Bond Dissociation Energies and Heats of Formation of Trimethylsilyl Compounds

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THIS Communication reports kinetic and electron impact results, obtained since those quoted in recent publications,[1–4] which lead to a more consistent and extensive collection of thermochemical data for trimethylsilyl compounds than has hitherto been available.

Our preliminary work with ethylpentamethyldisilane[2] has been followed by a detailed study of hexamethyldisilane.[5] Pressures of hexamethyldisilane from 0·2 to 0·8 mm.Hg were pyrolysed in a static system between 523° and 555°, up to not more than 4% decomposition. Under these relatively mild conditions, the product composition and approximate stoicheiometry (neglecting the small temperature-dependence, which was measured) were given by:

$$11\ \mathrm{Me_6Si_2} \rightarrow 5\ \mathrm{Me_3SiH} + \mathrm{Me_4Si} + 4\ \mathrm{Me_5Si_2CH_2SiMe_3} + (\mathrm{Me_5Si_2})_2\mathrm{CH_2}$$

Kinetic data were obtained by measuring the rate of formation of the trisilane. All the results were consistent with the non-chain scheme suggested earlier,[2] and the rate of dissociation of hexamethyldisilane was given by

$$k\ (\mathrm{sec.}^{-1}) = 10^{13\cdot5 \pm 1\cdot0}\exp-(67{,}300 \pm 2{,}200)/\boldsymbol{RT},$$

whence $D(\mathrm{Me_3Si{-}SiMe_3}) = 67 \pm 2$ kcal.mole^{-1}.

Earlier experiments on the pyrolysis of hexamethyldisilane between 660° and 770°, and up to at least 55% decomposition, have been described recently.[1] The activation energy was found to be 49 kcal.mole^{-1}, but in view of the extensive and presumably complex decomposition, there appears to be more difficulty than in our experiments in identifying the activation energy with $D(\mathrm{Me_3Si{-}SiMe_3})$.

Appearance potentials obtained by us are given in Table 1, along with those of previous workers. Where several alternative values exist, the lowest is most likely to be correct, because of the ease of forming fragments with excess energy in the mass spectrometer, and the difficulty of extrapolating ionization efficiency curves.

Bond dissociation energies, calculated from our value of $D(\mathrm{Me_3Si{-}SiMe_3})$ and our appearance potentials are given in Table 2. The most reliable heat of formation available is probably that of trimethylchlorosilane,[6] and the heats of formation in Table 2 were calculated from this and standard values for atoms and radicals.[7]

TABLE 1

Appearance potentials ($\mathrm{Me_3Si^+}$) *from* $\mathrm{Me_3Si{-}X}$ (ev)

X	This work	Ref. 3	Ref. 4
$\mathrm{SiMe_3}$	10·0 ± 0·1†	10·0 ± 0·1	10·69 ± 0·04
Me	10·4 ± 0·1	10·5 ± 0·1	10·63 ± 0·07
H	10·6 ± 0·1	10·7 ± 0·1	10·78 ± 0·07
Cl	10·9 ± 0·1	11·5 ± 0·2	12·40 ± 0·06
Br	10·5 ± 0·1	—	10·69 ± 0·06
I	10·1 ± 0·1	—	—

† Hence Ionization potential (I.P.) ($\mathrm{Me_3Si}$) = 7·1 ev

TABLE 2

Thermochemical data

	$D(\mathrm{Me_3Si{-}X})$ kcal.mole^{-1}	$\Delta H^0_f(\mathrm{Me_3SiX})_g$ kcal.mole^{-1}
$\mathrm{Me_3Si{\cdot}SiMe_3}$	67 ± 2	−118 ± 2
$\mathrm{Me_4Si}$	76 ± 2	−68 ± 2
$\mathrm{Me_3SiH}$	81 ± 2	−55 ± 2
$\mathrm{Me_3SiCl}$	88 ± 2	−84·7 (lit. value)
$\mathrm{Me_3SiBr}$	78·5 ± 2	−77 ± 2
$\mathrm{Me_3SiI}$	69 ± 2	−69 ± 2
$\mathrm{Me_3Si{\cdot}}$	—	−25·6 ± 2

The following supporting evidence exists for the results in Table 2:

(i) $D(\mathrm{Me_3Si{-}H})$ has been estimated as 81 ± 5 kcal.mole^{-1} from gas kinetic studies of the reactions between alkylsilanes and methyl radicals.[8]

(ii) A calculation based on the group equivalent method gave[4] $\Delta H^0_f(\mathrm{Me_6Si_2})_{(g)} = -126 \pm 10$ kcal.mole^{-1}.

(iii) Heats of formation of $\mathrm{Me_4Si}_{(g)}$ and $\mathrm{Me_3SiH}_{(g)}$ have been reported[9] as −69 and −60 kcal.mole^{-1} respectively, but there are good reasons[10] for believing that the latter value should be −55·5 kcal.mole^{-1}. If so, both heats of formation agree with those in Table 2.

Thus, the results in Tables 1 and 2 are internally consistent, and in good agreement with the limited amount of independent evidence available.

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