Bond Dissociation Energies in Organosilicon Compounds

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No direct determinations of bond dissociation energies in organosilicon compounds have hitherto been reported, and the values previously obtained by indirect electron impact methods seem too high to be reconciled with the chemical behaviour of some of these compounds, particularly those containing Si–Si or Si–H bonds. We report here a number of investigations on trimethylsilyl compounds which lead, by both direct and indirect methods, to bond dissociation energies substantially lower than those reported by other workers.[1]

Kinetic studies

Hexamethyldisilane.—The decomposition of hexamethyldisilane has been studied[2] by the conventional toluene carrier technique, and shown to be a first-order and homogeneous process at 650—710° C and reactant pressures of 0·1—1 mm. Hg in a 20- to 170-fold excess of toluene. Fission of the Si–Si bond gave trimethylsilyl radicals from which mainly trimethylsilane was formed. The activation energy of this process, 58 ± 4 kcal. mole^{-1}, is therefore the value of $D(\mathrm{Me_3Si{-}SiMe_3})$.

The decomposition has also been studied[3] at pressures of 10^{-5}—10^{-3} mm. Hg in a molecular flow system at 670—750° C, by leading the product gases directly to the ion-source of a mass spectrometer and measuring the reactant concentration as a function of temperature. Assuming that under these conditions the primary decomposition follows the same kinetics, $D(\mathrm{Me_3Si{-}SiMe_3})$ can be equated with the measured activation energy, 49 ± 6 kcal. mole^{-1}.

These two values are in reasonable agreement with each other, and are very much lower than the value of 86 kcal. mole^{-1} obtained indirectly from electron-impact results by Hess, Lampe, and Sommer[1] (see Table 1).

Bis(trimethylsilyl)mercury.—The decomposition of bis(trimethylsilyl)mercury was studied[3] at pressures below 10^{-5} mm. Hg and temperatures of 100—200° C, using the mass-spectrometric technique described above. On the basis of a mechanism involving the initial homolytic fission of the Hg–Si bond, the measured activation energy, 13·6 ± 1·5 kcal. mole^{-1}, may be equated with $D(\mathrm{Me_3SiHg{-}SiMe_3})$.

Electron-impact studies

Hexamethyldisilane and bis(trimethylsilyl)mercury.—The appearance potential of the trimethylsilyl radical ion [A.p.$(m/e = 73)$] from hexamethyldisilane has been redetermined,[3] to give a value much lower than that reported previously[1] (Table 1). Combination of this figure with the value for D(Me$_3$Si–SiMe$_3$) = 49 ± 6 kcal. mole^{-1} (see above) gives a value for the ionisation potential of the trimethylsilyl radical [I.p.(SiMe$_3$)]. Similarly, the same quantity can be obtained from the corresponding data for bis(trimethylsilyl)mercury, and it will be seen from Table 1 that these values agree well and are distinctly higher than the earlier[1] value. The ionisation potential of the trimethylsilyl radical can also be calculated using D(Me$_3$Si–SiMe$_3$) = 58 ± 4 kcal. mole^{-1}. Again the value obtained is significantly higher than that obtained by Hess *et al.*[1] but lower than the values reported above.

The error limits on these new figures are a measure of their reproducibility, and the discrepancy between them is probably due to systematic rather than random errors. The true value for I.p.(SiMe$_3$) is probably either 7·5$_4$ ± 0·2 or 7·9$_5$ ± 0·2 *ev*, and in either case is higher than the value of 6·94 *ev* derived previously.

TABLE 1

Values in italics are derived; others are directly measured.

Me$_3$Si–X X	D(Me$_3$Si–X) kcal. mole^{-1}	A.p.(m/e = 73) *ev*	I.p.(SiMe$_3$) *ev*	Ref.
SiMe$_3$	58 ± 4	10·0$_3$ ± 0·1	*7·5$_4$ ± 0·2*	2
SiMe$_3$	49 ± 6	10·0$_3$ ± 0·1	*7·9$_3$ ± 0·3*	3
Hg·SiMe$_3$	13·6 ± 1·5	8·5$_6$ ± 0·1	*7·9$_7$ ± 0·2*	3
SiMe$_3$	*86 ± 10*	10·6$_9$ ± 0·04	*6·9$_4$*	1

Other Compounds.—Table 2 compares appearance potential data for a series of trimethylsilyl compounds with the results obtained by other workers. The appearance potentials for the compounds where X = H, Me, or Et are in reasonable agreement with those obtained by Hess, Lampe, and Sommer. Although the appearance potential of chlorotrimethylsilane could not be determined with the same precision as for the other compounds, it is certainly very much lower than 12·4 *ev*.

Using the new values for I.p.(SiMe$_3$) (7·5$_4$ *ev* or 7·9$_5$ *ev*) the measured appearance potentials can be used to calculate the two series of bond dissociation energies shown in Table 2. Although there is a difference of 10 kcal. mole^{-1} between the two new sets of values they are both lower than those obtained previously.[1] In particular the new value for D(Me$_3$Si–Cl), at least 30 kcal. mole^{-1} lower than before, is now much closer to the energies of carbon–chlorine bonds.[4]

TABLE 2

Me$_3$SiX X	A.p.(m/e = 73) *ev* This work	 Ref. 1	D(Me$_3$Si–X) kcal. mole^{-1} This work (a)*	 (b)*	 Ref. 1
H	10·7$_2$ ± 0·1	10·78 ± 0·07	74 ± 5	64 ± 5	88 ± 10
Me	10·5$_3$ ± 0·1	10·63 ± 0·13	69 ± 5	59 ± 5	85 ± 10
Et	10·3$_4$ ± 0·1	10·53 ± 0·09	65 ± 5	55 ± 5	83 ± 10
CH$_2$Ph	10·0$_5$ ± 0·1	—	58 ± 5	48 ± 5	—
Cl	11·5 ± 0·2	12·40 ± 0·06	92 ± 10	82 ± 10	126 ± 10

* The values (a) and (b) are based on I.p.(SiMe$_3$) = 7·5$_4$ and 7·9$_5$ *ev* respectively.

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[1] G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Amer. Chem. Soc.*, 1964, **86**, 3174; 1965, **87**, 5327.

[2] G. Finney, R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, unpublished results.

[3] J. A. Connor, G. J. Leigh, R. N. Haszeldine, and R. D. Sedgwick, unpublished results.

[4] T. Cottrell, "The Strengths of Chemical Bonds", 2nd edn., Butterworths, 1958.