

FT-IR study of the gas phase thermolysis of trimethylsilyl acetate

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Received 18 June 1996; revised 13 August 1996

Abstract

Thermolysis of neat trimethylsilyl acetate has been investigated in the temperature range 723–818 K under static conditions using Fourier transform infrared spectroscopy. The principal gaseous products formed during the thermal decomposition are 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. Loss of trimethylsilyl acetate is first-order over the whole temperature range; the first-order rate constants vary from $1.66 \times 10^{-5} \text{ s}^{-1}$ at 723 K to $15.7 \times 10^{-5} \text{ s}^{-1}$ at 818 K, leading to an activation energy E_a of 104(5) kJ mol^{-1} . In the presence of methyl iodide the decomposition is substantially faster and the products are methane, hexamethyldisiloxane and ethanoic acid. Decomposition is also faster in the presence of nitric oxide and oxygen, although complete identification of the product mixtures was not possible in these cases. The mechanisms of the reactions are interpreted in terms of principally radical reactions involving initial homolytic dissociation of the $\text{Me}_3\text{SiO}-\text{C}(\text{O})\text{CH}_3$ bond.

Keywords: Gas phase thermolysis; Methane

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. Trimethylsilyl acetate is a very common precursor molecule from the synthesis of a multitude of silicon-containing materials. The solution chemistry of trimethylsilyl acetate is quite extensive and several modes of reaction have been characterised including inter alia acylation of the acetate methyl group [1], condensation [2,3], exchange reactions with reagents such as aluminium and titanium alkoxides [4–7], and cleavage reactions with reagents such as phosgene, zinc chloride or epichlorohydrin [8–10]. In contrast, however, essentially no chemistry is known either in the gas phase or at high temperature for this reagent. A brief UV photoelectron spectroscopic study at 1073 K at a pressure of 10^{-3} Torr has reported that thermal decomposition occurs to only a small extent, giving acetic acid as the only identified product [11]. Here we report the results of a detailed investigation of the thermolysis of neat, gaseous trimethylsilyl acetate as

well as the effects of added methyl iodide, nitric oxide and oxygen.

2. Experimental

The general experimental technique has been described in detail previously [12]. Prior to any qualitative or quantitative studies, the reaction cell was conditioned by allowing trimethylsilyl acetate (ca. 5 Torr) to decompose at 743 K several times.

3. Results

3.1. Infrared spectrum and Beer–Lambert characteristics of trimethylsilyl acetate at ambient temperature

The gas phase infrared spectrum of trimethylsilyl acetate at a pressure of 2.8 Torr is shown in Fig. 1, with band positions and assignments [13,14] summarised in Table 1. Quantitative measurements of the abundance of trimethylsilyl acetate were made using the intense carbonyl stretching band at 1741 cm^{-1} . A Beer–Lambert plot of the integrated peak envelope area of the $\nu(\text{C}=\text{O})$ band in the range $1773\text{--}1713 \text{ cm}^{-1}$ vs. gas phase abundance was constructed in the pressure range 0.0–

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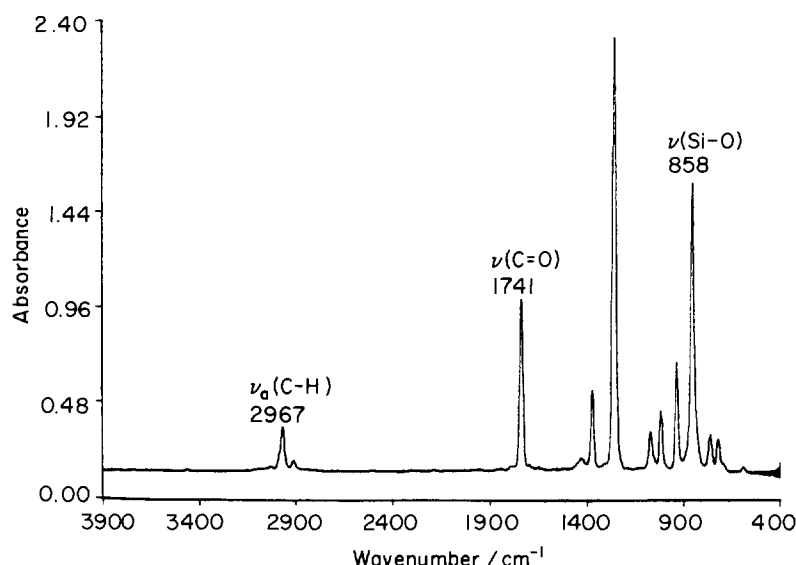


Fig. 1. Gas phase infrared spectrum of trimethylsilyl acetate (2.8 Torr) at ambient temperature.

10.3 Torr (Fig. 2), all measurements being made at ambient temperature. The least squares fit (correlation coefficient 0.985) of the linear plot was of the form

$$A = -0.0514 + 9.8086 \times 10^4 C$$

where A is the integrated peak envelope area for the $\nu(\text{C}=\text{O})$ (absorbance units cm^{-1}) band and C (mol l^{-1}) is the molar abundance. From the Beer–Lambert law, the gradient ϵl was determined as 9.81×10^4 (absorbance units cm^{-1}) $\text{mol}^{-1} \text{l}$, giving a value of $7.27(0.15) \times 10^5$ (absorbance units cm^{-1}) $\text{mol}^{-1} \text{m}^{-1}$ for the magnitude of the extinction coefficient ϵ .

3.2. Analysis of the gas phase reaction products after thermolysis in the temperature range 723–818 K

As the temperature is increased (but before a temperature sufficient to initiate decomposition is attained), the

infrared bands characteristic of trimethylsilyl acetate broaden and decrease in peak height, but suffer no diminution of integrated area. Thermal decomposition of neat trimethylsilyl acetate commences at an appreciable rate at ca. 723 K. As the thermal decomposition proceeds, the bands characteristic of trimethylsilyl acetate reduce in intensity and new bands appear. A typical series of infrared spectra recorded up to 50 000 s at 763 K are illustrated in Fig. 3. Time-resolved spectra (Fig. 4) in the region 1850–1650 cm^{-1} at this temperature show the steady decrease in intensity of the carbonyl stretching band. Fig. 5 illustrates the changes occurring in the 1600–400 cm^{-1} region at the same temperature. Peaks characteristic of hexamethyldisiloxane ($\nu_{\text{as}}(\text{SiOSi})$ 1067 cm^{-1} , $\delta_{\text{s}}(\text{CH}_3)$ 1260 cm^{-1} , $\rho(\text{CH}_3)$ 851 cm^{-1} , $\rho(\text{CH}_3)$ 759 cm^{-1} , $\nu_{\text{s}}(\text{SiC}_3)$ 690 cm^{-1} , $\nu_{\text{s}}(\text{SiC}_3)$ 620 cm^{-1} and $\nu_{\text{s}}(\text{SiOSi})$ 532 cm^{-1}) [15,16] are apparent. Additional low intensity bands also

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

Band position/ cm^{-1}	Assignment ^a
3025 vvw	$\nu(\text{C-H})$
2967 w	$\nu_{\text{a}}(\text{C-H})$ (C- CH_3)
2920 vw	$\nu_{\text{s}}(\text{C-H})$ (C- CH_3)
1741 s	$\nu(\text{C}=\text{O})$
1428 vw	$\delta_{\text{a}}(\text{C-H})$
1375 m	$\delta_{\text{s}}(\text{C-H})$ (C- CH_3)
1245 vvs	skeletal C-CO-O + $\delta_{\text{s}}(\text{CH}_3)$
1073 w	$\rho(\text{CH}_3)$ (C- CH_3)
1019 mw	skeletal C-CO-O + $\rho(\text{CH}_3)$
937 ms	skeletal C-CO-O + $\rho(\text{CH}_3)$
858 vs	$\nu(\text{Si-O})$
766 w	?
725 w	skeletal C-CO-O
590 vw	?

^a By comparison with data from Refs. [12,13].

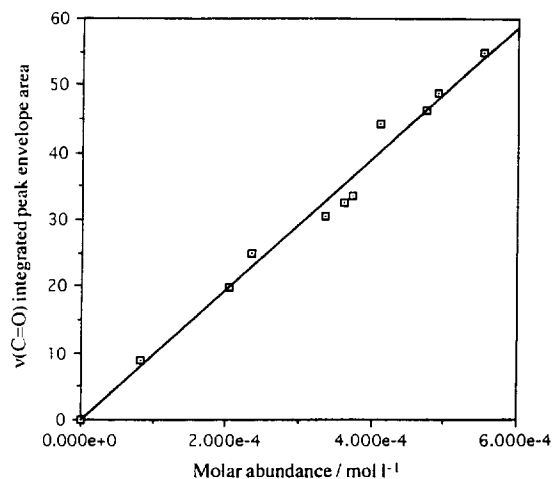


Fig. 2. Beer–Lambert plot of integrated area of the $\nu(\text{C}=\text{O})$ peak vs. gas phase molar abundance for trimethylsilyl acetate.

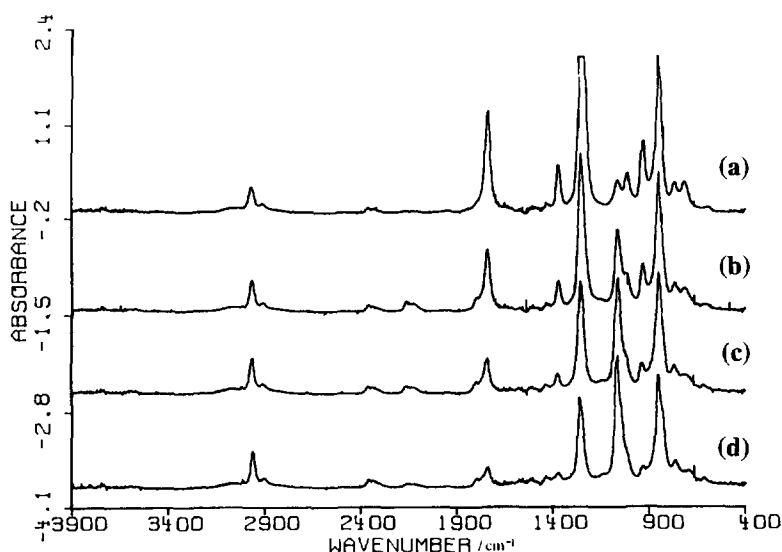


Fig. 3. Infrared spectra recorded during the thermolysis of trimethylsilyl acetate at 763 K after (a) 0, (b) 266.7, (c) 550, and (d) 833.3 min.

present as a shoulder at 1021 cm^{-1} at the lower wavenumber side of the $\nu_{\text{as}}(\text{SiOSi})$ stretching vibration at 1067 cm^{-1} due to cyclohexamethyltrisiloxane [17], and at 667 cm^{-1} $\delta(\text{CO}_2)$ due to carbon dioxide [18]. Bands due to water ($\delta(\text{H}_2\text{O})$ centred at 1595 cm^{-1}), ethanoic acid ($\nu(\text{O-H})$ 3580 cm^{-1} , $\nu(\text{C=O})$ 1788 cm^{-1} and $\nu(\text{C-O})$ 1182 cm^{-1} [19]), and methane ($\nu(\text{C-H})$ 3019 cm^{-1} and 1306 cm^{-1} ($\delta(\text{H}_3\text{C-H})$ [20]) are also observed. Absence of the bands at 3580 cm^{-1} , 1788 cm^{-1} and 1182 cm^{-1} when the reaction is carried out at 793 K indicates that no ethanoic acid is produced at that temperature.

The formation of the two siloxane products is corroborated by the mass spectrum of the reaction product mixture formed after near complete thermolysis at 818 K

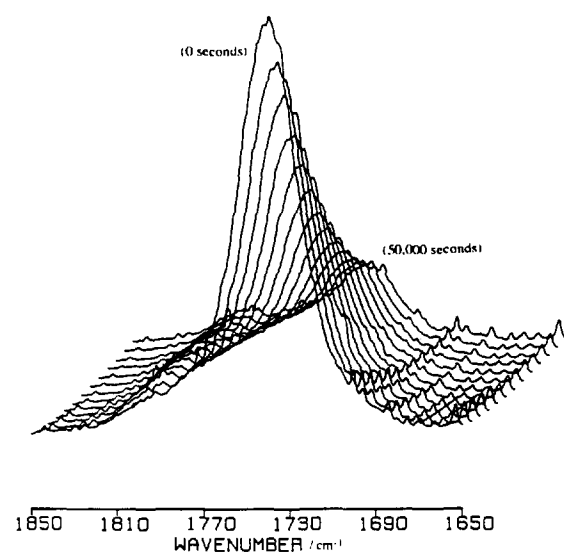
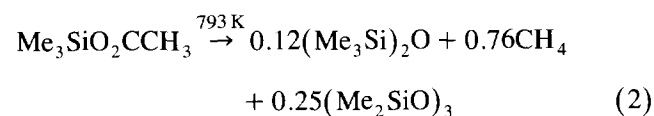
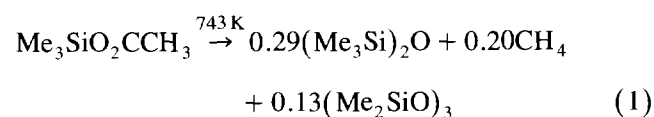


Fig. 4. Time-resolved spectra showing the decay of the $\nu(\text{C=O})$ peak of trimethylsilyl acetate during thermolysis at 763 K .

(16000 s). This shows peaks at m/e values of 221 ($(\text{M-H})^+$), 207 ($(\text{M-Me})^+$) and 147 resulting from fragmentation of cyclohexamethyltrisiloxane, and at m/e 131 due to loss of a methyl group from hexamethyldisiloxane.

Both carbon monoxide ($\nu(\text{CO})$ centroid 2144 cm^{-1}) [21] and carbon dioxide ($\nu_{\text{as}}(\text{CO}_2)$ centroid 2349 cm^{-1}) [18] are also formed, although the relative amounts of these products vary with both temperature and time. At temperatures of 763 K or less, more carbon monoxide than carbon dioxide is produced, the amount increasing with increasing temperature and reaching a maximum after ca. 25 min . At higher temperatures, however, the integrated peak envelope area for carbon monoxide is at a maximum value by the time the reaction temperature is attained, but decreases to zero with time whilst the amount of carbon dioxide increases steadily with time. Furthermore, carbon dioxide continues to be produced long after carbon monoxide has been lost from the reaction mixture, an observation which could indicate an heterogeneous process involving adsorption of carbon monoxide at the walls of the cell followed by subsequent slow desorption of carbon dioxide.

The overall stoichiometries for reactions carried out at 743 K and 793 K (from mass balance measurements obtained by spectral subtraction using spectra of authentic compounds) may be represented by the Eqs. (1) and (2)



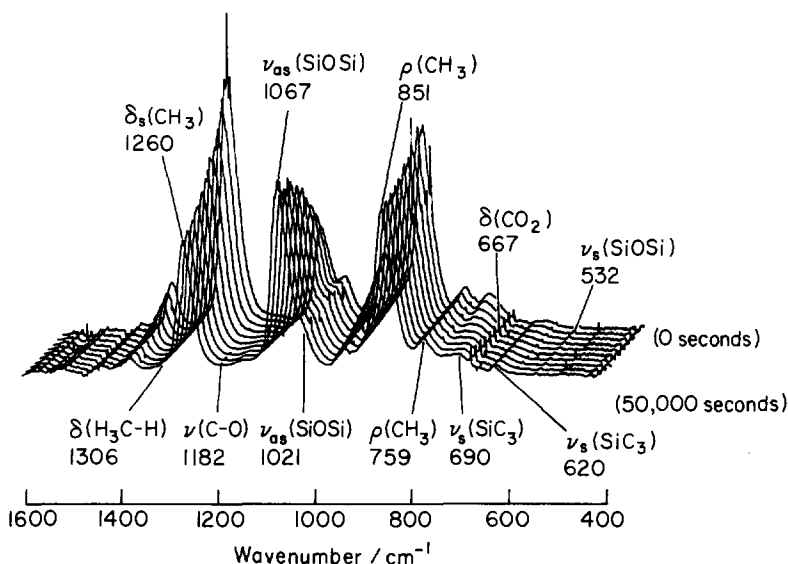


Fig. 5. Time-resolved spectra showing the appearance of peaks due to hexamethyldisiloxane during the thermolysis of trimethylsilyl at 763 K. Weak bands due to carbon dioxide, methane and cyclohexamethyltrisiloxane are also apparent.

Some residual trimethylsilyl acetate remains in each case (14.5% at 743 K and 2.6% at 793 K). Similar amounts of both hexamethyldisiloxane and hexamethylcyclotrisiloxane (on the basis of atom Si) are formed at 743 K, but the latter predominates at 793 K. More methane and carbon dioxide are also produced at higher temperatures.

3.3. Determination of rate data and the activation energy

From the time dependence of the integrated peak envelope area for the $\nu(\text{C}=\text{v})$ band over the region $1786\text{--}1663\text{ cm}^{-1}$ and the extinction coefficient ϵ , the loss of trimethylsilyl acetate with time was determined

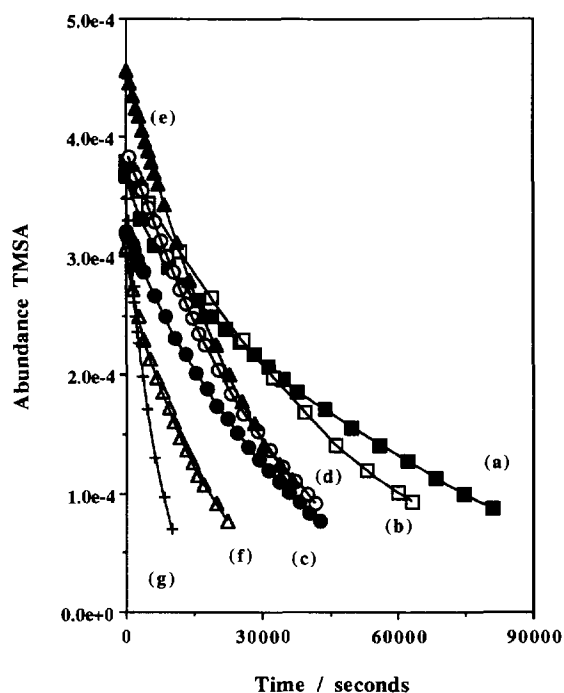


Fig. 6. Plot of gas phase molar abundance (mol l^{-1}) of trimethylsilyl acetate vs. time at (a) 723 K, (b) 733 K, (c) 743 K, (d) 753 K, (e) 763 K, (f) 793 K, and (g) 818 K.

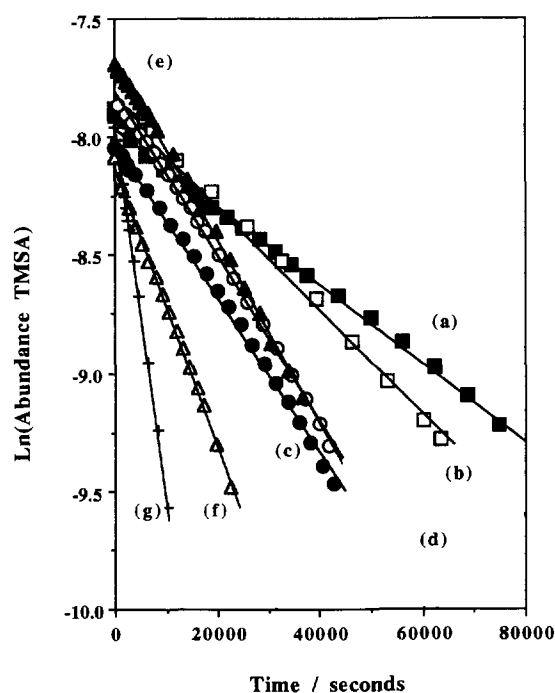


Fig. 7. First-order rate plots for the loss of trimethylsilyl acetate at (a) 723 K, (b) 733 K, (c) 743 K, (d) 753 K, (e) 763 K, (f) 793 K, and (g) 818 K.

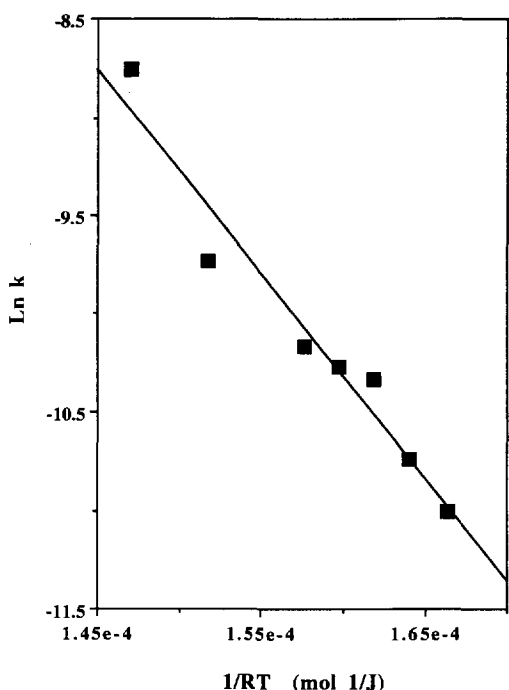


Fig. 8. Arrhenius plot for the loss of trimethylsilyl acetate in the temperature range 723–818 K.

for temperatures in the temperature range 723–818 K (Fig. 6). Plots of $\ln C$ vs. time (Fig. 7) are linear (correlation coefficients greater than 0.99) showing that the loss of trimethylsilyl acetate is first-order over the whole temperature range. First-order rate constants k vary from $1.66 \times 10^{-5} \text{ s}^{-1}$ at 723 K to $15.7 \times 10^{-5} \text{ s}^{-1}$ at 818 K. All kinetic runs were taken to ca. 75% completion (ca. two half-lives). Rate data are summarised in Table 2.

Table 2
First-order rate constant and Arrhenius data

Temperature/K	First order rate constant $k_1/\text{s}^{-1} (\times 10^5)$
723	1.66
733	2.17
743	3.25
753	3.46
763	3.86
793	5.96
818	15.7

Fig. 8 shows the corresponding Arrhenius plot from which the relationship

$$\ln k = 6.35 - 104.2/RT$$

(correlation coefficient 0.952) leads to values for the activation energy E_a and the pre-exponential factor A of $104(5) \text{ kJ mol}^{-1}$ and 572 s^{-1} , respectively.

3.4. Reaction with methyl iodide

Infrared spectra (Fig. 9) for the reaction of trimethylsilyl acetate and methyl iodide (molar ratio 5:1, combined pressure 12 Torr, 673 K, followed to greater than 75% loss of trimethylsilyl acetate) show the evolution of bands due to methane, hexamethyldisiloxane and ethanoic acid. Species *not* detected include carbon monoxide, carbon dioxide, cyclohexamethyltrisiloxane, water and hydrogen iodide or any other iodine-containing gaseous molecules. A very small reddy-brown deposit was formed but was not characterized.

When the reaction was carried using a 1:1 molar ratio of trimethylsilyl acetate and methyl iodide (combined pressure 16 Torr, 673 K) the products were

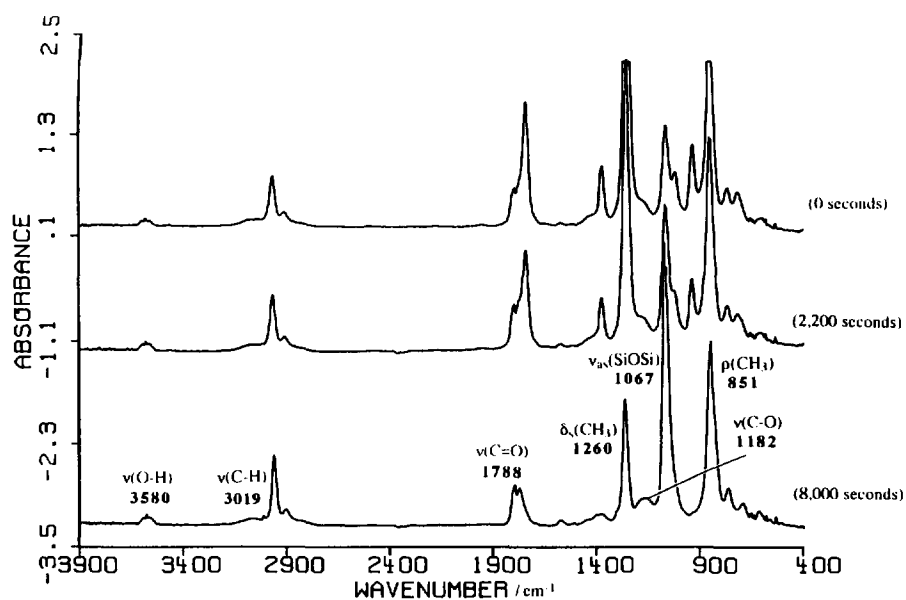


Fig. 9. Infrared spectra recorded during the thermolysis of trimethylsilyl acetate in the presence of methyl iodide (molar ratio 5:1) at 673 K showing the formation of hexamethyldisiloxane, ethanoic acid and methane.

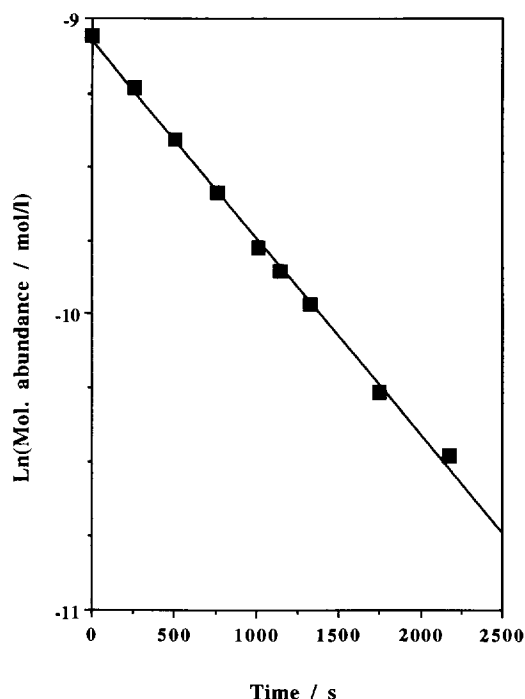


Fig. 10. First-order rate plot for the decomposition of trimethylsilyl acetate in the presence of methyl iodide (molar ratio 1:1) at 673 K.

methane, hexamethyldisiloxane and ethanoic acid, similar to the 5:1 reactant ratio experiment. Methyl iodide is totally consumed after ca. 2200 s, at which time ca. 75% of the trimethylsilyl acetate has decomposed. Bands associated with methane increase in intensity with time, whilst the bands associated with ethanoic acid and hexamethyldisiloxane decrease in intensity after 2200 s. Again, species *not* formed in the reaction include carbon monoxide, carbon dioxide, water, hydrogen iodide

and cyclohexamethyltrisiloxane, and the deposition of the reddish-brown solid is observed. With this ratio of reactants, the reaction also proceeds by first-order loss of trimethylsilyl acetate with a first-order rate constant of $6.66 \times 10^{-4} \text{ s}^{-1}$ (Fig. 10). Hence, the presence of an equal amount of methyl iodide causes the reaction to proceed ca. four times faster at 673 K than the rate of neat trimethylsilyl acetate decomposition at 818 K (cf. 75% depletion after ca. 10 000 s, $k_1 1.57 \times 10^{-4} \text{ s}^{-1}$), and the reaction is ca. 40 times faster at 723 K, the temperature at which decomposition of neat trimethylsilyl acetate commences at an appreciable rate (cf. 75% depletion after ca. 81 000 s, $k_1 1.66 \times 10^{-5} \text{ s}^{-1}$).

3.5. Reaction with nitric oxide

Infrared spectra of the reaction of trimethylsilyl acetate and nitric oxide (molar ratio 4:1, combined pressure 10 Torr) at 773 K show the growth of methane, ethanoic acid, water, carbon dioxide and trace amounts of carbon monoxide (Fig. 11). Although species containing SiOSi linkages are obviously formed, as indicated by the growth of new bands at 1060 cm^{-1} and 1018 cm^{-1} , their identification was not possible. However, hexamethyldisiloxane is not present. The trimethylsilyl acetate reacts more quickly under these reaction conditions (totally by ca. 3300 s) than for neat trimethylsilyl acetate at 793 K (only 75% decomposition after ca. 22 000 s).

With excess nitric oxide (molar ratio 1:10, combined pressure 88 Torr) at 773 K, methane, carbon dioxide, water, nitrous oxide ($\nu(\text{NN}) 2223 \text{ cm}^{-1}$, $\nu(\text{NO}) 1285 \text{ cm}^{-1}$, and $\nu(\text{NNO}) 588 \text{ cm}^{-1}$) [22], and traces of carbon monoxide are formed (Fig. 12). Transient hex-

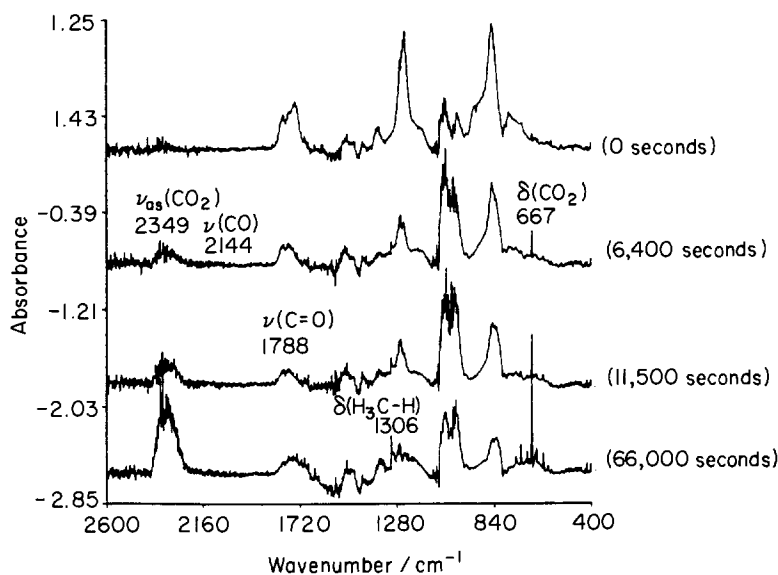


Fig. 11. Infrared spectra recorded during the thermolysis of trimethylsilyl acetate in the presence of nitric oxide (molar ratio 4:1) at 773 K showing the formation of ethanoic acid, carbon monoxide, carbon dioxide and methane.

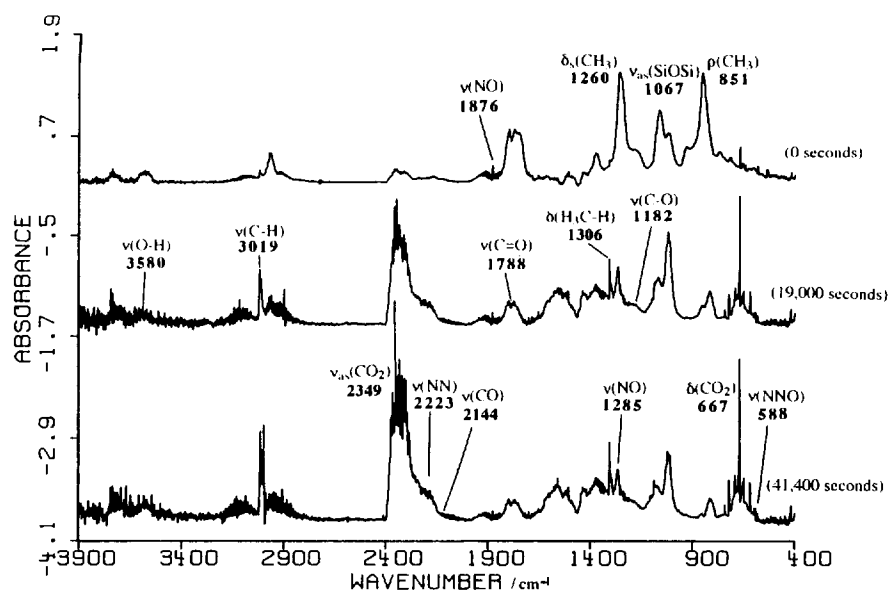


Fig. 12. Infrared spectra recorded during the thermolysis of trimethylsilyl acetate in the presence of nitric oxide (molar ratio 1:10) at 773 K showing the formation of nitrous oxide, ethanoic acid, carbon monoxide, carbon dioxide, methane, and transient hexamethyldisiloxane.

amethyldisiloxane (maximum value after 10000 s but then decreases to negligible amounts by 41 400 s), and ethanoic acid are also formed. Weak bands at 1072 cm^{-1} and 1017 cm^{-1} are probably $\nu_{\text{as}}(\text{SiOSi})$ vibrations but the species responsible could not be identified. Nitric oxide is still present after 41 000 s.

Trimethylsilyl acetate is completely consumed after ca. 19 000 s under these reaction conditions. Although this is a slower reaction than for the 4:1 molar ratio

experiment, it is still faster than the neat decomposition of trimethylsilyl acetate at 793 K.

3.6. Reaction with oxygen

Infrared spectra of a mixture of trimethylsilyl acetate and oxygen (molar ratio 1:4, combined pressure 40 Torr) shows that no reaction occurs at 733 K, but is totally consumed at 773 K. Spectra comprise bands due to

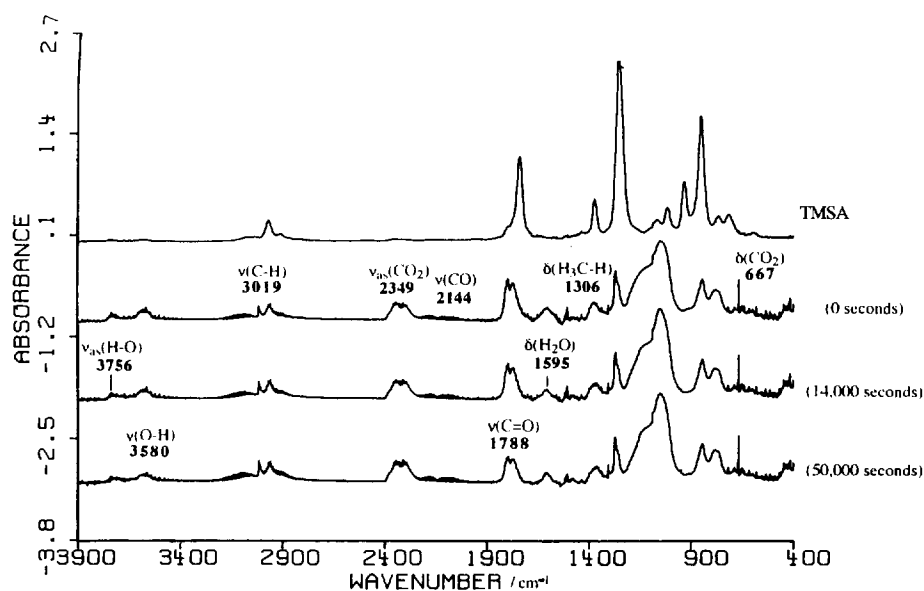


Fig. 13. Infrared spectra recorded during the thermolysis of trimethylsilyl acetate in the presence of oxygen (molar ratio 1:4) at 773 K showing the formation of ethanoic acid, carbon monoxide, carbon dioxide, methane and water.

ethanoic acid, carbon dioxide, methane, traces of carbon monoxide and water (Fig. 13). A broad band exists between the limits 1220–1000 cm⁻¹, which probably contain inter alia the $\nu_{\text{as}}(\text{SiOSi})$ bands due to hexamethyldisiloxane and cyclohexamethyltrisiloxane at 1067 cm⁻¹ and 1021 cm⁻¹ respectively. Carbon dioxide and carbon monoxide, although absent at 733 K, are present as soon as 773 K is reached, the relative amounts of each remaining approximately constant at 773 K. No further changes are observed in the spectra over 50 000 s at 773 K.

4. Discussion

A summary of the thermolysis data of trimethylsilyl acetate with the various reactants investigated is presented in Table 3.

Thermolysis of neat trimethylsilyl acetate in the temperature range 723–818 K gives the gaseous products hexamethyldisiloxane, cyclohexamethyltrisiloxane, methane, and carbon dioxide, whose proportions vary substantially with temperature, together with ethanoic acid, carbon monoxide and water. Loss of trimethylsilyl acetate follows first-order kinetics over the whole temperature range, and rate constants vary from $1.66 \times 10^{-5} \text{ s}^{-1}$ at 723 K to $15.7 \times 10^{-5} \text{ s}^{-1}$ at 818 K with an activation energy of 104(5) kJ mol⁻¹.

The observed acceleration in reaction rate in the presence of methyl iodide indicates that the mechanism is radical in nature, and a reaction scheme which accounts for the formation of all products is shown in Scheme 1. Owing to the strength of the Si–O bond, the expected initial process would be homolytic cleavage of the skeletal C–O bond generating trimethylsilyloxy and acetyl radicals (step 1), analogous to the generation of organosilyloxy radicals via the thermolysis of silylperoxides [23–25] and benzyloxydimethylsilane [26]. Three reaction pathways are possible for the further reaction of the trimethylsilyloxy radical:

(i) abstraction of hydrogen to form trimethylsilanol (step 2);

(ii) homolytic attack at the silicon atom of trimethylsilyl acetate displacing either a methyl radical and forming pentamethyl(acetato)disiloxane (step 3), or an acetoxy radical forming hexamethyldisiloxane (step 4);

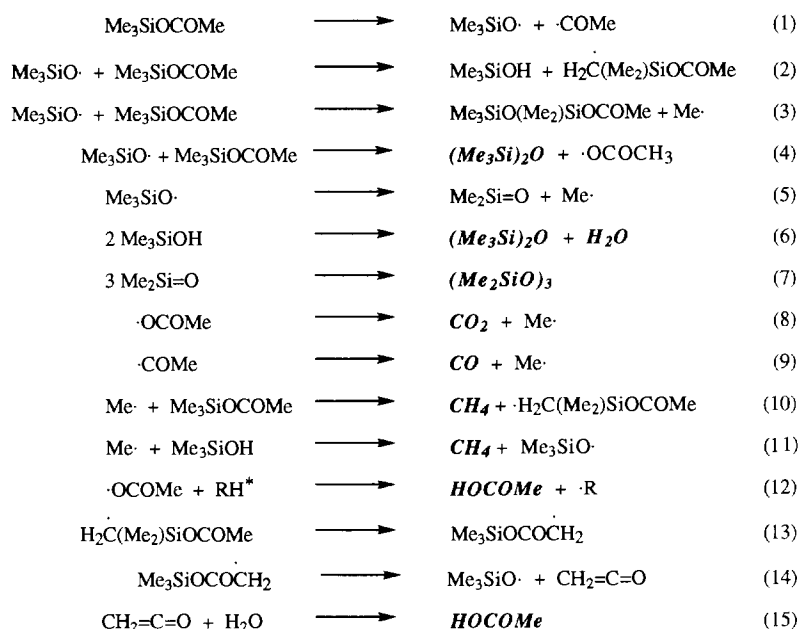
(iii) elimination of a methyl radical with the formation of dimethylsilanone (step 5).

Hydrogen-abstraction by trimethylsilyloxy radicals, is known to occur with a variety of substrates [24,25,27,28]. In particular, hydrogen-abstraction from bistrimethylsilyl peroxide giving the $\text{Me}_3\text{SiOOSiMe}_2\text{CH}_2$ radical has been observed, directly paralleling the process shown in step 2. The product of hydrogen-abstraction, trimethylsilanol, readily undergoes condensation to hexamethyldisiloxane and water [23] (step 6) and accounts for the formation of water in the system.

Silyloxy radical attack at a silicon centre, as far as we are aware, has not as yet been observed. However, interaction of trimethylsilyloxy radicals with the butyltin chlorides, $\text{Bu}_n\text{SnCl}_{4-n}$ ($n = 1-4$), proceeds via hydrogen-abstraction for Bu_4Sn , but $S_{\text{H}}2$ substitution at the tin centre displacing a butyl radical occurs with increasing chlorine substitution [24]. It would, therefore, not be unlikely for a similar $S_{\text{H}}2$ substitution, as shown in step 3, to occur in the present case, generating pentamethyl(acetato)disiloxane. Displacement of an acetoxy radical from silicon would give hexamethyldisiloxane directly. Although this process is unlikely in view of the high Si–O bond strength, the observation of ethanoic acid at lower temperatures, together with the absence of ethanoic acid but increased formation of carbon dioxide (only formed from the acetoxy radical by step 8), would indicate that this process does occur. The hexamethylcyclotrisiloxane observed almost certainly results from the trimerization of dimethylsilanone [29,30] (step 7) formed by methyl radical elimination from the trimethylsilyloxy radical (step 5). Although this process has not as yet been observed, it does have its parallel in the elimination of a methyl radical from the Me_3SiCH_2 and $\text{CMe}_2\text{SiCH}_2$ radicals affording the corresponding silaethenes [31]. The fate of any pentamethyl(acetato)disiloxane formed is uncertain. Ex-

Table 3
Summary of reactions for trimethylsilyl acetate

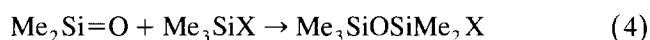
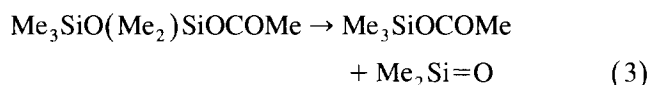
Reactant(s)	Thermolysis temperature/K	Gaseous products	Other species probably present	Order of reaction w.r.t. TSA	$E_a/\text{kJ mol}^{-1}$
TSA	723–818	$(\text{Me}_3\text{Si})_2\text{O}$, CH_4 , $(\text{Me}_2\text{SiO})_3$, CO_2 , MeCO_2H , CO , H_2O		First	104.2 (5.0)
TSA + MeI (1:1)	673	$(\text{Me}_3\text{Si})_2\text{O}$, MeCO_2H , CH_4		First	
TSA + NO (4:1)	773	CH_4 , MeCO_2H , CO_2 , CO	$(\text{Me}_2\text{SiO})_3$, $(\text{Me}_3\text{Si})_2\text{O}$		
TSA + NO (1:10)	773	CH_4 , MeCO_2H , CO_2 , CO , N_2O , $(\text{Me}_3\text{Si})_2\text{O}$	$(\text{Me}_2\text{SiO})_3$		
TSA + O_2 (1:4)	773	MeCO_2H , CO , CO_2 , CH_4 , H_2O	$(\text{Me}_2\text{SiO})_3$, $(\text{Me}_3\text{Si})_2\text{O}$		



* RH = any general species containing available hydrogen.

Scheme 1. Proposed reaction mechanism for the thermolysis of trimethylsilyl acetate in the temperature range 723–818 K (final products are in italicised bold font).

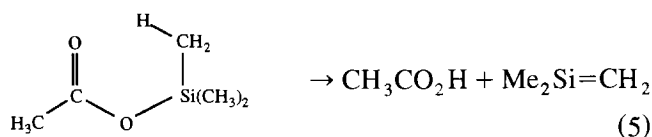
trusion of dimethylsilanone (Eq. (3)) could be possible, although this is perhaps unlikely since the reverse insertion reaction (Eq. (4)) might be expected to be favoured [32,33].



Thus, the formation of hexamethylcyclotrisiloxane is via steps 1, 2 and 6, whereas hexamethylcyclotrisiloxane arises from steps 1, 5 and 7. At lower temperatures both hexamethylcyclotrisiloxane and cyclohexamethyltrisiloxane are formed in similar amounts (on a Si atom basis), but at higher temperatures the latter predominates. Hence, at higher temperatures hydrogen-abstraction (step 2) is less important, and dimethylsilanone formation and trimerization is the major reaction pathway. Dimethylsilanone ($\nu(\text{Si=O})$ at 1209 cm^{-1}) [34] could not be observed in the infrared spectra in the present experiments, most probably because of its very low abundance as a transient intermediate and the presence of the $\delta_s(\text{CH}_3)$ band at 1260 cm^{-1} .

The acetyl radical formed in step 1 is known to eliminate carbon monoxide [35–38] (step 9). Methyl radicals are also formed in this step, the analogous elimination from acetoxy radicals (step 8), and additionally in the $S_{\text{H}2}$ process (step 3) and elimination from trimethylsilyloxy radicals (step 5), and lead to methane formation by hydrogen abstraction (steps 10 and 11). Ethanoic acid may be formed by an $S_{\text{H}2}$

displacement of an acetoxy radical (step 4) followed by hydrogen abstraction (step 12). An alternative pathway for the formation of ethanoic acid is via internal hydrogen abstraction from trimethylsilyl acetate [11] (Eq. (5)):



However, this process is unlikely to occur under the present conditions since it occurs to only a small extent at 1073 K and 10^{-3} Torr [11]. The production of acetoxy radicals in step 4 accounts for the formation of carbon dioxide (step 8) [39,40].

Whereas the hydrogen-abstraction process (step 2) is reasonable, the fate of the resulting $\text{H}_2\text{C}(\text{Me}_2)\text{SiOCOMe}$ radical formed is uncertain. Rearrangement to the $\text{Me}_3\text{SiOCOCH}_2$ radical (step 13) is a possibility, which could then eliminate ketene generating the trimethylsilyloxy radical (step 14). However, no ketene is observed, although it would be readily scavenged by water (step 15) providing an additional route for the formation of ethanoic acid.

In the presence of methyl iodide, the reaction is much faster and occurs at a much lower temperature than the neat reaction. The reaction product mixture is simpler, with only hexamethylcyclotrisiloxane, ethanoic acid and methane being formed. The principal difference under these conditions is that homolytic dissociation of

the C–I bond occurs at temperatures in excess of ca. 603 K, well below the temperature at which C–O bond homolysis of trimethylsilyl acetate occurs. Therefore step 1 in Scheme 1 cannot be the initiating process of the thermolysis in this case. That no carbon monoxide is formed (from the acetyl radical via step 9) corroborates this conclusion. Rather, hydrogen-abstraction by methyl radicals from trimethylsilyl acetate (step 10) forming methane is the principal process under these conditions. Subsequently, the ketene extrusion process (step 14) will occur. Since no hexamethylcyclotrisiloxane is observed, this indicates that dimethylsilanone is not formed. The simplified product distribution observed in the presence of methyl iodide lends some credence to the participation of the ketene extrusion step in the neat reaction also. Once generated by step 14, the trimethylsilyloxy radicals may then enter into the hydrogen-abstraction process of step 2 with subsequent condensation of trimethylsilanol to hexamethyldisiloxane (step 6), the water generated in this process being scavenged by ketene producing the ethanoic acid observed.

The loss of trimethylsilyl acetate is first-order over the whole temperature range studied, with first-order 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. The order with respect to trimethylsilyl acetate is also first-order in the presence of methyl iodide (molar ratio 1:1) at 673 K, with a rate constant of $6.66 \times 10^{-4} \text{ s}^{-1}$, i.e. a 40-fold increase in rate with a 50 K reduction in the thermolysis temperature compared with the neat reaction. The value of the activation energy ($104(5) \text{ kJ mol}^{-1}$) and the pre-exponential factor (572 s^{-1}) determined for the neat reaction are both relatively low. That the activation energy is much lower than is reasonable for the $\text{Me}_3\text{SiO}-\text{C}(\text{O})\text{CH}_3$ 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 [41,42], and propose that such enhancement is also occurring in the present case. That decomposition occurs to only a small extent at a pressure of 10^{-3} Torr even at 1073 K [11], conditions under which only unimolecular gas phase decomposition can occur, corroborates this conclusion.

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. However, in the presence of methyl iodide the reaction proceeds at a much lower temperature (673 K) and below the temperature at which $\text{Me}_3\text{SiO}-\text{C}(\text{O})\text{CH}_3$ bond homolysis occurs (723 K). Hence, the homolysis of methyl iodide exerts a dominating effect on the reaction kinetics, and hydrogen abstraction by methyl radicals is the rate determining process, which again would lead to first-order loss of trimethylsilyl acetate.

Surprisingly, nitric oxide (a known radical inhibitor) also enhances the reaction, especially at low molar ratios. Its usual reaction in the presence of hydrocarbons is to act as a radical scavenger, thus inhibiting radical reactions. Identified gaseous products in the reaction with trimethylsilyl acetate include methane, ethanoic acid, carbon dioxide, carbon monoxide, nitrous oxide and transient hexamethyldisiloxane. Other product(s) exhibiting $\nu_{\text{as}}(\text{SiOSi})$ bands in the infrared are present, but could not be characterized. Mercury sensitization of trimethylsilane in the presence of nitric oxide leads to the formation of siloxanes, nitrous oxide, nitrogen, hydrogen and nitric oxide [43]. In this case, $\text{Me}_3\text{Si}^\cdot$ radicals react with nitric oxide forming Me_3SiON : species which dimerise with subsequent elimination of either nitrogen or nitrous oxide from the intermediate $\text{Me}_3\text{SiON}=\text{NOSiMe}_3$. Since $\text{Me}_3\text{Si}^\cdot$ radicals will not be available in the present case, nitrous oxide cannot be formed by this particular pathway and we await further data in order to elucidate its formation. The other products are probably formed by the routes discussed for the neat reaction.

Oxygen also enhances the decomposition of trimethylsilyl acetate to such an extent that the reaction is complete by the time 773 K is achieved. Identified gaseous species include ethanoic acid, carbon monoxide, carbon dioxide, methane and water, along with unidentified siloxanes. Whilst it is not possible from the present data to ascertain with certainty the reaction pathways for oxidation processes, we have previously shown that the oxidation of trimethylgermane [44], tetramethyltin [41], and dimethyldivinyltin [21] proceed via surface-mediated reactions and involve reactive adsorbed oxygen species. Similar pathways are expected to operate in the present case.

Acknowledgements

We thank the EPSRC for a research studentship (to A.T.).

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