Dimethylsilanone from the Pyrolysis of Octamethylcyclotetrasiloxane

By I. M. T. DAVIDSON* and J. F. THOMPSON

(*Department of Chemistry, The University, Leicester* LE1 7RH)

Summary Dimethylsilanone, $Me_2Si:O$, is postulated as an intermediate in the gas-phase thermalde composition of octamethylcyclotetrasiloxane; a lower limit for the silicon–oxygen π-bond strength in dimethylsilanone is calculated.

As part of an investigation of the thermal and oxidative stability of simple model compounds for methylsiloxane polymers we have pyrolysed octamethylcyclotetrasiloxane, $(Me_2SiO)_4$, in the gas-phase between 766·5 and 842 K with initial pressures of between 66·5 and 1800 Nm^{-2} (0·5—13·5 mmHg). A static system with provision for g.l.c. analysis (gas density detector and nitrogen carrier gas) was used, and the reaction products were identified by g.l.c. and by mass spectrometry.

Pyrolysis of $(Me_2SiO)_4$ up to *ca.* 25% decomposition gave hexamethylcyclotrisiloxane, $(Me_2SiO)_3$, and decamethylcyclopentasiloxane, $(Me_2SiO)_5$, as the only products. Up to *ca.* 4% decomposition the reaction was kinetically simple. The two products were formed in similar amounts, the molar excess of $(Me_2SiO)_3$ over $(Me_2SiO)_5$ being about 1·3; while the decomposition of $(Me_2SiO)_4$ accurately followed the first-order rate law (the usual log-log plot of initial rate against concentration had a slope of 0·98 ± 0·03). Beyond 4% decomposition the relative rate of formation of $(Me_2SiO)_5$ decreased rapidly, the concentration–time curve for $(Me_2SiO)_5$ passing through a maximum at about 20% decomposition, while the rate of decomposition of $(Me_2SiO)_4$ and the rate of formation of $(Me_2SiO)_3$ showed fall-off from the first-order law. Ultimately, at high percentage decomposition, the only product was $(Me_2SiO)_3$.

The rate of formation of $(Me_2SiO)_3$ was measured up to 4% decomposition, first-order rate constants being given by: $\log k = 14{\cdot}85 \pm 0{\cdot}39 - (300{\cdot}9 \pm 6{\cdot}1)/2{\cdot}303RT$ (95% confidence limits), where k is in s^{-1} and the activation energy in kJ mol^{-1}. To see why no cyclic siloxanes higher than $(Me_2SiO)_5$ were observed, a few experiments on the pyrolysis of dodecamethylcyclohexasiloxane, $(Me_2SiO)_6$ were conducted. This compound decomposed to $(Me_2SiO)_3$ extremely rapidly at 766·5 K, probably by an intramolecular mechanism analogous to that suggested for the thermal degradation of polydimethylsiloxanes,[1] which has an activation energy of only 176 kJ mol^{-1}. We suggest the following mechanism for the overall decomposition of $(Me_2SiO)_4$:

$$(Me_2SiO)_4 \rightleftharpoons Me_2Si:O + (Me_2SiO)_3 \qquad (1)\ (-1)$$

$$Me_2Si:O + (Me_2SiO)_4 \rightleftharpoons (Me_2SiO)_5 \qquad (2)\ (-2)$$

$$Me_2Si:O + (Me_2SiO)_5 \rightleftharpoons (Me_2SiO)_6 \qquad (3)\ (-3)$$

$$(Me_2SiO)_6 \rightarrow 2\,(Me_2SiO)_3 \qquad (4)$$

Up to 4% decomposition reactions (1), (2), and (−2) suffice to describe the mechanism. The other reactions are responsible for the fall-off observed thereafter, and for the ultimate formation of $(Me_2SiO)_3$ as the only product; the steady-state concentration of $(Me_2SiO)_6$ was too small to be observed because of its instability at these temperatures.

Further evidence for describing the mechanism in the early stages by reactions (1), (2), and (−2) only was provided by trapping experiments; propene, buta-1,3-diene, and traces of silicone grease were all found to be effective in inhibiting the formation of $(Me_2SiO)_5$ but not of $(Me_2SiO)_3$. However, most of our trapping experiments made use of ethylene, since it produced no response on the gas density detector and therefore could be added in large excess without obscuring product peaks on the g.l.c The effect of a 90-fold excess of ethylene on the pyrolysis is summarised in the Figure, which shows that the first-order formation of $(Me_2SiO)_3$ is maintained up to at least 10% decomposition, while the formation of $(Me_2SiO)_5$ is almost completely suppressed. Peaks attributable to adduct formation were observed on the g.l.c. The discrepancy between the amounts of $(Me_2SiO)_3$ and $(Me_2SiO)_5$ formed in the absence of ethylene in the initial stages is probably due to some heterogeneous loss of $Me_2Si:O$ as well as to reaction (−2).

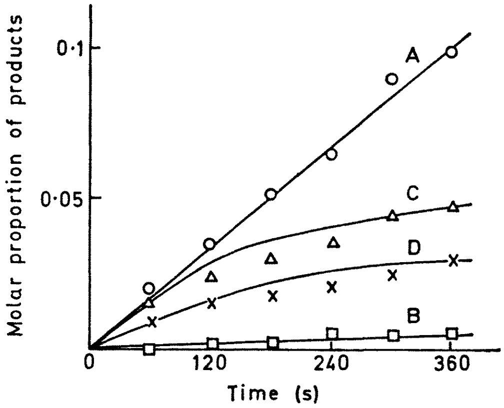

FIGURE. *Effect of an excess of ethylene on the rate of formation of pyrolytic products at* 842 K. (A) *Formation of* $(Me_2SiO)_3$ *with added ethylene*; (B) *Formation of* $(Me_2SiO)_5$ *with added ethylene*; (C) *Formation of* $(Me_2SiO)_3$, *absence of ethylene*; (D) *Formation of* $(Me_2SiO)_5$, *absence of ethylene.*

The experimental activation energy for the formation of $(Me_2SiO)_3$ equals E_1 and $\Delta H_1 = E_1 - E_{-1}$. E_{-1} is likely to be fairly low, but irrespective of its value a lower limit for the π-bond energy in $Me_2Si:O$ may be calculated by considering the energetics of reaction (1). Taking 444 kJ mol^{-1} for D(Si—O) in $(Me_2SiO)_4$ and $(Me_2SiO)_3$,[2-4] with 15 kJ mol^{-1} of strain energy in the latter,[4] we calculate the π-bond energy in $Me_2Si:O$ as: $444 + 15 - \Delta H_1$, and since $\Delta H_1 \leqslant E_1$, the π-bond energy $\geqslant 444 + 15 - 301 \geqslant 158$ kJ mol^{-1}. Thus the silicon–oxygen bond in $Me_2Si:O$ is at least 158 kJ mol^{-1} stronger than a simple silicon–oxygen σ-bond, and $Me_2Si:O$ is best thought of as a weakly double-bonded molecule rather than a biradical.

Jackson[5] has pointed out that the sum of the σ- and π-carbon–carbon bond energies for ethane and ethylene approximately equals the dissociation energy of C_2, and that similar reasoning applied to silicon carbide gives 117 kJ mol^{-1} for its π-bond energy, from the difference between its bond dissociation energy and that of the silicon–carbon σ-bond in tetramethylsilane (a value of 125—167 kJ mol^{-1} has been estimated[6] for the silicon–carbon π-bond energy in $Me_2Si:CH_2$ from kinetic arguments). This simple approach can be extended to molecules with two formal π-bonds, such as carbon monoxide. The dissociation energy of carbon monoxide is[7] 1069 kJ mol^{-1}, while that of a carbon–oxygen σ-bond is[3] 358 kJ mol^{-1}; hence the energy of each π-bond in CO is $\frac{1}{2}(1069 - 358) = 356$ kJ mol^{-1}, comparable with the π-bond energies of 337 kJ mol^{-1} in H_2CO, 379 kJ mol^{-1} in HMeCO, and 391 kJ mol^{-1} in Me_2CO. Taking the dissociation energy of silicon monoxide[7] (782 kJ mol^{-1}) in conjunction with the silicon–oxygen σ-bond energy (444 kJ mol^{-1}) we obtain, similarly, a value of 169 kJ mol^{-1} for each π-bond in silicon monoxide in good agreement with our value of $\geqslant 158$ kJ mol^{-1} for $Me_2Si:O$.

Thus $Me_2Si:O$, like $Me_2Si:CH_2$,[8] is formed pyrolytically as a weakly double-bonded molecule. An investigation of the pyrolysis of $(Me_2SiNH)_4$, which is known[9] to give $(Me_2SiNH)_3$, might reveal the existence of a similar silicon–nitrogen double-bonded molecule.

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