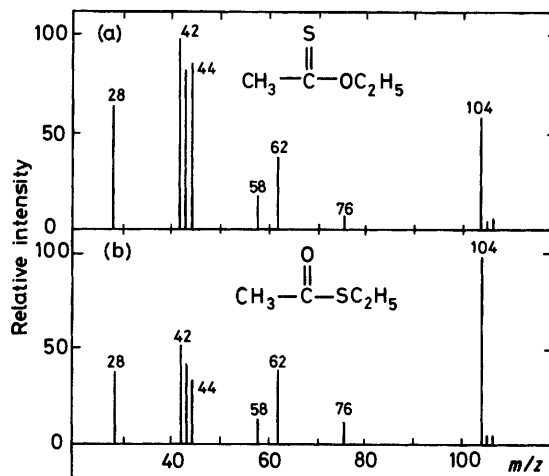


FIGURE 3 Field-ionization mass spectra of ethyl thionoacetate and ethyl thioacetate following thermolysis at 1 404 K

from the pure unthermolysed thiono-ester (Figure 4a) to the corresponding thiolo-ester (Figure 4e) as a function of temperature is observed. Based on these spectra we calculate that following the thermolysis at 1 404 K $>95\%$ of the so-called unreacted ethyl thionoacetate (7) has rearranged into the thermodynamically more stable thiolo-ester (8), *i.e.* the peak at *m/z* 104 in Figure 3a reflects the rearranged ester (8) and not unreacted (7). On the other hand the *m/z* 104 peak in Figure 3b truly

reflects unreacted (8), as no thio- thiono rearrangement has been observed in the temperature range studied.

As mentioned above the thermolysis products obtained from the ethyl monothioacetates include ethylene (11) (*m/z* 28) and acetaldehyde (12) (*m/z* 44) (*cf.* Figure

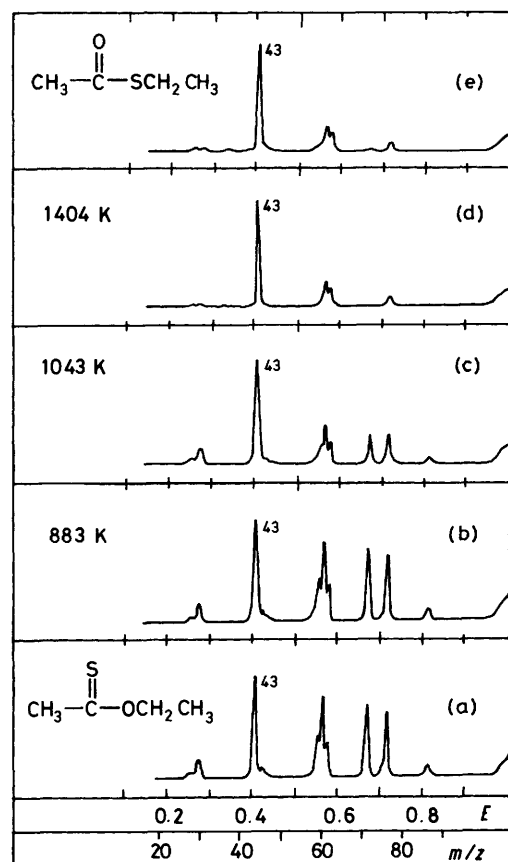


FIGURE 4 Collision activation mass spectra of the electron impact-induced molecular ions of ethyl thionoacetate without thermolysis (a), following thermolysis at 883 K (b), 1 043 K (c), and 1 404 K (d), respectively, and unthermolysed ethyl thioacetate (e)

3). Both products are likewise found after thermolysis of ethyl acetate. The ethylene formation is explained by the previously mentioned arrangement (*cf.* Scheme 1). The acetaldehyde is tentatively suggested to originate exclusively from the ester alkoxy moiety, partly based on analogy to ethyl acetate¹⁷ and partly due to the fact that no acetaldehyde is observed after thermolysis of the corresponding methyl esters (see above).

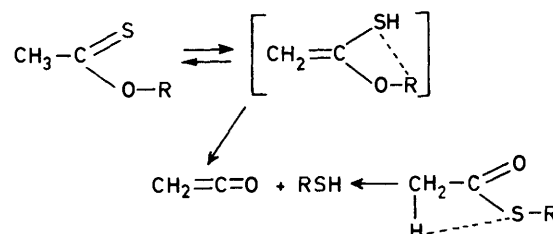
Finally the keten-ethanethiol formation is discussed. In contrast to keten-methanethiol formation following thermolysis of (5) and (6), the possible elucidation of the formation of (9) and (13) following thermolysis of (7) and (8) is somewhat complicated, owing to the concurrent formation of monothioacetic acid (14) (*cf.* Scheme 1), since a possible rethermolysis of the latter will lead to an additional keten formation.* However, studying the

* Flash vacuum thermolysis of (14) has been shown to lead to considerable amounts of keten¹⁸ apart from the previously described COS and methane.^{5,6}

ratios between the absolute yields of keten (9), ethylene (11), and ethanethiol (13) following thermolysis of (7) and (8), respectively, at 1 404 K, gives valuable information. These ratios were calculated, based on the mass spectra, to be keten *ca.* 5, ethylene *ca.* 4–5, and ethanethiol *ca.* 2.5, respectively. The value for ethylene formation is in close agreement with previously reported data by Bigley⁵ and Louw⁶ showing the higher decomposition rate for the thiono-ester. The crucial figure, however, is the value for ethanethiol formation, of necessity following keten formation, which unambiguously demonstrates that 2.5 times more keten-ethanethiol are generated from (7) than from (8), excluding a rethermolysis of primarily generated (8) as responsible for the major part of keten-ethanethiol detected following thermolysis of (7).

On the above background we are forced to consider a mechanism for keten formation by unimolecular gas-phase thermolysis of thionoacetates which does not involve a primary rearrangement to the thermodynamically more stable thioacetates, although the existence of the latter reaction has been demonstrated unequivocally. The only reasonable alternative appears to be the assumption of a primary 1,3 carbon to sulphur hydrogen migration, followed by elimination of the mercaptan. However, it is emphasized that we are unable to conclude whether the enethiolized structure can be regarded as an intermediate in the reaction or simply as a transition state.

The keten-mercaptan formation from the thio-esters, on the other hand, most probably takes place by



direct 1,2 elimination since no evidence has been obtained for a primary enolization, which similarly has been ruled out in the cases of methyl and ethyl acetate by ¹⁸O labelling experiments.^{15,17}

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