Bond Dissociation Energies of Trimethylsilyl Compounds

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Two series of appearance potential measurements of trimethylsilyl compounds have recently been reported.[1,2] They are summarized in Table 1, together with dissociation energy differences calculated from them.

The main difference between these two sets of values is in the appearance potential of the trimethylsilyl cation from hexamethyldisilane, and we have therefore repeated this determination. We obtained 10·1 ± 0·2 ev, in excellent agreement with Haszeldine and his co-workers.[1] We used the MS 9 mass spectrometer which revealed that the

TABLE 1

$\mathrm{Me_3SiX}$ X	*A.P.* ($\mathrm{Me_3Si^+}$) from $\mathrm{Me_3SiX}$ ev Ref. 1	Ref. 2	$\Delta D = D(\mathrm{Me_3SiX{-}}) - D(\mathrm{Me_3Si{-}SiMe_3})$ kcal.mole^{-1} Ref. 1	Ref. 2
$\mathrm{Me_3Si}$	10·0 ± 0·1	10·69 ± 0·04	0	0
H	10·7 ± 0·1	10·78 ± 0·07	+15	+2
Me	10·5 ± 0·1	10·63 ± 0·13	+10	−1
Et	10·3 ± 0·1	10·53 ± 0·09	+6	−3
Cl	11·5 ± 0·2	12·40 ± 0·06	+33	+40

ionization efficiency curve had a long tail, which might not have been observed in its entirety by the less sensitive apparatus of Hess, Lampe, and Sommer.[2]

Both groups of workers have attempted to put their relative dissociation energies on an absolute basis by evaluating $D(\mathrm{Me_3Si{-}SiMe_3})$. Hess *et al.*[2] obtained 86 kcal.mole^{-1} by a calculation which relied on an estimated value for the heat of formation of hexamethyldisilane, while Haszeldine and his co-workers[1] investigated the pyrolysis of hexamethyldisilane between 650 and 750°C; they reported two activation energies, 49 ± 6 and 58 ± 4 kcal.mole^{-1}, which they suggested could be identified with $D(\mathrm{Me_3Si{-}SiMe_3})$. We have obtained different results from gas kinetic experiments on a hexa-alkyldisilane, using a static system with continuous mass-spectrometric analysis. We heated low pressures (0·1—0·7 mm. Hg) of ethylpentamethyldisilane at temperatures below 545°C in the hope of seeing evidence for the recombination of trialkylsilyl radicals, thus:

$$\mathrm{Me_3SiSiMe_2Et} \rightleftharpoons \mathrm{Me_3Si\cdot} + \mathrm{EtMe_2Si\cdot} \rightarrow \mathrm{Me_3SiSiMe_3} + \mathrm{EtMe_2SiSiMe_2Et}$$

TABLE 2

Dissociation energies of $\mathrm{Me_3Si{-}X}$

X	$\mathrm{Me_3Si}$	H	Me	Et	Cl
$D(\mathrm{Me_3Si{-}X})$ kcal. mole^{-1}	69*	84	79	75	102

* Hence ΔH_f^0 ($\mathrm{Me_3Si\cdot}$) ~ − 25 kcal., and *I.P.* ($\mathrm{Me_3Si}$) = 7·0 ev.

We failed to observe these disilanes, but found alkytrisilanes and tetrasilanes instead, with smaller quantities of monosilanes and no hydrocarbon gases. The formation of higher silanes was first order, with an activation energy of 69 ± 2 kcal. mole^{-1}. The Arrhenius *A*-factor was between 10^{13} and $10^{13.5}$sec.$^{-1}$, the uncertainty being due mainly to mass-spectrometer calibration factors. The absence of hydrocarbon gases shows that no free alkyl radicals were formed, and we propose the following non-chain sequence:

$$\mathrm{R_3SiSiR_3} \rightarrow \mathrm{R_3Si\cdot} + \mathrm{R_3Si\cdot} \tag{1}$$

$$\mathrm{R_3SiSiR_3} + \mathrm{R_3Si\cdot} \rightarrow \mathrm{R_3SiH} + \mathrm{R_3SiSi(R_2)CH_2\cdot} \quad [\rightarrow \mathrm{R_3SiCH_2SiR_2\cdot}\text{(ref. 3)}] \tag{2}$$

$$\mathrm{R_3SiSiR_3} + \mathrm{R_3Si\cdot} \rightarrow \mathrm{R_4Si} + \mathrm{R_3SiSiR_2\cdot} \tag{3}$$

$$\mathrm{Si_2}\text{ radical} + \mathrm{R_3Si\cdot} \rightarrow \text{trisilanes} \tag{4}$$

$$2\ (\mathrm{Si_2}\text{ radical}) \rightarrow \text{tetrasilanes} \tag{5}$$

Relatively strong bonds are formed in reactions (2) and (3) and each is endothermic by only 3 kcal. (calculated from data in Table 2) so their activation energies are likely to be low. On the other hand, there is no reasonable process other than reaction (1) for the formation of trialkylsilyl radicals. The above sequence is rate-determined by reaction (1), so $D(\mathrm{Me_3Si{-}SiMe_2Et})$ is 69 kcal.mole^{-1}, and since the subsitution of methyl for ethyl would have a negligible effect on the dissociation energy, $D(\mathrm{Me_3Si{-}SiMe_3})$ is also 69 kcal.mole^{-1}. Our *A*-factor of about 10^{13} sec.$^{-1}$ is correct for a unimolecular dissociation.

It appears from our results that $D(\mathrm{Me_3Si{-}SiMe_3})$ cannot be less than 69 kcal.mole^{-1}, so we suggest that Haszeldine and his co-workers[1] were following a more complex process than the simple unimolecular dissociation. In their experiments, at appreciably higher temperature and lower pressure than ours, methyl radical chain reactions, heterogeneous processes, and even unimolecular fall-off may have been important.

If the appearance potentials recorded by Haszeldine and his co-workers[1] are combined with our value for $D(\mathrm{Me_3Si{-}SiMe_3})$, the dissociation energies listed in Table 2 are obtained.

The high value for the silicon–chlorine bond is consistent with a degree of back-donation, and the other dissociation energies are appreciably lower than their carbon analogues, as would be expected from the chemistry of organosilicon compounds.

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