A mechanistic study of cyclic siloxane pyrolyses at low pressures†

Matthew J. Almond,[a] Rosa Becerra,[b] Sarah J. Bowes,[c] John P. Cannady,[d] J. Steven Ogden*[c] and Robin Walsh*[a]

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Matrix isolation IR spectroscopy has been used to study the vacuum pyrolysis of hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4) and decamethyl cyclopentasiloxane (D5), and the results interpreted in the context of various kinetic models. In particular, it is shown that the significant pyrolysis products—which include CH_3, CH_4, C_2H_2, C_2H_4, C_2H_6 and SiO—may be satisfactorily accounted for by radical reactions involving dimethylsiloxane (D1), and estimates are made of the various chain lengths for the proposed reactions based on a range of ambient conditions.

1. Introduction

The pyrolysis of siloxanes is a much-studied area not least because of the widespread industrial use of the cyclic oligomers in numerous high temperature environments. Typical early studies[1] on the thermal degradation of polydimethylcyclosiloxanes drew attention to the interconversion of these molecules, and in an early kinetic study[2] on the pyrolysis of octamethylcyclotetrasiloxane (D4) it was proposed that the formation and subsequent ring-expanding reactions of (monomeric) dimethylsiloxane (D1) played a key role in these processes. A wide-ranging review of these and related early studies can be found in a comprehensive review in 1985 by Raabe and Michl.[3] During this period, however, attempts to isolate and characterise this important intermediate were generally unsuccessful, and D1 remained an elusive molecule. However, its involvement in siloxane chemistry remained paramount, and its role was reviewed again in 1998 by Voronkov.[4]

An early attempt to spectroscopically characterise the possible intermediates in the pyrolysis of siloxanes was carried out in 1989 by Khabashesku *et al.*,[5] who obtained argon matrix IR spectra of the pyrolysis products of D4. In this work, they identified D3, together with SiO, CH_3, CH_4, C_2H_2, C_2H_4, and trace amounts of D2 (tetramethylcyclodisiloxane), but failed to find evidence for D1. Rather, it was proposed that D1 was unstable under the low pressure and high temperature pyrolysis conditions used, and decomposed into SiO and the range of hydrocarbon species observed. Despite the failure to identify D1 by this route, Khabashesku was, however, able to identify this species as a pyrolysis product of 6-oxa-3-silabicyclohexane and other bicyclo- systems, and assigned seven of its vibrational fundamentals.[6] The most intense features were located at 1244 (s), 1210 (s) and 798 (*vs.*) cm^{-1}: the 1210 cm^{-1} band being assigned as the Si=O stretch. This band assignment was confirmed by Withnall and Andrews[7] in their ^{18}O enrichment studies on the matrix photolysis of $(CH_3)_3SiH–O_3$ mixtures, where D1 was identified as a minor reaction product.

Our principal interest in this field is to explore possible mechanisms which could lead to the variety of small molecules identified in the matrix pyrolysis experiments, and to extend the original studies on D4 by Khabashesku *et al.* to include also the pyrolyses of D3 and D5. This has entailed not only the accumulation of matrix IR data for all these systems, but has also involved quantum calculations (G3 level) to justify key steps in the proposed mechanisms.

2. Experimental

The general features of our matrix isolation ir equipment have been described elsewhere.[8] Samples of D5, D4 and D3 were obtained from Aldrich and used at their stated purities (all >97%). In a typical matrix pyrolysis study, a flux of siloxane vapour was admitted through a PTFE control needle valve into a silica chamber which was typically heated to *ca.* 1000 K. The pressure in the chamber was estimated to be in the range 10^{-3} to 10^{-4} Torr, and the effusing vapours were cocondensed with an excess (*ca.* ×1000) of inert matrix gas onto a caesium iodide window maintained at *ca.* 12 K. Experiments were carried out using both nitrogen and argon as matrix gases (stated purities >99.99%), but nitrogen routinely gave sharper and simpler spectra, and the results described below relate to nitrogen matrix studies.

Supporting matrix experiments were also carried out on SiO, CH_4, C_2H_2, C_2H_4, and C_2H_6 for comparative purposes in the identification of the pyrolysis products. In addition to establishing the vibration frequencies for these species when trapped in nitrogen matrices, these studies also showed that C_2H_4 and C_2H_6 did not themselves undergo pyrolysis under the conditions used in siloxane experiments.

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[a] *School of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading, UK RG6 6AD. E-mail: r.walsh@reading.ac.uk*
[b] *Instituto de Quimica-Fisica, "Rocasolano", C.S.I.C., C/Serrano 119, Madrid, 28006, Spain*
[c] *School of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ. E-mail: jso@soton.ac.uk*
[d] *Dow Corning Corporation, Mail Stop C012322200 West Salzburg Road, P.O. Box 994, Midland, Michigan, 48686-0994, USA*

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To assist mechanistic interpretation, quantum chemical (*ab initio*) calculations were carried out at the G3 level of theory[9] in the same way as in earlier papers.[10,11]

3. Results and discussion

3.1 Spectroscopic studies

A preliminary series of experiments for these siloxane studies involved establishing the nitrogen matrix ir absorptions of the parent D3, D4 and D5 compounds, together with the hydrocarbons CH_4, C_2H_2 and C_2H_4 anticipated from Khabashesku's work, and the results of these studies are summarised in Table 1. From this Table, it may be concluded that D3, together with all three hydrocarbons would be easily distinguished if present all together in a mixture, but that it might be more difficult to discriminate between D4 and D5. The nitrogen matrix IR spectra of these two species proved to be remarkably similar, being confidently distinguished only by the different positions of weak bands at 697 cm^{-1} (D4) and 702 cm^{-1} (D5), and the presence of a shoulder at 824 cm^{-1} for D5 on the strong 812 cm^{-1} absorption. Also routinely observed in all spectra were features due to matrix isolated H_2O (at *ca.* 3725, 3633 and 1597 cm^{-1}). The growth of these bands mirrored the rate of matrix gas deposition, and there was no evidence that H_2O was produced as a pyrolysis product.

3.1.A Pyrolysis of octamethylcyclotetrasiloxane (D4). The preliminary studies showed that the principal absorptions of D4 lie in the C–H stretching region (3400–2800 cm^{-1}) and in the region 1500–600 cm^{-1}, and typical spectra obtained from D4 are shown in Fig. 1. In particular, Fig. 1a and b show spectra in the C–H stretching region obtained before and after the pyrolysis of D4 at *ca.* 1000 K. The single D4 feature in this region (Table 1) is still present after pyrolysis, but this is now accompanied by several new bands. As might be anticipated from the original study on this system[5] the majority of these bands can be assigned to D3, CH_4, C_2H_2, and C_2H_4, and this was confirmed by supporting experiments. However, the presence of prominent additional features in Fig. 1b at 2950, and 2890 cm^{-1} shows that at least one more hydrocarbon is formed during pyrolysis. The detection of CH_3 in the original study suggests that C_2H_6 might be considered as a possible candidate, and the nitrogen matrix spectrum of C_2H_6 in this spectral region is reproduced in Fig. 1c. Band correlation is excellent, and it is evident that C_2H_6 has also been formed here as a result of pyrolysis.

Fig. 2 shows the spectral region 1500–600 cm^{-1} from the same experiments. Fig. 2a shows the D4 parent bands in this region, whilst Fig. 2b shows a typical spectrum obtained after pyrolysis at 1000 K. In addition to residual features arising from un-pyrolysed D4, this latter spectrum clearly shows the presence of D3 (at *ca.* 1030 cm^{-1}), together with the known absorptions of C_2H_2, CH_4, C_2H_4 and C_2H_6 in this region. D3 also provides the major contribution to the bands at 1262 and 816 cm^{-1}, which overlap almost exactly (Table 1) with parent D4 bands. The absorptions at 919 and 610 cm^{-1} signal the presence of D2 and the radical CH_3 respectively, as proposed by Khabashesku *et al.*[5] A very weak feature at 1224 cm^{-1} was also present after pyrolysis confirming the formation of SiO, but at a significantly lower intensity relative to the other products. C_2H_6 shows three IR bands in this region, but only one of these (at *ca.* 830 cm^{-1}) would have been present in Khabashesku's published spectrum, and it could well have been overlapped by the intense D3 band occurring near this value. This new pyrolysis product might therefore have been present in his system, whilst remaining undetected. Finally, a band at 870 cm^{-1} routinely appeared on pyrolysis, but it remains unassigned.

The wavenumbers and band assignments arising from the pyrolysis of D4 are included in Table 1, and it is evident that these results, with the additional identification of C_2H_6, are in very good agreement with the conclusions from the previous work.

3.1.B Pyrolysis of D5 and D3. Analogous experiments on the pyrolysis of D5 at *ca.* 1000 K resulted in the formation of D3 together with SiO and the same hydrocarbon decomposition products as were observed above for D4. There was no evidence for the intermediate formation of D4. It was also significant that the various hydrocarbon products were produced in much the same proportions as from D4, as indicated by relative band intensities.

The pyrolysis of D3 also gave the same hydrocarbon products (together with SiO), although this siloxane appeared relatively more resistant to decomposition under the conditions used. It may also be significant that the proportions of C_2H_2 and CH_4 produced from D3 were relatively lower than

Table 1 Assignments of significant infrared bands (cm^{-1}: N_2 matrix) observed during pyrolysis studies on D3, D4 and D5

Species	Observed wavenumbers[a]
D3	2972 (w), 1261 (s), 1029 (vs), 817 (vs), 690 (w), 606 (w)
D4	2973 (w), 1263 (s), 1098 (sh), 1078 (vs, br), 815 (vs), 697 (w)
D5	2971 (w), 1263 (s), 1094 (sh), 1067 (vs, br), 824 (sh), 812 (vs), 702 (w)
SiO	1224
CH_3	611
CH_4	3024 (br), 1305
C_2H_2	3280, 747
C_2H_4	3105, 2987, 1436, 947
C_2H_6	2985, 2950, 2921, 2890, 2859, 2835, 1465, 1376, 828
D2	919
(unassigned)	870

[a] Wavenumber accuracy (±)1 cm^{-1}.

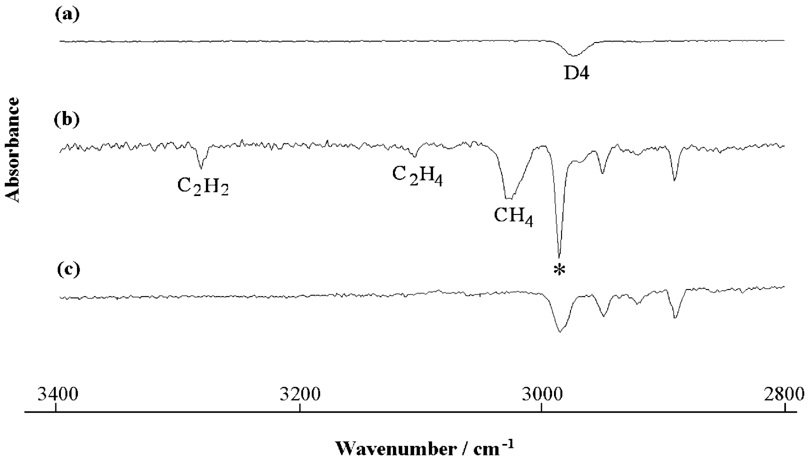

Fig. 1 Nitrogen matrix IR bands (3400–2800 cm^{-1}) observed in pyrolysis studies on D4 at 1000 K (a) D4 before pyrolysis; (b) D4 after pyrolysis; (c) spectrum of C_2H_6. The feature denoted by the asterisk is an accidental overlap of bands from C_2H_4 and C_2H_6.

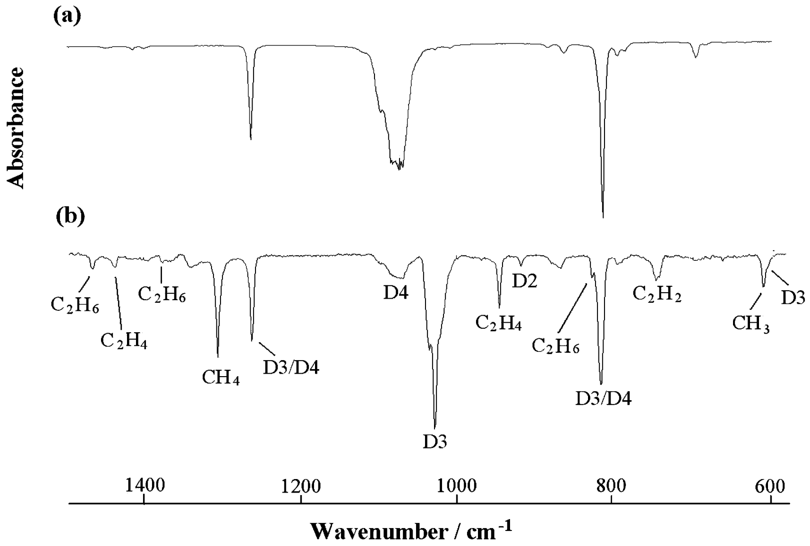

Fig. 2 Nitrogen matrix IR bands (1500–580 cm^{-1}) observed in pyrolysis studies on D4 at 1000 K. (a) D4 before pyrolysis; (b) D4 after pyrolysis, showing band assignments.

for C_2H_4 and C_2H_6. This is most easily seen in the C–H stretching region, and Fig. 3a and b show the comparison in band intensities between the products of D5 and D3 in this region.

3.1.C Formation of D1?. In his original work on the pyrolysis of D4, Khabashesku *et al.*[5] was unable to confirm the presence of D1 as a key intermediate, although its importance in the thermal decomposition process seemed almost self-evident. In this present work on D3, D4 and D5, we therefore looked closely in the region of 1244, 1210 and 798 cm^{-1} where the most intense fundamentals of D1 have been assigned,[6,7] in an attempt to find any evidence for the presence of D1. No new pyrolysis product features appeared at these expected positions in either argon or nitrogen matrices. The 798 cm^{-1} band would admittedly be quite close to the intense 810–820 cm^{-1} absorption found in all parent siloxane spectra, but our spectral band widths were sufficiently narrow to allow detection of any significant new product near 800 cm^{-1}. In the higher frequency region only the parent feature at *ca.* 1262 cm^{-1} might present a potential obstacle by way of reactant–product overlap, but only the SiO band at 1224 cm^{-1} was ever detected in the region 1200–1250 cm^{-1}. If any D1 had been isolated in these studies it would have been at very low concentrations.

3.2 Mechanistic studies

The initial study on the pyrolysis of D4 by Davidson and Thompson[2] established that under static conditions (766 to 842 K), D4 gave D3 in a unimolecular process with an activation energy of 301 kJ mol^{-1}. D5 was also produced in lower yield, suggesting that dimethylsilanone (D1) was a likely intermediate, and this intermediate was also proposed by Khabashesku *et al.*[5] Many of the hydrocarbon products found from this system have also been found in the pyrolysis of other plausible precursors of D1 at similar temperatures, but only one type of precursor, the epoxysilacycloalkanes, which

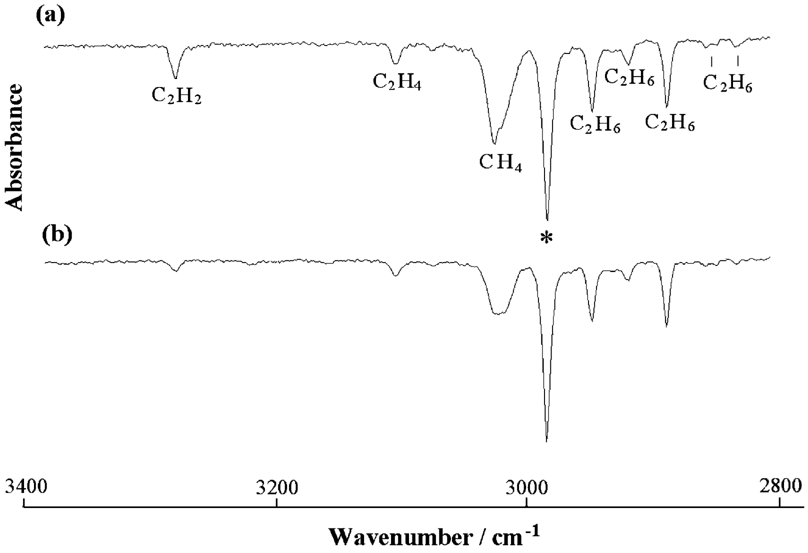

Fig. 3 Nitrogen matrix IR bands in the C–H stretching region. (a) D5 after pyrolysis at 1000 K; (b) D3 after pyrolysis at 1000 K. The feature denoted by the asterisk is an accidental overlap of bands from C_2H_4 and C_2H_6.

decompose at lower temperatures, has provided *direct evidence* for formation of D1 in the form of a matrix IR spectrum.[6,12] Clearly the evidence is strong that D1 is formed from D4. Our results show that D3 is formed from both D4 and D5 and that the array of small molecules (CH_4, CH_3, C_2H_6, C_2H_4, C_2H_2 and SiO) are formed from each of D3, D4 and D5. Thus it seems likely that the decomposition mechanisms of all three oligomers are similar. Our working hypothesis is therefore that each of the oligomers decomposes by elimination of D1 and that the larger ones effectively depolymerise. It seems therefore very likely that all the smaller products arise from the decomposition of D1, which is itself not stable at these high temperatures.

The similarity between D1 and acetone provides a useful starting point for consideration of the decomposition mechanism of D1. Rice and Herzfeld[13] proposed the original chain mechanism for the pyrolysis of acetone and Rice and Vollrath[14] confirmed that CH_4 and CH_2CO (ketene) are the major reaction products. Mousavipour and Pacey[15] have carried out the most recent study of the kinetics of acetone decomposition. Based on this we propose the following decomposition mechanism for D1:

$$(CH_3)_2SiO \rightarrow CH_3 + CH_3SiO \qquad (1a)$$

$$CH_3SiO \rightarrow CH_3 + SiO \qquad (1b)$$

$$CH_3 + (CH_3)_2SiO \rightarrow CH_4 + CH_2Si({=}O)CH_3 \qquad (2)$$

$$CH_2Si({=}O)CH_3 \rightarrow CH_2SiO + CH_3 \qquad (3)$$

$$2CH_3 \rightarrow C_2H_6 \qquad (4a)$$

$$CH_3 + CH_2Si({=}O)CH_3 \rightarrow C_2H_5Si({=}O)CH_3 \qquad (4b)$$

$$2CH_2Si({=}O)CH_3 \rightarrow (CH_2Si({=}O)CH_3)_2 \qquad (4c)$$

This mechanism would account for formation of CH_4, C_2H_6 and SiO (provided the chain reaction is short). The other hydrocarbon products could arise if CH_2SiO (a silicon analogue of ketene) were unstable and decomposed to give CH_2 ($^3B_1$) [CH_2(T) for short] + SiO. The following additional reactions could then occur:

$$CH_2SiO \rightarrow CH_2(T) + SiO \qquad (5a)$$

$$2CH_2(T) \rightarrow C_2H_2 + H_2 \text{ (or 2H)} \qquad (6a)$$

$$CH_2(T) + CH_3 \rightarrow C_2H_5^* \rightarrow C_2H_4 + H \qquad (6b)$$

$$H + CH_2SiO \rightarrow CH_3SiO^* \rightarrow CH_3 + SiO \qquad (7)$$

The combination process of CH_2(T), reaction (6a), is known to form C_2H_2[16] and CH_2(T) should be sufficiently unreactive with other molecules to accumulate in sufficient concentration to participate in combination processes.

In order to investigate further the feasibility of this mechanism we have undertaken quantum chemical calculations (G3 level) of the key steps in the mechanism. The results are shown in Table 2. Because of its potential significance we have also included reaction (8), the direct methane elimination process:

$$(CH_3)_2SiO \rightarrow CH_4 + CH_2{=}Si{=}O \qquad (8)$$

The energy values (ΔE_o or ΔH_{298}) show a number of important features. The breaking of the C–Si bond in $(CH_3)_2SiO$, reaction (1a), is the highest energy process. Reaction (1b) has only a low energy requirement and the radical CH_3SiO will

Table 2 Theoretically calculated ΔE_o and ΔH_{298} values (kJ mol^{-1}) for potentially important reaction steps in the thermal decomposition of dimethylsilanone (G3 level)

Reaction step		ΔE_o	ΔH_{298}
(1a)	$(CH_3)_2SiO \rightarrow CH_3 + CH_3SiO$	347	353
(1b)	$CH_3SiO \rightarrow CH_3 + SiO$	81	86
(2)	$CH_3 + (CH_3)_2SiO$ $\rightarrow CH_4 + CH_2Si({=}O)CH_3$	−22	−24
(3)	$CH_2Si({=}O)CH_3 \rightarrow CH_2SiO + CH_3$	270	276
(5a) (T)	$CH_2SiO \rightarrow CH_2(T) + SiO$	209	213
(5b) (S)	$CH_2SiO \rightarrow CH_2(S) + SiO$	248	253
(8)	$(CH_3)_2SiO \rightarrow CH_4 + CH_2SiO$	248	252
	$CH_3 + (CH_3)_2SiO \rightarrow TS2$	46	42
	$(CH_3)_2SiO \rightarrow TS8$	339	338

decompose readily under most conditions. The products CH_4 and $CH_2{=}Si{=}O$ could arise either from the chain propagation steps (reactions (2) and (3)) or directly *via* reaction (8). It should be noted that because reaction (8) is a molecular elimination process it has a significant energy barrier above the overall endothermicity. This is shown in the energy value for TS8 [the transition state of reaction (8)] which is only slightly less than the dissociation energy for step (1a). Which of the two sources of CH_4 + CH_2SiO is more likely is considered below. However, assuming CH_2SiO is formed, the relatively low energy required for its dissociation to give CH_2(T) means that its decomposition *via* reaction (5a) is inevitable (even despite the requirement for intersystem crossing). Once formed CH_2(T) should react *via* the barrierless combination reactions (6a) and (6b).

To decide between the different sources of CH_4 + $CH_2{=}Si{=}O$, we have compared the rate constants for each process with those of $(CH_3)_2SiO$ dissociation [reaction (1a)]. For these purposes RRKM calculations[17] were necessary, because under reaction conditions (low pressure, high temperature) the unimolecular reactions are pressure dependent.

3.2.A Comparison of rate constants for steps (1a) and (8).

RRKM calculations (for details see appendix and ESI)† were carried out in order to calculate values for the rate constants k_{1a} and k_8 over a range of pressures at 950, 983 and 1000 K. Table 3 gives values for the relative rate constants under experimental conditions. The ratio k_{1a}/k_8 has values in the range 100–1000. It is thus clear that in the gas phase reaction (8) cannot compete with (1a) as a decomposition pathway for $(CH_3)_2SiO$ and therefore cannot be a significant source of CH_4 + CH_2SiO. The only way reaction (8) could compete would be through wall catalysis.

3.2.B Calculation of the chain length of reaction cycle (1)–(4).

Based on the assumption that CH_3 is the dominant propagation radical, the chain length, L_C, can be calculated from the expression:[18,19]

$$L_C = k_2[(CH_3)_2SiO]^{1/2}/\sqrt{(k_1k_{4a})}$$

Of the rate constants k_1, k_2 and k_{4a}, only the last has been investigated experimentally. Using estimated values for k_1 and k_2 based on the quantum chemical calculations and other kinetic information (see supporting information) we have calculated values for L_C. Table 4 gives these values for the range of experimental conditions. The figures have values in the range 30–250 and suggest substantial yields of CH_4 + CH_2SiO produced *via* the chain propagation cycle of steps (2) and (3). However, because of the number of assumptions involved in estimating these numbers they should be regarded as indicative rather than definitive. The observation of C_2H_6 suggest that chain lengths might not be as large as this.

Table 3 Relative values for k_{1a}/k_8 in the experimental pressure and temperature ranges

	Press./Torr			
Temp./K	10^{-1}	10^{-2}	10^{-3}	10^{-4}
950	713	465	270	136
983	733	475	275	138
1000	745	483	279	140

Table 4 Relative values for the chain length, L_C, in the experimental pressure and temperature ranges

	Press./Torr			
Temp./K	10^{-1}	10^{-2}	10^{-3}	10^{-4}
950	52	67	111	226
983	45	49	82	170
1000	30	41	70	145

Conclusions

These experiments have established that the three cyclic siloxanes D3, D4 and D5 produce essentially the same hydrocarbon decomposition products when undergoing vacuum pyrolysis, indicating that a common precursor is almost certainly involved in the process. The combination of quantum chemical calculations and kinetic estimates shows that the proposed mechanism for decomposition of $(CH_3)_2SiO$ (and CH_2SiO) is a viable one to explain the observed products in this reaction. More quantitative direct rate studies on $(CH_3)_2SiO$ itself would be required to further validate this mechanism. Finally, it is interesting to note that in these high temperature systems, the $Si{=}O$ unit would appear to remain intact during the reactions of $(CH_3)_2SiO$, with decomposition proceeding essentially *via* the CH_3 groups. In R_2SiO molecules where R cannot itself undergo decomposition, (*e.g.* R = Cl), the analogous Cl_2SiO species is found[22] to be stable to at least 1500 K.

Appendix

RRKM calculations on steps (1a) and (8) employed a two channel model. For step (1a) the vibrational assignment of the transition state was based on an *A* factor estimated from the thermodynamics of step (1a)[20] and the *A* factor for reverse (radical combination) reaction.[21] For step (8), the vibrational assignment of the transition state was available.[20] Weak collisions ($\langle \Delta E \rangle_{\text{down}}$ = 1000 cm^{-1}, stepladder model) were assumed. Further details are given in the ESI.†

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