The Thermolysis of Hexamethyldisilane

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DAVIDSON and his colleagues found the pyrolysis of hexamethyldisilane (I), in a static system at 523—550° and 0·2—0·8 mm. Hg, to have the approximate overall stoicheiometry of equation (1).[1]

$$\begin{aligned} & 11\mathrm{Me_6Si_2} \rightarrow 5\mathrm{Me_3SiH} + \mathrm{Me_4Si} \\ & \qquad + \underset{\text{(I)}}{4\mathrm{Me_5Si_2CH_2SiMe_3}} + \underset{\text{(II)}}{(\mathrm{Me_5Si_2})_2\mathrm{CH_2}} \end{aligned} \qquad (1)$$

Sakurai, Hosomi, and Kumada[2] have pointed out that this finding is apparently in conflict with Shiina and Kumada's observation[3] that the major product of the thermolysis of (I) in a flow system at 600° is the isomeric compound (II), and have shown that the reaction in a sealed tube at 400° produces (II) in high yield, along with a small amount of trimethylsilane. They appreciate that the decomposition may have a different mechanism at low pressure than at the high pressure of the sealed-tube reaction, and conclude that the thermolysis of (I) needs further investigation.[2] We present results which largely account for the apparent anomaly.

We have pyrolysed hexamethyldisilane in a static system between 444—507° at 10—125 mm. The major product is the compound (II), which is formed in over 80% yield, along with a small amount of trimethylsilane [$\mathrm{Me_3SiH}$: (II) = *ca.* 0·06] and traces of tetramethylsilane, methane, and an unidentified high-boiling material. The order of the reaction is 1·56 ± 0·06 (taken to be 1·50), the activation energy is 60 ± 2 kcal./mole, and the value of the pre-exponential factor, A, in mole^{-1} ml.$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$, is given by $\log A = 16{\cdot}65 \pm 0{\cdot}7$. The rate is unchanged by a 15-fold increase in the surface : volume ratio, or by addition of argon or benzene, but is lowered by addition of toluene, which does not change the yield of the major product (II). At 537° the rate of decomposition of (I) is *ca.* 20 times greater than that of (II).

These results are consistent with the chain process (2)—(6) for the main reaction with an approximate chain length, as indicated by the (II) : $\mathrm{Me_3SiH}$ product ratio of 17. The initiation step, (2), and the propagation steps, (3)—(5),

$$\mathrm{Me_3Si{\cdot}SiMe_3} \rightarrow 2\mathrm{Me_3Si}\cdot \qquad (2)$$

$$\begin{aligned} & \mathrm{Me_3Si}\cdot + \mathrm{Me_3Si{\cdot}SiMe_3} \rightarrow \mathrm{Me_3SiH} \\ & \qquad + \mathrm{Me_3Si{\cdot}SiMe_2{\cdot}CH_2}\cdot \end{aligned} \qquad (3)$$

$$\mathrm{Me_3Si{\cdot}SiMe_2{\cdot}CH_2}\cdot \rightarrow \mathrm{Me_3Si{\cdot}CH_2{\cdot}SiMe_2}\cdot \qquad (4)$$

$$\begin{aligned} & \mathrm{Me_3Si{\cdot}CH_2{\cdot}SiMe_2}\cdot + \mathrm{Me_3Si{\cdot}SiMe_3} \rightarrow \\ & \qquad \mathrm{Me_3Si{\cdot}CH_2{\cdot}SiMe_2H} + \mathrm{Me_3Si{\cdot}SiMe_2{\cdot}CH_2}\cdot \end{aligned} \qquad (5)$$

$$2\mathrm{Me_3Si{\cdot}CH_2{\cdot}SiMe_2}\cdot \rightarrow (\mathrm{Me_3Si{\cdot}CH_2{\cdot}SiMe_2})_2 \qquad (6)$$

are those originally suggested by Shiina and Kumada, while the possible termination step (6) is of the type required by the kinetics; the compound

$(Me_3Si{\cdot}CH_2{\cdot}SiMe_2)_2$ could certainly have been formed in the very small yield necessary, even though it was not identified. (If the scheme (2)—(6) were strictly followed, twice as much compound (II) would be formed as trimethylsilane.] Tetramethylsilane may be formed by abstraction of a methyl group by a trimethylsilyl radical,[1] and the formation of methane shows that a little C–Si bond cleavage occurs. The reaction scheme suggested by Davidson *et al.* involved steps (2) and (3), followed, under their conditions, by radical combination rather than step (5); there was no chain-propagation but instead a non-chain reaction, with the rate determined by the initial dissociation (2).

The difference between the course of the thermolysis reported by Davidson *et al.* on the one hand, and that observed by Kumada *et al.* and ourselves on the other, can be largely explained by the difference in the pressures used. It seems that a first-order non-chain process, of the stoicheiometry of equation (1), and a higher-order chain process occurs concurrently, the former dominating at very low pressures, the latter at higher pressures. Change from a pressure of 50 mm. to 0·5 mm. would lower the rate of the chain process by a factor of about 2000, but that of the non-chain process by a factor of only 100, which would serve to switch the predominant course of the reaction from one to the other. If this were the only factor operating, a significant yield of (II) would still be expected under the conditions used by Davidson and his colleagues, but the higher activation energy (67 kcal./mole) of their non-chain process, and possibly also a higher rate of decomposition of (II) relative to (I) at low pressures, would serve to reduce the yield of (II) further. Since Davidson *et al.* studied only the first 5% of the decomposition of (I), they would have had difficulty in detecting a small proportion of (II) in their products unless they had taken special steps to do so; the formation of a small proportion of (II) would not, in fact, significantly affect their arguments and conclusions.

We have confirmed that pyrolysis of (I) in a sealed tube at 300—450° gives (II) in high yield [at 350°, *ca.* 80% of (I) was decomposed in one week; no liquid phase was visible at this temperature], and we have used this reaction as a convenient preparative method.[5] Small amounts of trimethylsilane are also produced, and at 190° this was the only detectable product from the small amount of (I) decomposed in several months, which is consistent with the report that the $Me_3Si{\cdot}SiMe_2{\cdot}CH_2{\cdot}$ radical does not rearrange at lower temperatures.[4]

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