

FTIR study of thermally induced transformations of trimethylsilylmethyl acetate in the temperature range 623–813 K

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Abstract

The chemistry of trimethylsilylmethyl acetate in the gas phase in the temperature range 623–813 K has been investigated under static conditions using Fourier transform IR spectroscopy. Little change occurs at temperatures lower than 623 K, at which temperature a thermally induced isomerization to form ethyldimethylsilyl acetate occurs. Some ethanoic acid is also produced at this temperature. The ethyldimethylsilyl acetate produced undergoes thermolysis at temperatures > 723 K giving methane, ethene, carbon monoxide, carbon dioxide, ethanoic acid, 1,3-diethyl-1,1,3,3-tetramethyldisiloxane, cyclohexamethyltrisiloxane, and cyclo-octamethyltetrasiloxane as products. Loss of ethyldimethylsilyl acetate is first order over the whole temperature range, and first-order rate constants vary from $4.87 \times 10^{-5} \text{ s}^{-1}$ at 723 K to $33.5 \times 10^{-5} \text{ s}^{-1}$ at 813 K, respectively, leading to an activation energy, E_a , of 110(4) kJ mol $^{-1}$. An intramolecular five-centre process is proposed for the isomerization reaction. The thermolysis is interpreted in terms of principally radical reactions involving initial homolytic dissociation of the EtMe $_2$ SiO–C(O)CH $_3$ bond. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Trimethylsilylacetate; Thermal decomposition; FTIR

1. Introduction

The increasing use of high-temperature gas-phase conditions for new material formation has led to a need for information concerning the behaviour of organosilicon compounds under these conditions. We have previously [1] shown that trimethylsilyl acetate decomposes by a radical process in the temperature range 723–818 K giving as principal gaseous products methane, hexamethyldisiloxane, cyclohexamethyltrisiloxane, carbon dioxide, and carbon monoxide, the relative amounts of which vary with the temperature. Small amounts of water and ethanoic acid are also formed. Trimethylsilylmethyl acetate is another potential precursor for the formation of siloxane films by MOCVD, although in this molecule the silicon is insulated from the oxygen of the acetate group by a methylene group. Previous studies of this molecule have all been in the solution phase, and have concentrated on reduction/substitution reactions [2–5] of the acetyl group and the nature of the

α -effect [6,7]. No chemistry is known either in the gas phase or at high temperature for this reagent, and hence we report here the results of a detailed investigation of the thermolysis of neat, gaseous trimethylsilylmethyl acetate.

2. Experimental

The general experimental technique has been described in detail previously [8]. Prior to any qualitative or quantitative studies, the reaction cell was conditioned by allowing trimethylsilylmethyl acetate (Aldrich) (ca. 5 Torr) to decompose at 743 K several times.

3. Results

3.1. IR spectrum and Beer–Lambert characteristics of trimethylsilylmethyl acetate at ambient temperature

The gas-phase IR spectrum of trimethylsilylmethyl acetate at a pressure of 10.8 Torr is shown in Fig. 1,

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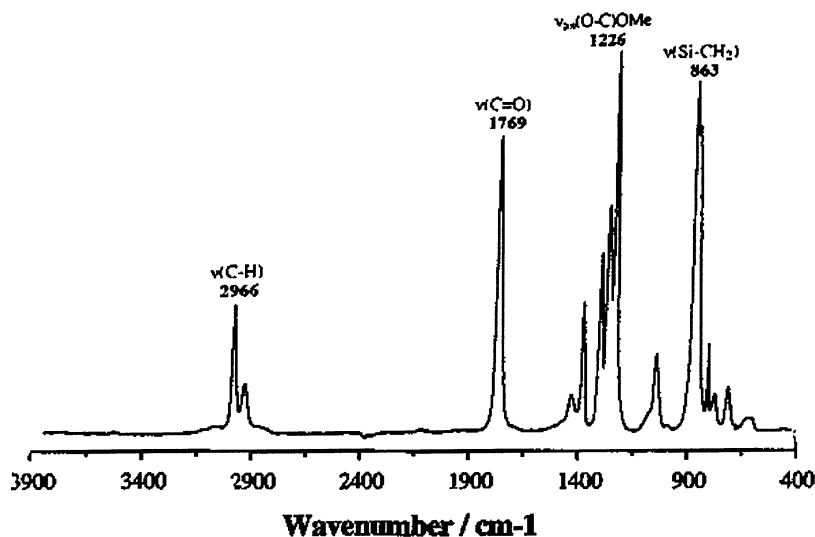


Fig. 1. Ambient-temperature infrared spectrum of trimethylsilylmethyl acetate in the gas phase (10.8 Torr).

with band positions and assignments [7] summarised in Table 1. Quantitative measurements of the abundance of trimethylsilylmethyl acetate were made using the intense carbonyl stretching band at 1769 cm^{-1} . A Beer–Lambert plot of the integrated peak envelope area of the $\nu(\text{C}=\text{O})$ band in the range $1702\text{--}1826\text{ cm}^{-1}$ versus gas-phase abundance was constructed in the pressure range $0.0\text{--}6.1\text{ Torr}$ (Fig. 2), all measurements being made at ambient temperature. The least-squares fit (correlation coefficient = 0.965) of the linear plot was of the form:

$$A = -0.8867 + 1.2614 \times 10^5 C$$

where A is the integrated peak envelope area for the $\nu(\text{C}=\text{O})$ band (absorbance units cm^{-1}) and C is the molar abundance (mol l^{-1}). From the Beer–Lambert law the gradient, ϵl , was determined to be 1.26×10^5 (absorbance units cm^{-1}) $\text{mol}^{-1}\text{ l}$, giving a value of 9.34 (0.33) $\times 10^5$ (absorbance units cm^{-1}) $\text{mol}^{-1}\text{ l m}^{-1}$ for the magnitude of the extinction coefficient, ϵ .

3.2. Analysis of the gas-phase reaction products

3.2.1. Effects of thermal treatment prior to decomposition

As the temperature is increased the IR bands characteristic of trimethylsilylmethyl acetate begin to broaden and decrease in intensity. At 373 K , very little change occurs in the IR. However, when a temperature of ca. 623 K is attained, these bands exhibit subtle but distinct differences from the bands recorded at ambient temperature, and are illustrated in the series of IR spectra shown in Fig. 3. The carbonyl stretching band of trimethylsilylmethyl acetate is observed to broaden from 1826 to 1702 cm^{-1} at ambient temperature to $1831\text{--}1695\text{ cm}^{-1}$ when heated to 373 K . On heating to 623 K , the carbonyl band shifts down wavenumber. The new

position has a maximum at 1740 cm^{-1} (cf. 1769 cm^{-1} $\nu(\text{C}=\text{O})$ at ambient temperature). Also present in this region is a new band centred at 1788 cm^{-1} (due to ethanoic acid $\nu(\text{C}=\text{O})$ [9]). After 600 s at 623 K , the reaction cell was cooled to ambient temperature when the characteristic bands of trimethylsilylmethyl acetate at 1425 , 1373 , 1292 , 1259 , 1226 , 1068 , 1034 , 977 , 863 , 848 , 795 , 765 , 703 and 614 cm^{-1} reduce in intensity and eventually disappear. After 600 s at 623 K and cooling to ambient temperature, the spectrum exhibits new bands at 1426 , 1372 , 1290 , 1260 , 1182 , 1069 , 1012 , 964 , 935 , 888 , 838 , 829 , and 802 cm^{-1} .

Table 1
Infrared assignment data for trimethylsilyl methylacetate in the gas phase at ambient temperature

Band position (cm^{-1})	Assignment ^a
3052 vvw	$\nu(\text{C-H})$
2966 m	$\nu(\text{C-H})$
2916 w	$\nu(\text{C-H})$
2859 vvw	$\nu(\text{C-H})$
1769 vs	$\nu(\text{C}=\text{O})$
1425 w	$\delta_{\text{as}}(\text{C-H})$ (Si-CH_3)
1373 m	$\delta_{\text{s}}(\text{C-H})$ (Si-CH_3)
1292 ms	$\gamma(\text{CH}_2)$
1259 s	$\delta_{\text{s}}(\text{CH}_3)$
1226 vvs	$\nu_{\text{as}}(\text{O-C})\text{OCH}_3$
1068 w	$\rho(\text{CH}_3)$
1034 mw	$\nu(-\text{CH}_2-\text{O}-)$
977 vvw	$\rho(\text{CH}_3)$
863 vvs	$\nu(\text{Si-CH}_2)$
848 vs	?
795 mw	?
765 w	$\nu_{\text{as}}(\text{Si-CH}_2-\text{O})$
703 w	$\nu_{\text{as}}(\text{Si-CH}_3)$
614 vw	$\nu_{\text{s}}(\text{Si-CH}_3)$

^a By comparison with data from Refs. [6,7], and A.L. Smith, Spectrochim. Acta 16 (1960) 87.

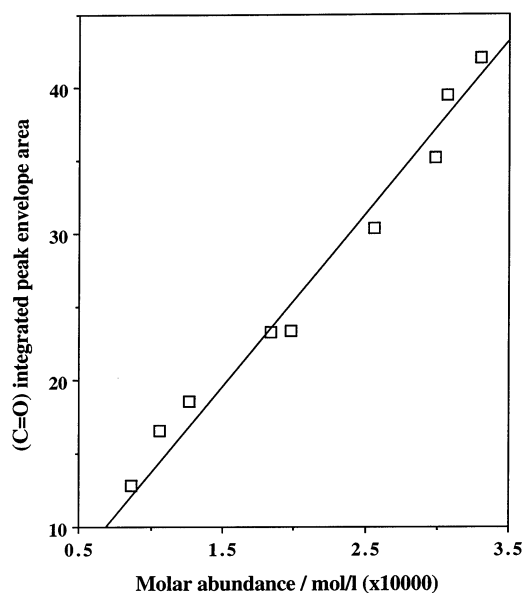


Fig. 2. Beer-Lambert plot of integrated area of the $\nu(\text{C}=\text{O})$ peak vs. gas-phase molar abundance for trimethylsilylmethyl acetate.

It is interesting to note that the position of the new acetate carbonyl band at 1740 cm^{-1} is almost identical to that of trimethylsilyl acetate (1741 cm^{-1}), suggesting a structural similarity. This is further highlighted in Fig. 4, where the spectrum of the product of heating trimethylsilylmethyl acetate to 623 K for 600 s is compared with the ambient-temperature IR spectra of trimethylsilyl acetate and trimethylsilylmethyl acetate. In particular, characteristic bands in the IR spectrum of trimethylsilylmethyl acetate at 1034 cm^{-1} ($\nu(-\text{H}_2\text{C}-\text{O})$), 1226 cm^{-1} ($\nu_{\text{as}}(\text{O}-\text{C})\text{OMe}$), and 1769 cm^{-1} ($\nu(\text{C}=\text{O})$) are lost, while

new bands appear at 838 cm^{-1} ($\nu(\text{Si}-\text{O})$), 964 cm^{-1} ($\nu(\text{C}-\text{C})$), 1260 cm^{-1} ($\nu(\text{C}-\text{CO}-\text{O}) + \delta_{\text{s}}(\text{CH}_3)$), and 1740 cm^{-1} ($\nu(\text{C}=\text{O})$). The similarity of the IR spectra of the product of heating trimethylsilylmethyl acetate and trimethylsilyl acetate is illustrated in Table 2. Hence, both have similar structures with the former containing an additional carbon-carbon bond ($\nu(\text{C}-\text{C})$ at 964 cm^{-1}) [10]. Isomerisation is possible for molecules containing $\text{Si}-\text{CH}_2-\text{O}$ linkages [3], and it would appear that such a process is occurring producing dimethylethylsilyl acetate.

Traces of ethanoic acid are also observed at 623 K ($\nu(\text{C}=\text{O})\ 1788\text{ cm}^{-1}$, $\nu(\text{C}-\text{O})\ 1182\text{ cm}^{-1}$) [11], and its formation probably arises from homolytic cleavage of the skeletal $\text{Si}-\text{CH}_2(\text{CO})\text{OMe}$ bond, followed by hydrogen abstraction by the $\cdot\text{CH}_2(\text{CO})\text{OMe}$ radical so formed.

3.2.2. Thermolysis in the temperature range 723–813 K

The decomposition of neat trimethylsilylmethyl acetate was investigated quantitatively in the temperature range 723–813 K. A typical series of IR spectra for the decomposition at 773 K is illustrated in Fig. 5. When isothermal conditions are attained (773 K), the trimethylsilylmethyl acetate has isomerised completely, and it is the decomposition of dimethylethylsilyl acetate (with characteristic IR bands at 1740 cm^{-1} $\nu(\text{C}=\text{O})$, 1372 cm^{-1} $\delta_{\text{s}}(\text{C}-\text{H})$, 1260 cm^{-1} [skeletal $\text{C}-\text{CO}-\text{O} + \delta_{\text{s}}(\text{Si}-\text{O})$], 1069 cm^{-1} $\nu(\text{CH}_3)$, 1012 cm^{-1} [skeletal $\text{C}-\text{CO}-\text{O} + \rho(\text{CH}_3)$], 964 cm^{-1} $\nu(\text{C}-\text{C})$, 935 cm^{-1} [skeletal $\text{C}-\text{CO}-\text{O} + \rho(\text{CH}_3)$], 838 cm^{-1} $\nu(\text{Si}-\text{O})$) which is observed. Interpretation of the spectra shown in Fig. 5 demonstrates that the products of decomposition are

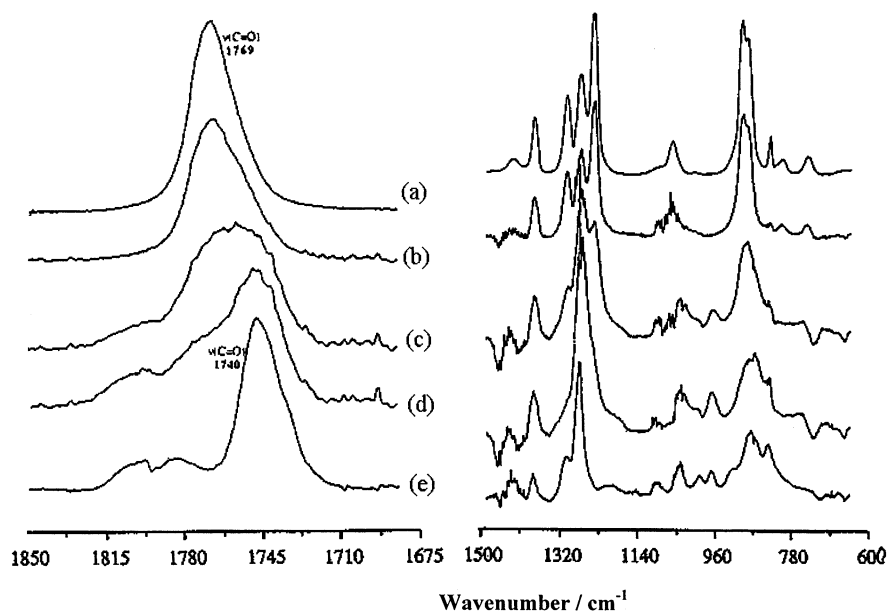


Fig. 3. Infrared spectra of trimethylsilylmethyl acetate in the gas phase: (a) at ambient temperature; (b) after heating to 375 K; (c) after heating to 623 K; (d) after heating to 623 K for 600 s, and (e) as for (d), followed by cooling to ambient temperature.

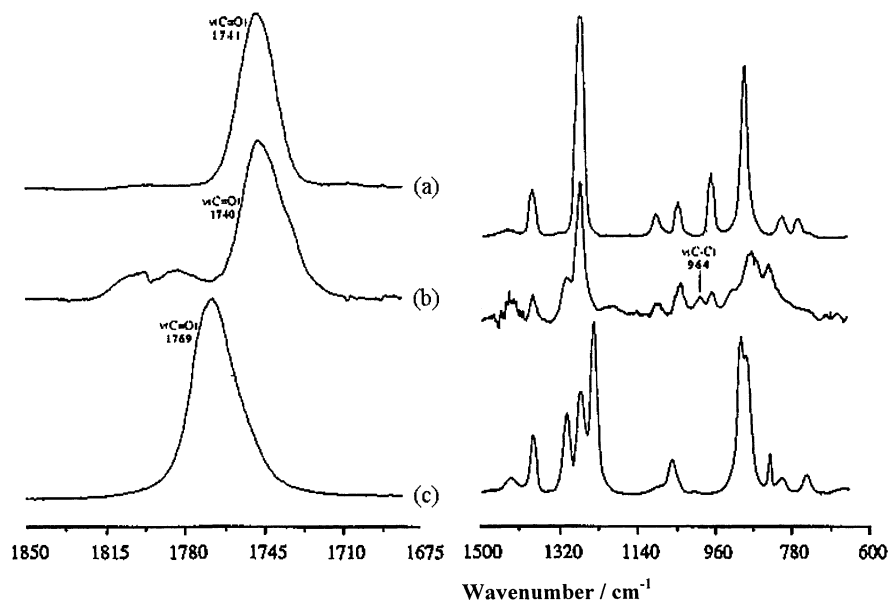


Fig. 4. Comparison of the gas-phase infrared spectra of trimethylsilyl acetate at ambient temperature (a) and trimethylsilylmethyl acetate at ambient temperature (c) and after heating to 623 K for 600 s, followed by cooling to ambient temperature (b).

Table 2

Comparison of the infrared spectra (1800–800 cm^{-1}) of trimethylsilyl acetate (TSA) and the product obtained by the thermal rearrangement of trimethylsilylmethyl acetate

Trimethylsilyl acetate (cm^{-1})	Assignment	Rearranged product (cm^{-1})	Tentative assignment
1741 s	$\nu(\text{C}=\text{O})$	1740 s	$\nu(\text{C}=\text{O})$
1428 vw	$\delta_a(\text{C}-\text{H})$	1426 vw	$\delta_a(\text{C}-\text{H})$
1375 m	$\delta_s(\text{C}-\text{H})$	1372 mw	$\delta_s(\text{C}-\text{H})$
—	—	1290 m	? ^a
1245 vvs	$\text{C}-\text{CO}-\text{O} + \delta_s(\text{CH}_3)$	1260 vs	$\text{C}-\text{CO}-\text{O} + \delta_s(\text{CH}_3)$
—	—	1182 vw	$\nu(\text{C}-\text{O})$ ^b
1073 w	$\rho(\text{CH}_3) (\text{C}-\text{CH}_3)$	1069 vw	$\rho(\text{CH}_3) (\text{C}-\text{CH}_3)$
1019 mw	$\text{C}-\text{CO}-\text{O} + \rho(\text{CH}_3)$	1012 mw	$\text{C}-\text{CO}-\text{O} + \rho(\text{CH}_3)$
—	—	964 w	$\nu(\text{C}-\text{C}) (\text{SiC}-\text{C})$
937 ms	$\text{C}-\text{CO}-\text{O} + \rho(\text{CH}_3)$	935 w	$\text{C}-\text{CO}-\text{O} + \delta(\text{CH}_3)$
—	—	888 mw	? ^a
858 vs	$\nu(\text{Si}-\text{O})$	838 s	$\nu(\text{Si}-\text{O})$
—	—	829 ms	? ^a
—	—	802 m	? ^a

^a Unassigned bands.

^b Ethanoic acid.

methane (3019 cm^{-1} ($\nu(\text{C}-\text{H})$), 1306 cm^{-1} ($\delta(\text{H}_3\text{C}-\text{H})$), ethanoic acid (3580 cm^{-1} ($\nu(\text{O}-\text{H})$), 1788 cm^{-1} ($\nu(\text{C}=\text{O})$), 1182 cm^{-1} ($\nu(\text{C}-\text{O})$), ethene (949 cm^{-1} (CH_2 wag)), carbon dioxide (2349 cm^{-1} ($\nu_{\text{as}}(\text{CO}_2)$), 667 cm^{-1} ($\delta(\text{CO}_2)$)), cyclohexamethyltrisiloxane (1025 cm^{-1} ($\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$)) and carbon monoxide (2144 cm^{-1} ($\nu(\text{CO})$)). A band at 1073 cm^{-1} is also observed, probably due to the $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ vibration of another siloxane product. A typical ambient-temperature ratio (after thermolysis) of methane:ethene:carbon dioxide is ca. 8:5:3.

Corroboration of the formation of the siloxane species cyclooctamethyltetrasiloxane, cyclohexamethyl-

trisiloxane, and diethyltetramethyldisiloxane is obtained from the mass spectrum (70 eV) of the gaseous product mixture after thermolysis at 773 K (12 000 s, > 75% reaction), which exhibits principal peaks at m/e values of 207, 175, 161, 147, 133, 119, 117, 89, 75, 73, 66, 61 and 59. Assignments and probable origins for these fragments are shown in Table 3. The highest m/e fragment occurs at 281 and can be attributed to $(\text{Me}_7\text{Si}_4\text{O}_4)^+$, which is derived from cyclooctamethyltetrasiloxane. The m/e fragment at 207 corresponds to $(\text{Me}_5\text{Si}_3\text{O}_3)^+$ due to cyclohexamethyltrisiloxane. The series of five m/e fragments with maxima at 175, 161, 147, 133 and 119 are attributed to $(\text{Me}_3\text{Et}_2\text{Si}_2\text{O})^+$,

$(\text{Me}_4\text{EtSi}_2\text{O})^+$, $(\text{Me}_3\text{Et(H)Si}_2\text{O})^+$, $(\text{Me}_3\text{Et(H)}_2\text{Si}_2\text{O})^+$, and $(\text{Me}_3(\text{H})_2\text{Si}_2\text{O})^+$, respectively, derived from diethyltetramethyldisiloxane, $(\text{Me}_2\text{EtSi})_2\text{O}$, which is most probably responsible for the band observed at 1073 cm^{-1} in the IR.

Plots of the integrated peak envelope areas with time showing the production of carbon monoxide and carbon dioxide as the thermolysis temperature increases are

Table 3

Summary of the mass spectrum fragmentation (70 eV) of the gaseous products from the thermolysis of trimethylsilylmethyl acetate at 773 K for 12 000 s

<i>m/e</i>	% Base	Fragment ^a	Molecule of origin
281	1.3	$(\text{Me}_7\text{Si}_4\text{O}_4)^+$	$(\text{Me}_2\text{SiO})_4$
207	7.8	$(\text{Me}_5\text{Si}_3\text{O}_3)^+$	$(\text{Me}_2\text{SiO})_3$
175	10.7	$(\text{Me}_3\text{Et}_2\text{Si}_2\text{O})^+$	$(\text{EtMe}_2\text{Si})_2\text{O}$
161	80.9	$(\text{Me}_4\text{EtSi}_2\text{O})^+$	$(\text{EtMe}_2\text{Si})_2\text{O}$
147	26.4	$(\text{Me}_3\text{Et(H)Si}_2\text{O})^+$	$(\text{EtMe}_2\text{Si})_2\text{O}$
133	100.0	$(\text{Me}_3\text{Et(H)}_2\text{Si}_2\text{O})^+$	$(\text{EtMe}_2\text{Si})_2\text{O}$
119	24.2	$(\text{Me}_3(\text{H})_2\text{Si}_2\text{O})^+$	$(\text{EtMe}_2\text{Si})_2\text{O}$
89	12.8	$(\text{Me}_3\text{SiO})^+$	—
75	39.5	$(\text{Me}_3\text{SiH}_2)^-$	—
73	21.0	$(\text{Me}_3\text{Si})^+$	—

^a Based on ^{28}Si .

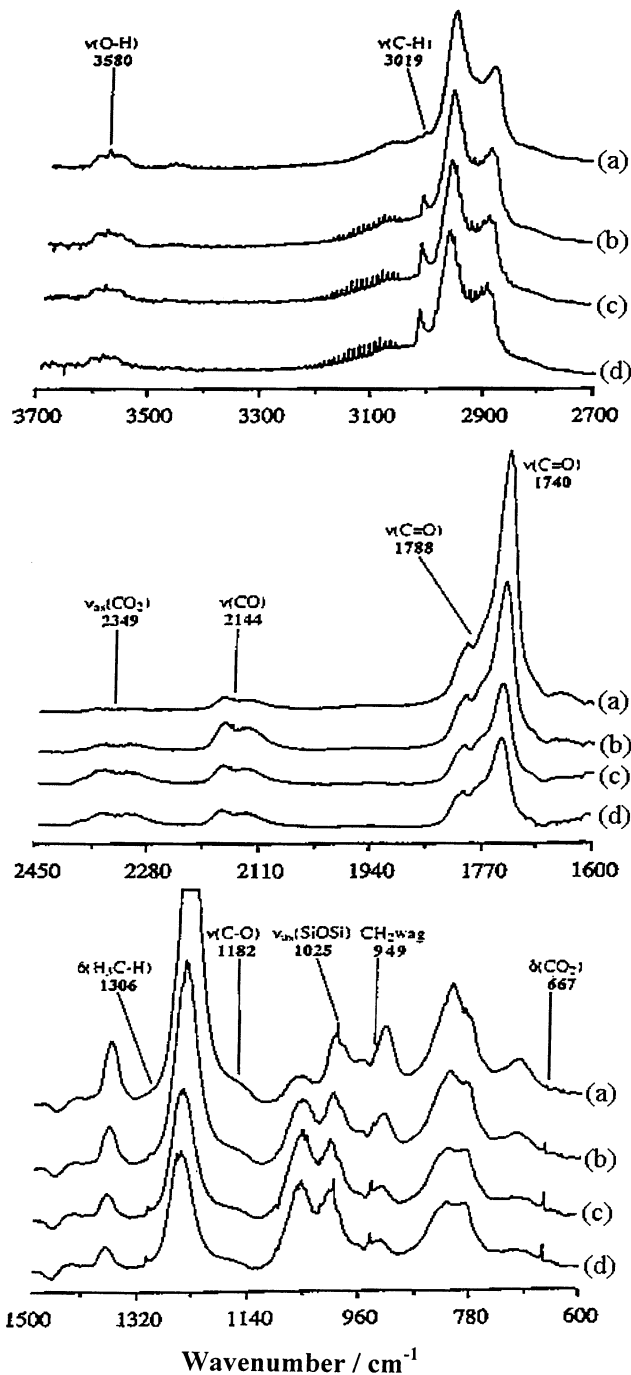


Fig. 5. Time-resolved infrared spectra of the thermolysis of trimethylsilylmethyl acetate at 773 K and (a) 0 s; (b) 2900 s; (c) 6700 s, and (d) 7200 s.

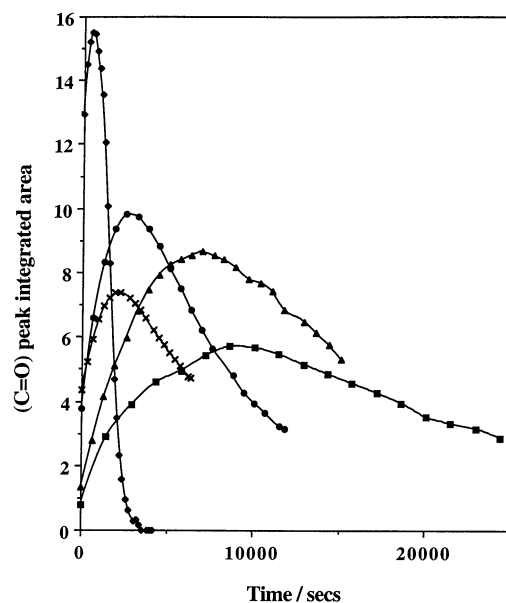


Fig. 6. Plot of integrated area of the $\nu(\text{C}=\text{O})$ peak vs. time for carbon monoxide production at 733 K (■), 753 K (▲), 773 K (●), 803 K (X) and 813 K (◆).

illustrated in Figs. 6 and 7, respectively. The profiles observed for each are quite different. At each temperature, the production of carbon monoxide initially increases to a maximum value before declining, whereas the production of carbon dioxide increases steadily with time. At low thermolysis temperatures no carbon dioxide is observed until the thermolysis has been underway for some considerable time. The maximum observed in the profiles for the production of carbon monoxide is very broad at low thermolysis temperatures, but steadily sharpens as the temperature is increased. At the highest temperature studied, the amount of carbon monoxide rapidly decreases to zero. From these observations we conclude that it is carbon monoxide that is produced initially in the reaction, and is subsequently converted to carbon dioxide as the thermolysis processes.

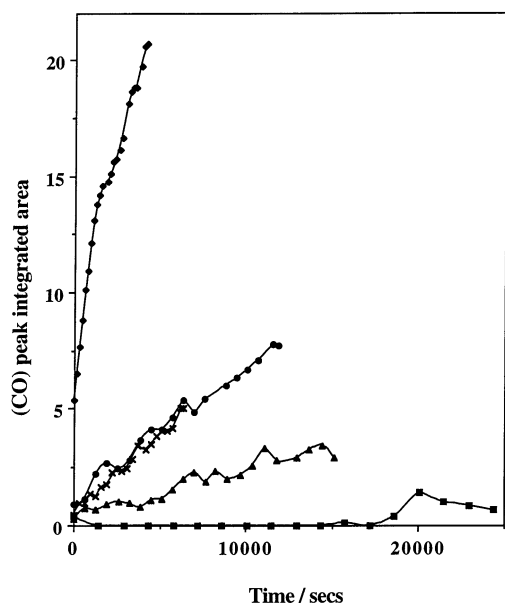


Fig. 7. Plot of integrated area of the $\nu(\text{C}=\text{O})$ peak vs. time for carbon dioxide production at 733 K (■), 753 K (▲), 773 K (●), 803 K (X) and 813 K (◆).

3.3. Determination of rate data and activation energy of decomposition

The integrated peak envelope area of the carbonyl stretching vibration characteristic of ethyldimethylsilyl acetate, derived by the isomerization of trimethylsilylmethyl acetate after molecular rearrangement, was partially masked on the higher wavenumber side by the

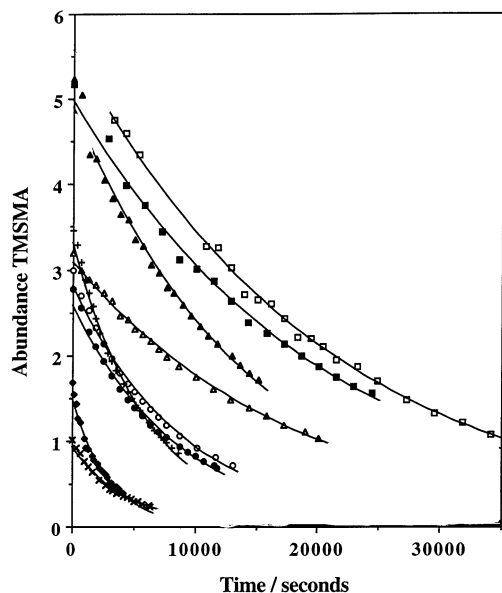


Fig. 8. Plot of gas-phase molar abundance (mol l^{-1}) of trimethylsilylmethyl acetate vs. time at 723 K (□), 733 K (■), 743 K (△), 753 K (▲), 763 K (○), 773 K (●), 783 K (+), 803 K (×), and 813 K (◆). Solid lines represent least-squares best fits.

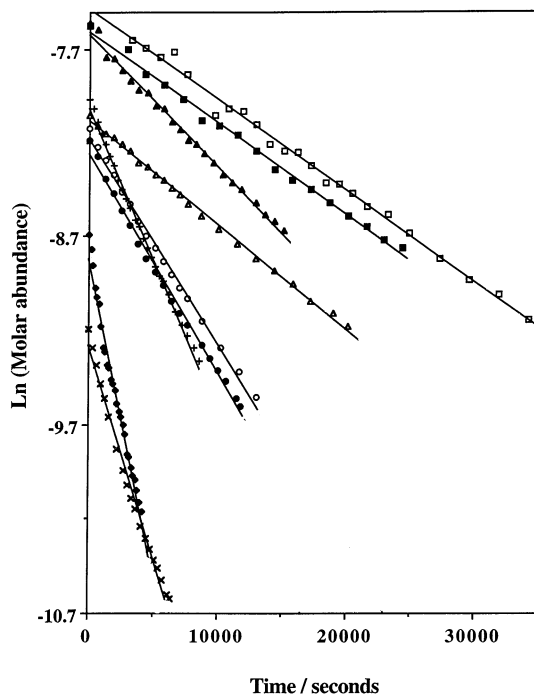


Fig. 9. First-order plots for the decomposition of trimethylsilylmethyl acetate at 723 K (□), 733 K (■), 743 K (△), 753 K (▲), 763 K (○), 773 K (●), 783 K (+), 803 K (×), and 813 K (◆). Solid lines represent least-squares best fits.

carbonyl stretching band $\nu(\text{C}=\text{O})$ of ethanoic acid. Hence, the integrated peak envelope area was calculated using the range $1740\text{--}1673\text{ cm}^{-1}$ (i.e. the lower wavenumber half band area) and then doubled. Using the extinction coefficient derived from the Beer–Lambert plot (Fig. 2), the time dependence of the loss of the rearranged acetate was determined for each temperature in the range 723–813 K. Plots of molar abundance versus time are illustrated in Fig. 8, and show exponential loss (correlation coefficients > 0.98) of the isomerized product. Plots of $\ln C$ versus time are linear (correlation coefficients > 0.99) (Fig. 9) showing that the loss of dimethylethylsilyl acetate is first-order over the whole temperature range studied. Rate constants vary from 4.87×10^{-5} to $33.5 \times 10^{-5}\text{ s}^{-1}$ in the temperature range 723–813 K. All kinetic runs were taken to ca. 75% completion. Rate data are summarised in Table 4.

Fig. 10 shows the corresponding Arrhenius plot from which the relationship

$$\ln C = 8.23 - 110.3/RT$$

was derived by least-squares analysis ($R^2 = 0.961$) leading to values for the activation energy, E_a , and the pre-exponential factor, A , of $110(4)\text{ kJ mol}^{-1}$ and $3.8 \times 10^3\text{ s}^{-1}$, respectively.

Table 4
First-order rate constant data

Temperature (K)	First-order rate constant (k_1) ($s^{-1} \times 10^5$)	Temperature (K)	First-order rate constant (k_1) ($s^{-1} \times 10^5$)
723	4.87	773	11.6
733	4.90	783	16.2
743	5.57	803	22.5
753	7.11	813	33.5
763	11.0		

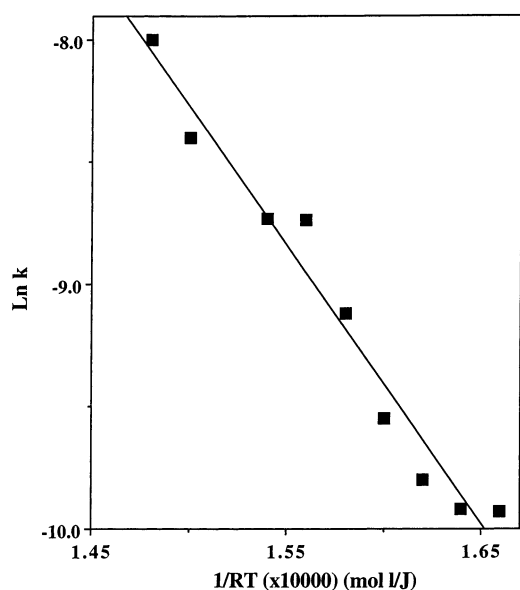
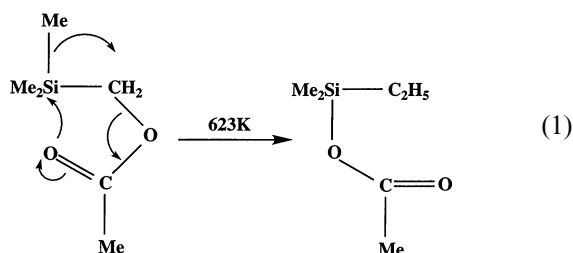


Fig. 10. Arrhenius plot for the loss of trimethylsilylmethyl acetate in the temperature range 723–813 K.

4. Discussion

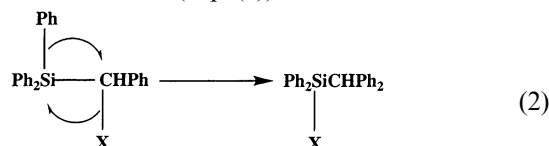
When trimethylsilylmethyl acetate is heated to 623 K it undergoes an isomerisation to give dimethylethylsilyl acetate, most probably via a concerted, five-centred, transition state (Eq. (1)):



No substantial isomerisation occurs below this temperature. The driving force for the isomerisation is the strength of the incipient Si–O bond, the polarity of the bond $\text{Me}_3\text{Si}^{\delta+}-\delta-\text{CH}_2-$ allowing nucleophilic attack by the carbonyl oxygen at silicon. Some ethanoic acid is also produced at this temperature. This may arise from the homolytic fission of the $\text{Me}_3\text{SiCH}_2\text{-OCOME}$ bond,

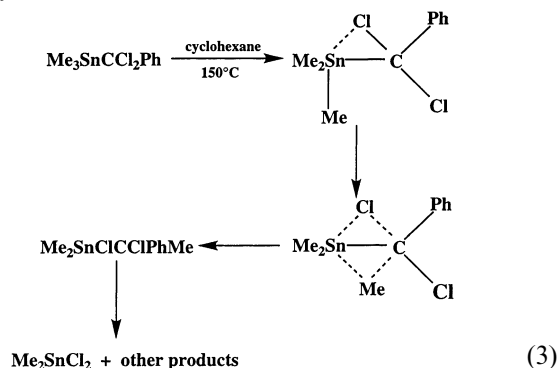
followed by hydrogen abstraction by the resulting acetoxy radical.

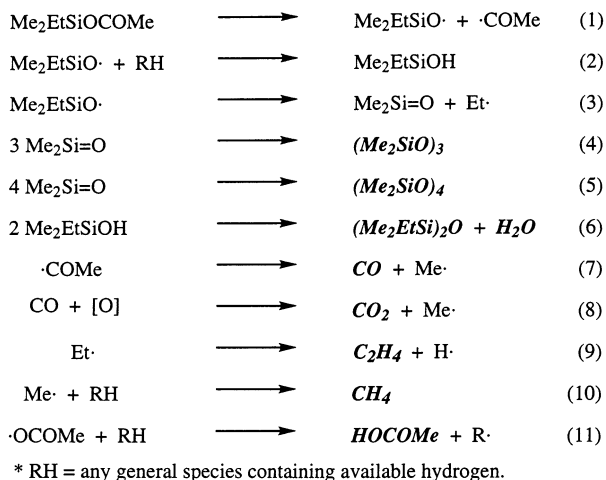
A similar rearrangement to that proposed here for trimethylsilylmethyl acetate has also been observed for benzyltriphenylsilanes [13] in which there is an exchange of groups between the silicon atom and the adjacent carbon atom (Eq. (2)):



The ease of migration of the group (X) from carbon to silicon decreases in the order $\text{X} = \text{F} > \text{OTs} > \text{OAc} > \text{Cl} > \text{Br} \gg \text{OMe}$, which coincides with the expected order of stabilisation of a penta-coordinated silicon atom based on bond energies and the electronegativities of X. It was observed that α -chlorobenzyltriphenylsilane rearranged faster than the analogous germanium compound, probably reflecting the greater bond energy of Si–X compounds and the lower energy of the silicon d orbitals.

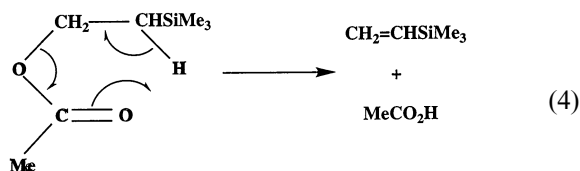
Thermal rearrangements involving [1,2]-shifts have also been observed for tin-containing compounds. Seyferth and Armbrecht [14] reported that dimethyldichlorostannane was one of the products of the thermolysis of trimethyl(α,α -dichlorobenzyl)tin at 150°C in cyclohexene. The reaction course proposed was initial $\text{Sn}\cdots\text{Cl}$ attraction, followed by a four-centre transition state involving the tin atom, a methyl group associated with tin, the carbon α to tin and a chloride atom (Eq. (3)). The exchange of methyl and the chloride was followed by a further step and yielded dimethyldichlorostannane.



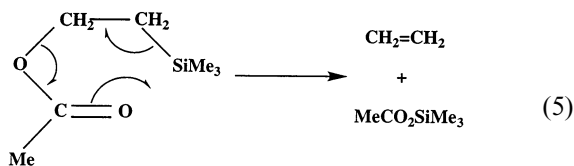


Scheme 1. Proposed reaction mechanism for the thermolysis of dimethylethylsilylmethyl acetate in the temperature range 723–813 K (final products are in italicised bold font).

Two elimination pathways are possible in the pyrolysis of 2-trimethylsilylethyl acetate in the temperature range 600–800 K [12]. The products of thermolysis at the lower end of the temperature region studied were due solely to the elimination of ethanoic acid and vinyltrimethylsilane (Eq. (4)):

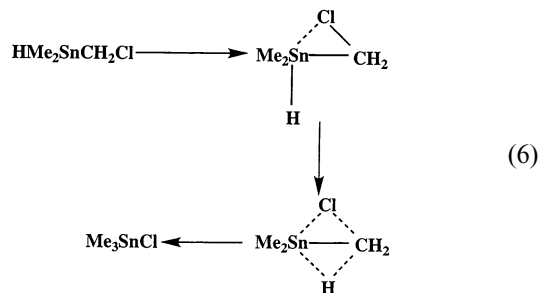


At higher temperature (> 750 K) however, another type of elimination occurs, the extrusion of ethene (Eq. (5)), but which contributed only one-third of the overall elimination. This process has a higher activation energy and only occurs at the higher temperatures studied. Both eliminations from 2-trimethylsilylethyl acetate were proposed to involve normal six-centre reactions.

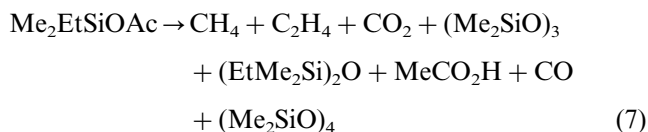


Another reported rearrangement is the gas-phase isomerisation of (chloromethyl)dimethylsilane to trimethylchlorosilane [15] in a static reactor between 636 and 690

K. The neat reaction was shown to occur by two parallel reaction pathways: a concerted dyotropic rearrangement and a free radical chain, which appeared to be wall initiated. Davidson and Ijadi-Maghsoodi [16] also studied the rearrangement of this molecule in a stirred flow apparatus with nitrogen as carrier gas between 467 and 550°C. The rearrangement followed first-order kinetics and was insensitive to added radical traps. The assumption was made that the unimolecular rearrangement followed a three-centre transition state with hydrogen migration rather than methyl migration (Eq. (6)).



Trimethylsilylmethyl acetate undergoes a molecular rearrangement prior to decomposition and the major products of this rearrangement are dimethylethylsilyl acetate and ethanoic acid. After the thermally induced isomerisation, the isomerization product, dimethylethylsilyl acetate, undergoes decomposition in the temperature range 723–813 K. Gas-phase products include methane, ethene, carbon dioxide, cyclohexamethyltrisiloxane, diethyltetramethyldisiloxane, ethanoic acid, carbon monoxide and cyclooctamethyltetrasiloxane (Eq. (7)):



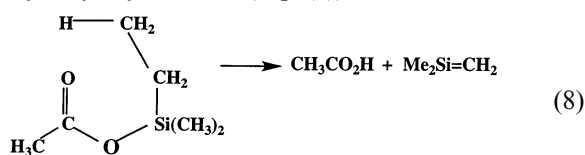
Loss of dimethylethylsilyl acetate follows first-order kinetics over the whole temperature range studied, and rate constants vary from $4.87 \times 10^{-5} \text{ s}^{-1}$ at 723 K to $33.5 \times 10^{-5} \text{ s}^{-1}$ at 813 K, respectively, leading to an activation energy, E_a , of 110(4) kJ mol⁻¹. This behaviour is very similar to that of trimethylsilyl acetate [1], which also exhibited first-order kinetics with rate constants varying from $1.66 \times 10^{-5} \text{ s}^{-1}$ at 723 K to $15.7 \times 10^{-5} \text{ s}^{-1}$ at 818 K, respectively, leading to an activation energy, E_a , of 104(5) kJ mol⁻¹. In that case, the behaviour in the presence of radical initiators indicated strongly the operation of a free radical mechanism involving the initial generation of the trimethylsilyloxyl radical, $\text{Me}_3\text{SiO}\cdot$, and a similar process is also thought to occur in the present case.

A reaction scheme that accounts for the formation of all products is shown in Scheme 1. Due to the strength of the Si–O band, the initial process would be homolytic cleavage of the skeletal C–O bond generating trimethylsilyloxy and acetyl radicals (step 1). Two reaction pathways are possible for the further reaction of the dimethylethylsilyloxy radical:

1. abstraction of hydrogen to form trimethylsilanol (step 2),
2. elimination of an ethyl radical with the formation of dimethylsilanone (step 3).

A third possible reaction pathway, silyloxy radical attack at a silicon centre, as far as we are aware, has not as yet been observed. Hydrogen abstraction by trimethylsilyloxy radicals is known to occur with a variety of substrates [18–21]. In particular, hydrogen abstraction from bistrimethylsilyl peroxide giving the $\text{Me}_3\text{SiOOSiMe}_2\text{CH}_2^\bullet$ radical has been observed. The product of hydrogen abstraction, trimethylsilanol, readily undergoes condensation to hexamethyldisiloxane and water [17], and an analogous process (step 6) accounts for the formation of diethyltetramethyldisiloxane in the present system. The hexamethylcyclotrisiloxane and octamethyltetrasiloxane observed almost certainly result from the oligomerization of dimethylsilanone [22,23] (steps 4 and 5), formed by ethyl radical elimination from the dimethylethylsilyloxy radical (step 3).

The acetyl radical formed in step 1 is known to eliminate carbon monoxide [24–27] (step 7). Methyl radicals are also formed in this step, leading to methane formation by hydrogen abstraction (step 10). Ethanoic acid may be formed by the formation of an acetoxyl radical, followed by hydrogen abstraction as described above. An alternative pathway for the formation of ethanoic acid is via internal hydrogen abstraction from dimethylethylsilyl acetate (Eq. (8)):



The loss of dimethylethylsilyl acetate is first order over the whole temperature range studied. The value of the activation energy ($110(4) \text{ kJ mol}^{-1}$) is relatively low. The fact that the activation energy is much lower than is reasonable for the $\text{SiO}-\text{C}(\text{O})\text{CH}_3$ bond dissociation energy indicates that step 1 cannot be a totally gas-phase process. We have previously observed that the presence of available surfaces can facilitate dissociative processes with a decrease in activation energy [28,29], and propose that such enhancement is also occurring in the present case.

If $\text{Me}_3\text{SiO}-\text{C}(\text{O})\text{CH}_3$ bond homolysis is the rate-determining step and the rates of all other subsequent

processes are fast relative to this, then loss of trimethylsilyl acetate in the neat reaction will be first-order as observed.

As carbon monoxide is present at the start temperature and rises to a maximum, the acetyl radical formed in step 1 must thermally decompose to give carbon monoxide and a methyl radical (step 7). After reaching a maximum value, the carbon monoxide abundance then decreases with time. Oxidation, presumably at the wall surface where there is a large presence of oxide, provides carbon dioxide (step 8).

Ethene is not present at the start, but grows in continuously with time later in the thermolysis. Ethyl radicals, produced into the reaction sphere, can propagate to form ethene (step 9). Methane forms later than ethene in the reaction and is probably produced from a methyl radical hydrogen abstraction (step 10).

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