A Kinetic Study of the Pyrolysis of Trimethylsilane

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Summary Hydrogen and methane are formed in the pyrolysis of trimethylsilane by radical non-chain mechanisms, rate-determined by the dissociation of silicon–hydrogen and silicon–methyl bonds; radical disproportionations leading ultimately to cyclic products are important, but reactions forming silenes apparently are not.

THE Rice–Herzfeld mechanism for the pyrolysis of hydrocarbons, in which olefins are formed in a radical chain sequence, is unlikely to apply to the pyrolysis of organosilanes, because stable compounds containing a silicon–carbon double bond are unknown. We have discussed this point previously in relation to the pyrolysis of hexamethyldisilane, which we have shown to proceed at low pressure by a radical non-chain sequence, rate-determined by the dissociation of the silicon–silicon bond[1] (although at higher pressures a radical chain reaction does occur,[2] leading to the formation of a rearrangement product[3]).

Trimethylsilane was pyrolysed in a quartz stirred-flow reactor[4] between 670° and 758°. The initial rates of formation of methane and of hydrogen were measured mass-spectrometrically. First-order rate constants were given by:

$$k(\mathrm{H_2})\ (\mathrm{sec.}^{-1}) = 10^{15\cdot 8 \pm 0\cdot 5}\ e^{-80{,}300 \pm 500/RT}$$

$$k(\mathrm{CH_4})\ (\mathrm{sec.}^{-1}) = 10^{16\cdot 1 \pm 0\cdot 5}\ e^{-76{,}500 \pm 500/RT}$$

where activation energies are in kcal. mole^{-1}. The most recent measurements of bond dissociation energies in methylsilanes by electron impact[5] gave $D(\mathrm{Me_3Si{-}H}) = 81$ kcal. mole^{-1} and $D(\mathrm{Me_3Si{-}Me}) = 76$ kcal. mole^{-1}. The excellent agreement between these bond dissociation energies and the activation energies reported here strongly suggests that hydrogen and methane were formed by non-chain processes rate-determined by the dissociation of silicon–hydrogen and silicon–methyl bonds, respectively. This conclusion is supported by the high *A* factors, which are characteristic of unimolecular bond fissions[6] and are, like the activation energies, inconsistent with the formation of hydrogen and methane by direct molecular elimination, thus: $\mathrm{Me_3SiH \rightarrow (Me_2Si\!:\!CH_2) + H_2}$ and $\mathrm{Me_3SiH \rightarrow Me_2Si\!: + CH_4}$.

Reasonable reactions leading to the formation of hydrogen and methane are:

$$\mathrm{Me_3SiH \rightarrow Me_3Si\cdot + H\cdot} \qquad (1a)$$

$$\mathrm{Me_3SiH \rightarrow HMe_2Si\cdot + CH_3\cdot} \qquad (1b)$$

$$\mathrm{H\cdot + Me_3SiH \rightarrow \cdot CH_2SiMe_2H + H_2} \qquad (2a)$$

$$\mathrm{\cdot CH_3 + Me_3SiH \rightarrow \cdot CH_2SiMe_2H + CH_4} \qquad (2b)$$

At the high temperatures of this work, the radical $\cdot\mathrm{CH_2SiMe_2H}$ would be formed in reactions (2) in preference to the radical $Me_3Si\cdot$, because of the higher *A* factors for abstraction from carbon.[7]

The mass spectra of the reaction products revealed the presence of the following groups of silicon-containing compounds: (a) tetra- to hexa-methyldisilanes; (b) tetra- and penta-methyldisilamethylenes; (c) 1,2-dimethylsilylethane; (d) di- to tetra-methyldisilacyclobutanes. The members of the first three groups were identified by characteristic features of their mass spectra,[8] while the last group was identified by peaks at *m/e* 144 (1,1,3,3-tetramethyl-1,3 disilacyclobutane), *m/e* 130 (1,1,3-trimethyl-1,3-disilacyclobutane), and *m/e* 116 (1,3-dimethyl-1,3-disilacyclobutane), which were shown to correspond to molecular ions by their increase in relative intensity with decrease in ionising energy. The spectra were also compared with that of an authentic sample of 1,1,3,3-tetramethyl-1,3-disilacyclobutane.

Silyl radicals are poor hydrogen abstractors because of the low strength of the silicon–hydrogen bond, and the kinetic evidence indicates that the $\cdot CH_2SiMe_2H$ radicals do not dissociate. In these circumstances the silicon-containing radicals formed in reactions (1) and (2) are likely to undergo combination and disproportionation reactions, the latter possibly being quite important because of the low efficiency of the former.[9] Self- and cross-combination of the three silicon-containing radicals would give all of the products in groups (a) to (c). The remaining products, the disilacyclobutanes, were probably formed by combination of the "double-bonded" intermediates[10] $CH_2{:}SiMeH$ and $CH_2{:}SiMe_2$, produced in disproportionations, thus:

$$\cdot CH_2SiMe_2H + HMe_2Si\cdot \rightarrow Me_3SiH + CH_2{:}SiMeH$$

$$\cdot CH_2SiMe_2H + Me_3Si\cdot \rightarrow Me_3SiH + CH_2{:}SiMe_2$$

$$\cdot CH_2SiMe_2H + \cdot CH_2SiMe_2H \rightarrow Me_3SiH + CH_2{:}SiMe_2$$

in which the substituted methyl radical, $\cdot CH_2SiMe_2H$, abstracts hydrogen from the other radicals.

Although there is growing evidence for silene intermediates in the photolysis[11] and pyrolysis[12] of silicon compounds, they do not seem to be important here; certainly the main route to methane and hydrogen is not molecular elimination (with the concomitant formation of silenes and unsaturated silicon compounds), but rupture of the silicon–methyl and silicon–hydrogen bonds to give monoradicals. Since the errors in these kinetic experiments were lower than in our electron-impact experiments,[5] the activation energies give the best available values for the bond dissociation energies in trimethylsilane, *i.e.*, $D(Me_3Si{-}H) = 80{\cdot}3 \pm 0{\cdot}5$ kcal. mole^{-1} and $D(HMe_2Si{-}Me) = 76{\cdot}5 \pm 0{\cdot}5$ kcal. mole^{-1}.

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