

new compositions and structures that have been found in the last few years in halide systems of the earlier transition elements, in spite of both considerable synthetic difficulties and earlier evidence that none existed. Additional extended structure types certainly exist and, likely as not, unprecedented configurations as well. Microcrystalline products have been discovered in MCl_3 -M systems with powder patterns which cannot be reconciled with those calculated for known structure types. And attention should be called once again to the fact that these wonderful materials occur in what are often considered "simple" binary metal-halogen sys-

tems. The likelihood that all stable bonding arrangements can be achieved electron precise in binary systems seems remote. Ternary systems involving low-field cations or other metals or anions with different oxidation states would also appear to provide bright prospects for the solid-state chemists' future.

The research described from my laboratory has been made possible only through both the enthusiasm and persistence of the excellent group of co-workers listed in the references and the continued support of the U.S. Department of Energy, Basic Energy Sciences (and its predecessor agencies), through the Ames Laboratory.

Bond Dissociation Energy Values in Silicon-Containing Compounds and Some of Their Implications

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Silicon occupies a special position in the hierarchy of elements. On the one hand the tetravalency of many of its compounds, which show remarkable stability, resembles that of saturated carbon compounds. On the other hand, its lack of ability to form obviously stable multiple-bonded compounds, its poor ability to catenate, its many crystalline compounds, and its ability to expand its coordination sphere are all more characteristic of other elements. Its chemistry may also be said to lie between that of organic and inorganic chemistry. Moreover, silicon is the second most abundant element of earth's crust and is today the vital component of the microchip technological revolution. Thus it need be no surprise that there is currently an expanding interest in silicon chemistry.

In the field of reaction mechanisms there has been an explosion of research on chemical intermediates in the last two decades, and silicon chemistry is no exception to this. There is active work now going on into silicon-containing free radicals, the π -bonded silicoolefins, the divalent silylenes, and unstable silicon-containing ring compounds such as silacyclopropane and silabenzene as well as much else. One of the more powerful ways to bring coherence to this field is through the establishment of reliable thermochemistry. With this objective in mind we embarked, some 7 years ago, on a program of bond dissociation energy¹ measurements in silanes.

Bond dissociation measurements are of assistance to this endeavour in two ways. First of all they provide the fundamental information on the strengths of bonds in important key molecules. Consequent upon this, much other information becomes available, for example,

the magnitudes of substituent effects and specific stabilizing influences in free radicals. There is the inevitable, yet fruitful, comparison of bonds strengths in silanes with their counterpart organic compounds. The second way in which such measurements are valuable is in providing a framework of free-radical heats of formation. This information has always been of immense use in mechanistic chemistry. Put simply, knowing the enthalpy change of reaction is the essential first stage in deciding whether such-and-such a proposed process is likely to go or not. It is sometimes surprising to this author how much time and effort has been devoted to the *theoretical* calculation of these quantities when measurement (or even crude estimation) of a few heats of formation will provide the answers desired. In this Account results obtained for silicon compounds are reviewed and discussed both for their intrinsic interest and for their bearing on questions of stability and reactivity of intermediates.

Our method of approach has been to study the gas-phase kinetics of the reaction of iodine with a series of silanes. This technique was pioneered by Sidney Benson in 1961 and has been reviewed by Benson and Golden.² It is not our purpose to review the possible methods by which bond dissociation energies may be determined or to discuss their applicability or relative merits.³ However, it is worth recalling that our method has been applied extensively to organic molecules to give values for C-H bonds which are generally agreed⁴⁻⁶

(1) A bond dissociation energy $D(A-B)$ is defined as the standard enthalpy change for process $A-B(g) \rightarrow A\cdot(g) + B\cdot(g)$. Despite the illogicality of the use of the word energy to describe enthalpy, we stick to tradition in the name. We also retain D as the symbol although others have preferred DH .^{2,3}

(2) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

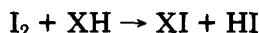
(3) For general information the reader is referred to S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965), and references cited therein.

(4) Tabulations are given by (a) K. W. Egger and A. T. Cocks, *Helv. Chim. Acta*, **56**, 1516, 1537 (1973); (b) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976. Where slight disagreements occur, (b) is preferred as being more up to date.

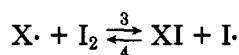
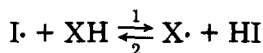
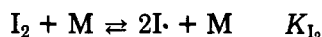
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to be reliable within ± 1 or 2 kcal mol⁻¹.⁷ The only other method of wide applicability is that of electron impact, and this has had in general a poor track record.

The reaction of iodine with a hydrogen-containing species, XH, in the gas phase follows the stoichiometry²



in the initial stages and in some cases over the whole extent of reaction. The mechanism, in the vast majority of cases studied, is as follows:



This is an I atom propagated chain reaction, maintained by a thermodynamic concentration of I atoms. In the early stages when step 4 is not important eq 1 applies.

$$-\frac{d[\text{I}_2]}{dt} = k_1 K_{\text{I}_2}^{1/2} [\text{I}_2]^{1/2} [\text{XH}] \quad (1)$$

By a spectrophotometric technique I_2 can be monitored as a function of time and the results fitted to an integrated form of eq 1 (or suitably modified rate equation which allows additionally for step 2 competing with step 3 to yield $k_1 K_{\text{I}_2}^{1/2}$). From the known value⁸ for $K_{\text{I}_2}^{1/2}$, k_1 is extracted, and its temperature dependence yields the activation energy. Although E_2 cannot be obtained directly, there are good reasons^{2,9} to believe that it is small (0–2 kcal mol⁻¹) and relatively invariant to the nature of X. Thus E_1 (usually in the range 5–40 kcal mol⁻¹) provides a good approximation to $\Delta H^\circ_{1,2}$ ($=E_1 - E_2$). E_1 can usually be measured with a precision of ± 1 kcal mol⁻¹. E_2 is estimated, based partly on experimental results which can add a maximum uncertainty of ± 1 kcal mol⁻¹. The adjustment of $\Delta H^\circ_{1,2}$ from the temperature of study to room temperature, carried out by use of standard thermodynamic formulas, is usually very small, and does not affect the uncertainty.

The enthalpy change $\Delta H^\circ_{1,2}$ for the iodine atom abstraction step provides the key to the result since it is related to bond dissociation energies, i.e.,

$$\Delta H^\circ_{1,2} = D(\text{X-H}) - D(\text{H-I})$$

Since $D(\text{H-I})$ is known¹⁰ (71.34 ± 0.05 kcal mol⁻¹); $D(\text{X-H})$ may be determined. Accessible values for $D(\text{X-H})$ usually lie within 75–110 kcal mol⁻¹ range, and so one of the advantages of this method becomes apparent, viz., ca. 75% of the desired quantity is known with high precision. It is like setting base camp three-quarters of the way up the mountain.

(5) There have been recent suggestions⁸ that C–H bonds might be a little stronger than those measured earlier.² This question is by no means settled, but, if true, upward revision would be required by at most 2 kcal mol⁻¹ for $D(\text{C}_2\text{H}_5\text{-H})$, $D(\text{i-Pr-H})$, and $D(\text{t-Bu-H})$, on the limit of the margin of the earlier uncertainty.

(6) (a) W. Tsang, *Int. J. Chem. Kinet.*, **10**, 821 (1978); (b) R. R. Baldwin, R. W. Walker, and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, **76**, 825 (1980), and references therein.

(7) 1 cal = 4.184 J. Despite some misgivings, calories are chosen as the units of energy here because this unit most conveniently represents the uncertainty margin in these measurements.

(8) "J.A.N.A.F. Thermochemical Tables", *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)*, NSRDS-NBS 37, (1971); see also supplements.

(9) (a) K. Lorenz, H. Gg. Wagner, and R. Zellner, *Ber. Bunsenges. Phys. Chem.*, **83**, 556 (1979); (b) M. Rossi and D. M. Golden, *J. Am. Chem. Soc.*, **101**, 1230 (1979).

(10) Based upon known⁸ ΔH_f° values for HI, H, and I.

Table I
Measured Si–H^a and Analogous C–H Bond
Dissociation Energies (kcal mol⁻¹)

bond	D	ref	bond	D	ref
H ₃ Si–H	90.3	11	H ₃ C–H ^b	104.8	2
MeSiH ₂ –H	~89.6	12	MeCH ₂ –H ^b	98	2, 4
Me ₂ SiH–H	~89.4	12	Me ₂ CH–H ^b	95	2, 4
Me ₃ Si–H	90.3	13	Me ₃ C–H ^b	92	2, 4
SiH ₃ SiH ₂ –H	86.3	24	SiH ₃ CH ₂ –H		
C ₆ H ₅ SiH ₂ –H	88.2	25	C ₆ H ₅ CH ₂ –H	87.9	9b
Cl ₃ Si–H	91.3	27	Cl ₃ C–H	96	4
F ₃ Si–H	100.1	28	F ₃ C–H	106	4
Me ₃ SiCH ₂ –H	99.2	29	Me ₃ CCH ₂ –H	99.7	29

^a The tenths of kcal mol⁻¹ shown are merely to indicate slight differences, not to claim spurious precision. ^b References 2 and 4 are quoted for consistency (iodination studies), but see also ref 5 and 6.

A couple of added complications arise in the mechanism when X is a carbon-centered radical.¹ In this case the overall iodination reaction is highly reversible as a result of the importance of step 4 in the mechanism. In addition, the iodide XI is often unstable, undergoing the elimination reaction



When X is a silicon-centered radical, however, neither of these situations pertain. Step 4 is unimportant, largely because Si–I bonds are stronger than C–I bonds and the elimination reaction does not occur as a result of the weakness of the π bond in sila olefins. Thus the reactions of I_2 with silanes are, in general, mechanistically and kinetically simpler than its reactions with hydrocarbons.

Measured Si–H Bond Dissociation Energies

In order to form the basis of discussion, the values we have obtained are collected in Table I together with the C–H bond dissociation energies in analogous hydrocarbons for reference purposes. These are discussed first in relation to other measurements and secondly from the standpoint of the presence or absence of "effects" in the silane or the derived silyl radical.

A striking feature of monosilane¹¹ and the methylsilanes^{12,13} is the almost constant Si–H bond strength. At the outset of our work there was a wide disparity in values. The most commonly quoted figures for $D(\text{SiH}_3\text{-H})$ and $D(\text{Me}_3\text{Si-H})$ were 95¹⁴ and 81 kcal mol⁻¹,¹⁵ respectively. The first was based on the electron-impact method, which as already noted has not been very reliable. The most recent electron-impact data, however, by Potzinger and co-workers¹⁶ are consistent with our kinetic values. The earlier low value for $D(\text{Me}_3\text{Si-H})$ was based upon a determination of the activation energy for H_2 formation in Me_3SiH pyrolysis.¹⁵ More recently Baldwin, Davidson, and Reed¹⁷ have reinter-

(11) A. M. Doncaster and R. Walsh, *Int. J. Chem. Kinet.*, **13**, 503 (1981); preliminary communication, *J. Chem. Soc., Chem. Commun.*, 904 (1979).

(12) A. M. Doncaster and R. Walsh, preliminary (unpublished) results.

(13) A. M. Doncaster and R. Walsh, *J. Chem. Soc., Faraday Trans. 1*, **75**, 1126 (1979); see also R. Walsh and J. M. Wells, *ibid.*, **72**, 100 (1976).

(14) F. E. Saalfeld and H. J. Svec, *J. Phys. Chem.*, **70**, 1753 (1966); see also W. C. Steele, L. D. Nicholls, and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 4441 (1962).

(15) I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc. A*, 882 (1971).

(16) P. Potzinger, A. Ritter, and J. Krause, *Z. Naturforsch. A*, **30A**, 347 (1975).

preted the kinetics of this complex pyrolysis in terms of a mechanism which is more consistent with a higher Si-H bond strength in Me_3SiH than the 81 kcal mol⁻¹ originally proposed. An approximate constancy of Si-H bond strength is strongly indicated by other work. Hosaka and Rowland¹⁸ found little variation in HT yields in recoil tritium abstractions with these silanes. Methyl radicals abstract H (bonded to silicon) with activation energies¹⁹ which all lie in the narrow range 7.0–7.8 kcal mol⁻¹. Although not all studies bearing on these Si-H bond strengths have been discussed here, there no longer appears to be any important body of research in substantial disagreement with the figures quoted in Table I.

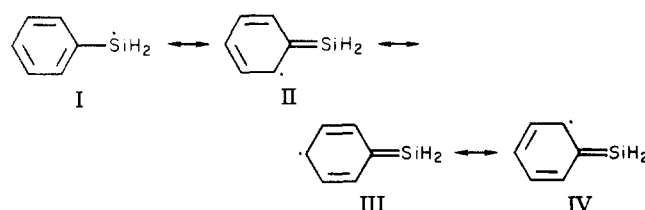
The C-H bond weakening by substituent methyl groups in the simple alkanes is commonly interpreted as arising from the methyl group inductive effect.²⁰ The absence of such an effect on Si-H bonds is perhaps not surprising in view of the differing electronegativities of C and Si (2.6 and 1.8 on the Pauling scale). These make CH_3 a less likely donor to, and therefore stabilizer of, an Si radical center than a C radical center. Although alternative explanations of the methyl group effect on C-H bond strengths may be offered (e.g., hyperconjugation in the radicals²¹), it is clear that whatever the effect it is absent in the methylsilanes and their radicals.

It is also worthy of note that Si-H bonds are in general not much weaker than their C-H analogues, despite the generally greater reactivity of silanes and Si-H bonds. It seems that the H(1s) orbital is capable of achieving substantial overlap with the appropriate Si orbital. Another feature, not apparent from Table I, is that $D(\text{H}_3\text{Si-H})$ is somewhat stronger than the average thermochemical Si-H bond energy of 77 kcal mol⁻¹.²² This indicates that there are bond-weakening effects operative on removal of one or more H atoms subsequent to the first in SiH_4 (vide infra). The existence of such bond-weakening effects is not limited to compounds of silicon. The variability of S-F bond strengths in SF_6 , recently discussed by Kiang and Zare,²³ is another example. Thus the often-used assumption that, in homoleptic compounds, the average bond energy is a reasonable approximation to the first bond dissociation energy is quite unreliable.

The Si-H bond in disilane²⁴ is ca. 4 kcal mol⁻¹ weaker than that in monosilane. Thus an SiH_3 substituent, unlike a CH_3 , does induce an Si-H bond weakening. The reason for this is not known, but again, probably an inductive or polarization mechanism will explain it. It will be interesting to see whether, as seems likely,

cumulative SiH_3 substitution will produce a greater weakening.

Si-H bond weakening by phenyl substitution²⁵ is very slight, ca. 1.5–2 kcal mol⁻¹. This is a measure of the "silabenzyl" stabilization energy, to be contrasted with the benzyl stabilization energy^{9b} ($=D(\text{MeCH}_2\text{-H}) - D(\text{C}_6\text{H}_5\text{CH}_2\text{-H})$) of ca. 10 kcal mol⁻¹. The small size of the silabenzyl stabilization is not unexpected in view of weakness of π bonding in sila olefins which makes the contribution to stabilization by structures such as II, III, and IV very slight. It is anticipated similarly that



the 1-silaallyl radical will not show much stabilization, and it is already evident from the high reactivity of silabenzene^{26a} and silatoluene^{26b} that they do not possess the classical aromatic stability.

Halogen substitution appears to strengthen Si-H bonds, as judged by Cl_3SiH ²⁷ and F_3SiH .²⁸ The comparison with the analogous halocarbons, whose C-H bonds are once again only very slightly stronger, shows that whereas F is strengthening, Cl lies between H and Me in its effect. One way of rationalizing this is to suppose that the general electron-withdrawing properties of F and Cl (leading to bond strengthening) are opposed by nonbonded repulsions (leading to bond weakening) in the X_3MH compounds. In the case of the larger $\text{M}\equiv\text{Si}$, the repulsions are less than the smaller $\text{M}\equiv\text{C}$, and so in the silanes, at least, the general electron-withdrawing effect is more likely to win out. However, the effects are sufficiently small that this kind of argument is probably a gross oversimplification.

Measured C-H Bond Dissociation Energies in Silanes

To our knowledge the only known value for a C-H bond strength in a silane is that in tetramethylsilane.²⁹ We made this measurement to probe the effect of α -silicon substitution on a carbon-centered radical. The analogous C-H bond strength in neopentane was also measured and found to be only ca. 0.5 kcal mol⁻¹ stronger. This indicates that there is little, if any, interaction of a p_π - d_π type between the singly occupied p orbital and the silicon d orbital. The indications from ESR measurements³⁰ are that there may be stronger interactions in β -silicon-substituted rather than α -silicon-substituted alkyl radicals. It will be interesting to see whether bond dissociation energy measurements bear this out.

(17) A. C. Baldwin, I. M. T. Davidson, and M. D. Reed, *J. Chem. Soc., Faraday Trans. 1*, 74, 2171 (1978).

(18) A. Hosaka and F. S. Rowland, *J. Phys. Chem.*, 77, 705 (1973).

(19) Reviewed by (a) I. M. T. Davidson, *Gas Kinet. Energy Transfer*, 1, 212 (1975); (b) N. L. Arthur and T. N. Bell, *Rev. Chem. Intermediates* 2, 37 (1978). (c) Critical Evaluation by J. A. Kerr and M. J. Parsonage, "Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals", Butterworths, London, 1976.

(20) (a) For the flavor of the original discussion, see C. K. Ingold, "Structure and Mechanism in Organic Chemistry", G. Bell and Sons, London, 1953. (b) For a more quantitative discussion, see M. Luria and S. W. Benson, *J. Am. Chem. Soc.*, 97, 3342 (1975).

(21) See, for example, A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance", Harper and Row, London, 1967, p 83.

(22) $D(\text{Si-H}) = 1/4(\text{heat of atomization of } \text{SiH}_4)$. ΔH_f° for SiH_4 and Si from Table II and ΔH_f° for H from ref 8.

(23) T. Kiang and R. N. Zare, *J. Am. Chem. Soc.*, 102, 4024 (1980).

(24) A. M. Doncaster and R. Walsh, unpublished results.

(25) M. Barber, A. M. Doncaster, and R. Walsh, unpublished results.

(26) (a) B. Solouki, P. Rosmus, H. Bock, and G. Maier, *Angew. Chem., Int. Ed. Engl.*, 19, 51 (1980); G. Maier, G. Mihm, and H. P. Reisenauer, *ibid.*, 19, 52 (1980); (b) C. L. Kreil, O. L. Chapman, G. T. Burns, and T. J. Barton, *J. Am. Chem. Soc.*, 102, 841 (1980).

(27) R. Walsh and J. M. Wells, *J. Chem. Soc., Faraday Trans. 1*, 72, 1212 (1976).

(28) A. M. Doncaster and R. Walsh, *Int. J. Chem. Kinet.*, 10, 101 (1978).

(29) A. M. Doncaster and R. Walsh, *J. Chem. Soc., Faraday Trans. 1*, 72, 2908 (1976).

(30) (a) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 93, 846 (1971); (b) T. Kawamura and J. K. Kochi, *ibid.*, 94, 648 (1972).

Table II
Heats of Formation of Silicon-Containing Species (kcal mol⁻¹)

compd	ΔH_f°	ref	compd	ΔH_f°	ref
SiH ₄	8.2	32	SiH ₃	46.4	derived
Si ₂ H ₆	19.1	32	Si ₂ H ₅	53.3	derived
Si ₃ H ₈	28.9	32			
n-Si ₄ H ₁₀	38.7	a	MeSiH ₃	30.5	derived
MeSiH ₂	-7	see text and 35	Me ₂ SiH	14.3	derived
Me ₂ SiH ₂	-23		Me ₃ Si	-0.8	derived
Me ₃ SiH	-39				
Me ₄ Si	-55.4		Cl ₃ Si	-76.0	derived
		33	F ₃ Si	-245	derived ^b
Me ₃ SiCl	-84.5	32			
Me ₃ SiBr	-70.3	32	SiH ₃	58	c
Me ₃ SiI	-52.2	35	SiCl ₂	-39.5	8, 32
Me ₃ SiOH	-119.3	32	SiF ₂	-140.5	8, 32
Me ₃ SiNHMe	-55.3	32	SiMe ₂	26	derived
Me ₃ SiSC ₄ H ₉	-81.3	32			
			SiH	90	8, 32
SiCl ₃ H	-115.2	32	SiCl	46.8	8, 32
SiF ₃ H	-293	b	SiF	-4.6	8, 32
SiCl ₄	-158.4	32	SiMe	74	derived
SiF ₄	-386.0	32			
			Si	108	8, 32
Me ₂ Si=CH ₂	7 ± 5	see text			
MeSiH=CH ₂	23 ± 5				
SiH ₂ =CH ₂	39 ± 5				

^a Assuming bond additivity in the linear polysilanes. ^b ΔH_f° values for SiF₃H and SiF₂ differ from those we have quoted previously.²⁸ This is because the new ΔH_f° (SiF₃H) (M. Farber and R. D. Srivastava, *Chem. Phys. Lett.*, 51, 307, (1977)) is presumed more reliable. There remain inconsistencies, however, for ΔH_f° (SiF₃). ^c P. John and J. H. Purnell, *J. Chem. Soc., Faraday Trans. 1*, 69, 1455 (1973).

Derived Bond Dissociation Energies

One of the useful byproducts of a determination of $D(R-H)$ is the radical heat of formation $\Delta H_f^\circ(R\cdot)$ which may be derived via the thermodynamic relationship

$$\Delta H_f^\circ(R\cdot) = \Delta H_f^\circ(RH) - \Delta H_f^\circ(H\cdot) + D(R-H) \quad (2)$$

This may then itself be used to generate other bond dissociation energies $D(R-X)$ via

$$D(R-X) = \Delta H_f^\circ(R\cdot) + \Delta H_f^\circ(X\cdot) - \Delta H_f^\circ(RX) \quad (3)$$

where X may be one of a variety of groups. Thus a single direct bond dissociation energy measurement may be used to generate many others. However, to apply eq 2 and 3 requires a knowledge of the molecular heats of formation $\Delta H_f^\circ(RH)$ and $\Delta H_f^\circ(RX)$ as well as those of the radicals $\Delta H_f^\circ(H\cdot)$ and $\Delta H_f^\circ(X\cdot)$. Whereas the latter are quite widely available, the thermochemistry of silicon-containing compounds is not only rather sparse but subject to uncertainty and controversy. Thus this approach is not yet as profitable as it ought to be. However, it seems worthwhile to present some values even if examples are necessarily limited. To facilitate this, those molecular heats of formation which are felt to be of reasonable reliability and relevance are collected in Table II together with the derived radical heats of formation. Other thermochemical data (atomic heats of formation) are taken from standard sources.^{4,8}

Some of these data are by no means universally accepted and deserve special mention. We single out the methylsilanes whose heats of formation have recently been discussed by Davidson.³¹ Davidson favors the mass spectrometrically determined values of Potzinger, Krause, and Ritter¹⁶ which show a self-consistency lacking in data from other sources.³² Unfortunately the value recommended for $\Delta H_f^\circ(\text{Me}_4\text{Si})$ of -42.4 kcal

Table III
Derived Carbon-Silicon Bond Dissociation Energies (kcal mol⁻¹)^a

bond	D^b	bond	D^c
H ₃ Si-CH ₃	88.2	CH ₃ -CH ₃	88
MeSiH ₂ -CH ₃	88.3	MeCH ₂ -CH ₃	85
Me ₂ SiH-CH ₃	88.1	Me ₂ CH-CH ₃	84
Me ₃ Si-CH ₃	89.4	Me ₃ C-CH ₃	82

^a ΔH_f° for methylsilanes in Table II; $\Delta H_f^\circ(\text{CH}_3\cdot)$ from ref 8. ^b Tenths of kcal mol⁻¹ are shown for consistency, not to claim spurious accuracy. ^c Reference 4b.

mol⁻¹ is not supported by a recent measurement using fluorine bomb calorimetry by Steele who obtained -55.4 kcal mol⁻¹.³³ $\Delta H_f^\circ(\text{Me}_4\text{Si})$ is a key quantity since other heats of formation may be derived from it. Chemical intuition, supported by studies of catalyzed disproportionation equilibria among the methylsilanes,³⁴ suggests an approximately constant increment in ΔH_f° upon H for Me substitution in methylsilanes. Assuming this and the values for $\Delta H_f^\circ(\text{Me}_4\text{Si})$ and $\Delta H_f^\circ(\text{SiH}_4)$, the ΔH_f° values for the other methylsilanes shown in the table were derived.³⁵ For the reasons given we favor these values over Davidson's, although the arguments cannot be regarded as resolved until more corroborative values are available.

Table III shows the Si-C bond dissociation energies based on the above discussion. It must be emphasized that, quite apart from the questions discussed above, these figures are only reliable to within ±3 kcal mol⁻¹ on the basis of purely experimental uncertainties. There is slight but not substantial disagreement with the only reliable direct measurement of a carbon-silicon bond dissociation energy, $D(\text{Me}_3\text{Si}-\text{CH}_3) = 85$ kcal

(33) W. C. Steele, unpublished results (private communication).

(34) (a) A. Hoffman, *Diss. Abs. Int. B*, 31, 4613 (1971); J. M. Most, *ibid.*, 3230 (1975); (b) A. M. Doncaster and R. Walsh, unpublished results.

(35) A. M. Doncaster and R. Walsh, *J. Phys. Chem.*, 83, 3037 (1979).

(31) I. M. T. Davidson, *J. Organometal. Chem.*, 170, 365 (1979).

(32) J. B. Pedley and B. S. Iseard, "CATCH Tables", University of Sussex, 1972.

Table IV
Bond Dissociation Energies in Polysilanes^a and Carbon Analogues (kcal mol⁻¹)

bond	D	bond	D ^c
SiH ₃ -SiH ₃	74	CH ₃ -CH ₃	88
Si ₂ H ₅ -SiH ₃	71	C ₂ H ₅ -CH ₃	85
Si ₃ H ₇ -Si ₂ H ₅	68	C ₂ H ₅ -C ₂ H ₅	82
Me ₃ Si-SiMe ₃	80.5 ^b	Me ₃ C-CMe ₃	70

^a ΔH_f° for silanes and radicals in Table II. ^b Reference 37. ^c Reference 4b.

mol⁻¹, by Davidson and co-workers.¹⁷ Moreover, despite the disagreement over $\Delta H_f^\circ(\text{Me}_4\text{Si})$, Potzinger, Ritter, and Krause's values¹⁶ of $D(\text{Si}-\text{C}) = 85 \pm 4$ kcal mol⁻¹ are also not in major disagreement. What is clear is that carbon-silicon bonds are stronger than was once thought¹⁵ (ca. 76 kcal mol⁻¹), and indeed they appear stronger than the analogous carbon-carbon bonds in some cases.

Si-Si bond dissociation energies are shown in Table IV, and it can be seen that in the linear polysilanes there is substantial attenuation of the Si-Si bond strength with SiH₃ substitution. This follows from the weakness of $D(\text{Si}_2\text{H}_5-\text{H})$ compared with $D(\text{SiH}_3-\text{H})$. At first sight this appears to parallel the situation in linear alkanes. However, this parallel may disappear on further substitution of a branching nature. In hexamethylethane, part of the central C-C bond weakness is due to nonbonded methyl repulsions. That, in the absence of such repulsions, the bond would be stronger can be seen in the ultimate branched structure, diamond, where the average C-C bond energy³⁶ is 85 kcal mol⁻¹. By contrast, the average Si-Si bond energy³⁶ in crystalline silicon is 54 kcal mol⁻¹, and this suggests that the electronic effects causing Si-Si bond weakening on SiH₃ for H substitution will augment with further substitution making the central Si-Si bond in $(\text{SiH}_3)_3\text{Si}-\text{Si}(\text{SiH}_3)_3$ very weak indeed and perhaps close to that in crystalline silicon itself. The directly measured bond dissociation energy in hexamethyldisilane³⁷ is worthy of note in that it shows that methyl groups (in disilanes) can act as bond-strengthening substituents. The effect is not large (ca. 1 kcal mol⁻¹ per methyl group) but serves to show that methyl groups are not invariably bond weakening, as is often assumed.

Si-halogen bond dissociation energies are best illustrated by the trimethylsilyl halides for which the data derived are collected in Table V. Silicon-halogen bonds show the same trends in strength with halogen as do carbon-halogen bonds, but are much stronger. In fact the Si-F bond in SiF₄ is probably the strongest formally single bond known.³⁸ The origin of this strengthening has been attributed either to $p_\pi-d_\pi$ back bonding or an increased ionic contribution to bonding.³⁹ It may be that the increased size of silicon simply facilitates better bonding orbital overlap by reducing lone-pair, bond-pair, and other intramolecular repulsions. In other words, maybe an explanation should be sought for the weak carbon-halogen rather than the strong silicon-halogen bonds. A more detailed theo-

(36) $D(\text{X}-\text{X}) = \frac{1}{2}(\text{heat of atomization of elemental X})$. This can be derived from $\Delta H_f^\circ(\dot{\text{C}})$ and $\Delta H_f^\circ(\text{Si})$ (Table II).

(37) I. M. T. Davidson and A. V. Howard, *J. Chem. Soc., Faraday Trans. 1*, 71, 69 (1975).

(38) Although the value quoted here differs from that in the earlier paper,²⁶ (see Table II), this does not affect the comment here.

(39) B. G. Gowenlock and J. Stevenson, *J. Organometal. Chem.*, 13, P13 (1968).

Table V
Bond Dissociation Energies in the Trimethylsilyl Halides, Analogous *tert*-Butyl Halides, and Selected Other Compounds^a (kcal mol⁻¹)

bond	D	bond	D ^b
Me ₃ Si-Cl	113	Me ₃ C-Cl	80
Me ₃ Si-Br	96	Me ₃ C-Br	64
Me ₃ Si-I	77	Me ₃ C-I	51
Cl ₃ Si-Cl	111	Cl ₃ C-Cl	70
F ₃ Si-F	160	F ₃ C-F	130
Me ₃ Si-OH	128	Me ₃ C-OH	91
Me ₃ Si-NHMe	100 ^c	Me ₃ C-NHMe	80
Me ₃ Si-SC ₄ H ₉	99 ^d	Me ₃ C-SC ₄ H ₉	71 ^e

^a ΔH_f° for silanes in Table II. ΔH_f° for F, Cl, Br, I, and OH from ref 8. ^b Reference 4. ^c Based on $\Delta H_f^\circ(\text{NHMe}) = 45.2$ kcal mol⁻¹ (ref 4). ^d Based on $\Delta H_f^\circ(\text{SC}_4\text{H}_9) = 19$ kcal mol⁻¹ (derived from data in S. W. Benson, *Chem. Rev.*, 78, 23 (1978)). ^e Based on analogous C-S bond strengths (same reference as (d)).

Table VI
Successive Bond Dissociation Energies in SiX₄ Compounds (Compared with Carbon Counterparts)^{a, b} (kcal mol⁻¹)

bond	D	bond	D
SiH ₃ -H	90	CH ₃ -H	104.8
SiH ₂ -H	64	CH ₂ -H	111.0
SiH-H	84	CH-H	100.4
Si-H	70	C-H	81.0
SiCl ₃ -Cl	111	CCl ₃ -Cl	71
SiCl ₂ -Cl	66	CCl ₂ -Cl	67
SiCl-Cl	114	CCl-Cl	92
Si-Cl	91	C-Cl	80
SiF ₃ -F	160	CF ₃ -F	130
SiF ₂ -F	123	CF ₂ -F	88
SiF-F	155	CF-F	123
Si-F	132	C-F	129

^a ΔH_f° for Si species in Table II. ^b ΔH_f° for C species in ref 8 apart from $\Delta H_f^\circ(\text{CH}_3)$ from R. K. Lengel and R. N. Zare, *J. Am. Chem. Soc.*, 100, 7495 (1978).

retical analysis of these bond strength differences would seem worthwhile. Other silicon bond dissociation energies are fairly sparse, but the remaining data in Table V show that silicon-oxygen, silicon-nitrogen, and silicon-sulfur bonds are all stronger than their carbon counterparts, and as with the bonds to halogens, by substantial amounts. It is the strengths of the bonds between silicon and electronegative elements which provides the driving force which influences so much of the chemistry of silicon.

Consecutive Bond Dissociation Energies and Silylene Stabilization Energies

Other useful byproducts of these measurements are the sequential dissociation energies in SiX₄ compounds. For any fragment SiX_n, we can write

$$D(\text{SiX}_{n-1}-\text{X}) = \Delta H_f^\circ(\text{SiX}_{n-1}) + \Delta H_f^\circ(\text{X}) - \Delta H_f^\circ(\text{SiX}_n)$$

Thus if $\Delta H_f^\circ(\text{SiX}_n)$ are known for $n = 0-4$, then the dissociation energies can be evaluated. The data required are again sparse and not of uniform quality. However, they are probably good enough now for the cases X = H, Cl, and F to warrant presentation. The heats of formation are collected in Table II and the bond dissociation energies calculated are in Table VI. These data update figures in earlier papers.^{27,28} Although there are a lot of figures, we discuss only one

point. The second dissociation energies for all the silicon-containing species are significantly the lowest even allowing for some uncertainties in the data. This suggests a specific stabilizing effect in the divalent SiX_2 species. We have suggested that this stability is associated with the lone-pair orbital containing substantial s character.^{11,27,28} This is thermodynamic evidence high up in the periodic table for what is known lower down in group 4 (Sn and Pb) as the *inert pair effect*.⁴⁰ If the difference between the first and second dissociation energies is used as an operational definition, then this lone-pair stabilization effect has energies of from 26 kcal mol⁻¹ (SiH_2) to 44 kcal mol⁻¹ (SiCl_2). The magnitude of the effect is, therefore, quite substantial. If we assume a constant Me for H replacement energy in SiH_2 (as in SiH_4), then we derive $\Delta H_f^\circ(\text{Me}_2\text{Si}) = 26$ kcal mol⁻¹⁴¹ and a lone-pair stabilization energy of 27 kcal mol⁻¹ in SiMe_2 . This last figure should be sufficiently transferable for nonpolar groups, R, to make thermodynamic estimates of $\Delta H_f^\circ(\text{SiR}_2)$ which may be useful for the analysis of mechanistic organosilicon chemistry.

This stabilization energy is also equal to the energy by which the disproportionation reaction (or equilibrium)



is exothermic. Some apparently direct studies⁴² of this equilibrium using a Knudsen cell technique appear to give erroneously low values for $-\Delta H^\circ$ (for the cases X = Cl and F) on the basis of the figures we have derived.⁴³ It is worth pointing out that the existence of the silylene stabilization effect partly illustrates why divalent intermediates are more commonly encountered as intermediates in thermal (and to some extent photochemical) decompositions in silicon chemistry than in carbon chemistry.

π -Bond Energies in Sila Olefins

In spite of their transient nature, the sila olefins are now well on their way to becoming well-characterized species.^{44,45} The strengths of their π bonds are important indexes of their reactivity. We made the first estimate of these π -bond dissociation energies, D_π , of 37 ± 9 kcal mol⁻¹ in 1972,⁴⁶ but since then a number of other estimates both experimental⁴⁷ and theoretical⁴⁸

have appeared, not all of them within the limits of uncertainty of our estimate. Limitations of space preclude a detailed analysis of these numbers here. However, some of the inputs to our original thermochemical calculation are now better known, and we have refined our estimate to 39 ± 5 kcal mol⁻¹⁴⁹ (for $\text{MeSi}=\text{CH}_2$). The analysis is based on bond strengths and kinetic arguments and not on the more uncertain heats of formation, which we feel are the reason for excessively low estimates of Gusel'nikov and Nametkin (28 kcal mol⁻¹)^{47b} and John, Gowenlock, and Co-workers^{47d} (23 kcal mol⁻¹). Davidson and Potzinger,^{47a} using bond energy arguments analogous to these but with slightly different figures, derive a mean value for D_π of 37 kcal mol⁻¹. Thus although they prefer somewhat different heats of formation, the π -bond energy they derive is hardly affected. For completeness, but at the risk of producing too many numbers, we use this π -bond energy to generate heats of formation for sila olefins based on the reaction of the type



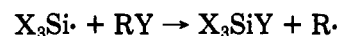
for which one may write

$$\Delta H = D(\text{Si-H}) + D(\text{C-H}) - D_\pi(\text{Si=C}) - D(\text{H-H})$$

Using the figures from this account and standard sources,^{4b} we obtain $\Delta H = 46$ kcal mol⁻¹. If this is reasonably assumed to be independent of methyl substitution, then heats of formation for the sila olefins, based on those for the methylsilanes, may be obtained. They have been included for three sila olefins in Table II. These numbers are not in very good agreement with those from other sources,⁴⁷ but they are based on our preferred, consistent heats of formation of the methylsilanes.

Some Applications

Abstraction by radicals from silanes has been studied extensively and reviewed.¹⁹ Abstraction by silicon-centered radicals from other molecules has been less widely discussed. Two subjects seem worthy of note. First Trotman-Dickenson, Cadman, and co-workers⁵⁰ have carried out a series of studies of reactions of the type



where X = Me, Cl, and F; RY is a series of alkyl halides. In competitive studies selectivities S were found to vary in the order $\text{S}(\text{F}_3\text{Si}\cdot) > \text{S}(\text{Cl}_3\text{Si}\cdot) > \text{S}(\text{Me}_3\text{Si}\cdot)$. This indicates that reactivity in these reactions is dominated by polar effects, such as $\text{X} \leftrightarrow \text{Y}$ repulsions in the transition state, since if bond energies were the determining factor, one might expect from our measured dissociation energies (Table I) an opposite ordering.

The second subject concerns a recent claim by Tokach and Koob⁵¹ that Me_3Si radicals may react up to 20 times faster than CH_3 in certain reactions. Bond dissociation energies show this is unlikely in general and

(40) For an illuminating discussion of the inert pair effect, see W. Dasent, "Non-existent compounds", Marcel Dekker, New York, 1965.

(41) Listed in Table II along with $\Delta H_f^\circ(\text{MeSi})$ based on the same argument.

(42) (a) M. Farber and R. D. Srivastava, *J. Chem. Soc., Faraday Trans. 1*, **73**, 1672 (1977); (b) M. Farber and R. D. Srivastava, *ibid.*, **74**, 1089 (1978).

(43) For a discussion on this point for the case X = Cl, see A. M. Doncaster and R. Walsh, *J. Chem. Soc., Faraday Trans. 1*, **76**, 272 (1980).

(44) For a comprehensive review, see L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, **79**, 529 (1979).

(45) Characterization has been made recently by (a) matrix isolation IR: O. M. Nefedov, A. K. Maltsev, V. N. Kabashchuk, and V. A. Korablev, *J. Organometal. Chem.*, **201**, 123 (1980); L. E. Gusel'nikov, V. V. Volkova, V. G. Avakyan, and N. S. Nametkin, *ibid.*, **201**, 137 (1980); (b) electron diffraction: P. G. Mahaffy, R. Gutowsky, and L. K. Montgomery, *J. Am. Chem. Soc.*, **102**, 2854 (1980); (c) UV and NMR: A. G. Brook, J. W. Harris, J. Lennon, and M. El Sheikh, *J. Am. Chem. Soc.*, **101**, 83 (1979).

(46) R. Walsh, *J. Organometal. Chem.*, **38**, 245 (1972).

(47) (a) S. Basu, I. M. T. Davidson, R. Laupert, and P. Potzinger, *Ber. Bunsenges. Phys. Chem.*, **83**, 1282 (1979); (b) L. E. Gusel'nikov and N. S. Nametkin, *J. Organometal. Chem.*, **169**, 155 (1979); (c) W. J. Pietro, S. K. Pollack, and W. J. Hehre, *J. Am. Chem. Soc.*, **101**, 7126 (1979); (d) P. John, B. G. Gowenlock, H. C. Low, and G. Peters, paper presented at The Chemical Society Gas Kinetics Discussion Group meeting in Keele, U.K., Sept 24, 1979.

(48) (a) M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *J. Am. Chem. Soc.*, **97**, 1311 (1975); (b) O. P. Strausz, L. Gammie, G. Theodorakopoulos, P. G. Mezey, and I. G. Cizmadias, *ibid.*, **98**, 1622 (1976); (c) R. Ahlrichs and R. Heinzman, *ibid.*, **99**, 7452 (1977).

(49) R. Walsh, unpublished results.

(50) (a) J. A. Kerr, B. J. A. Smith, and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 510 (1968); (b) P. Cadman, G. M. Tilsley, and A. F. Trotman-Dickenson, *ibid.*, 1370 (1969); (c) P. Cadman, G. M. Tilsley, and A. F. Trotman-Dickenson, *J. Chem. Soc., Faraday Trans. 1*, **69**, 914 (1973); (d) P. Cadman and H. L. Owen, private communication.

(51) S. K. Tokach and R. D. Koob, *J. Phys. Chem.*, **83**, 774 (1979).

impossible in at least the case of the substrate Me_4Si where the abstraction by Me_3Si is 9 kcal mol⁻¹ endothermic, with a probable activation energy of 17 kcal mol⁻¹, whereas abstraction by Me is 5 kcal mol⁻¹ exothermic, with an activation energy of 10 kcal mol⁻¹.^{19c} The system studied by Tokach and Koob, viz., the vacuum-UV photolysis of Me_4Si , is considerably more mechanistically complex than their interpretation suggests.^{52,53}

Chemically activated methylsilanes formed by $^1\text{CH}_2$ insertion reactions have been studied by Simons, Hase, and co-workers.⁵⁴ The decomposition processes of these hot silanes are in need of reinterpretation in the light of increased Si-C bond strengths. RRKM calculations⁵⁵ show that the experimental results can be fitted with the new energies for bond-breaking reactions with looser transition states than hitherto. These transition states correspond to thermal A factors of ca. 10^{17} s^{-1} rather than the 10^{15} s^{-1} previously found. This is in accord with recent thermal decomposition data for bond breaking.^{17,56,57}

Among silicon-containing small-ring pyrolyses, silacyclobutanes and their derivatives have been well studied,^{44,47a,d} and the finding by Barton et al.⁵⁸ that the initial site of ring cleavage is the C-C bond rather than the Si-C bond is supported by the bond dissociation energies. The comparison for small rings with their all-carbon analogues is interesting. Whereas silacyclobutanes have about the same thermal stability and decomposition parameters as cyclobutanes,⁵⁹ silacyclopropane (silirane) appears to be very much less stable⁶⁰ than cyclopropane.⁶¹ Of course, silacyclopropanes apparently decompose by a different mechanism from cyclopropanes, viz., a silylene extrusion reaction. Nevertheless we estimate a rather high activation energy of at least ca. 52 kcal mol⁻¹ based on a strain energy of 28 kcal mol⁻¹ in silacyclopropane.⁶² It seems unreasonable that the strain energy should be very much greater when the four-membered rings are so similar⁶³

and, therefore, we suspect that the true isolated molecule gas-phase study of a silacyclopropane may show it to be much more stable than suggested by Seyferth's solution studies of hexamethylsilane decomposition.^{60,64}

One or two further comments concerning silylenes, sila olefins, and biradicals seem appropriate. The ΔH_f° values deduced in this Account (Table II) back up theoretical calculations which show that isomeric silylenes and sila olefins lie extremely close in energy.⁶⁵ In view of this, it is very interesting that Conlin⁶⁶ has recently obtained evidence that $\text{CH}_3\text{SiH}=\text{CH}_2$ isomerizes to $\text{Me}_2\text{Si}^\cdot$ (by 1,2-H shift). It would be fascinating to see whether the reverse process also occurs. These possibilities may further complicate interpretations of thermal rearrangements of organosilicon molecules for which a bewildering variety of possible pathways often seems to exist. In reactions where the choice of pathways seems to lie between those involving silylene intermediates and those involving biradicals, the former seem to offer a definite energetic advantage. Therefore, if activation barriers permit, silylene-type mechanisms are likely to be favored.⁶⁷ In this respect Barton's explanation⁶⁸ of the rearrangements of the dimethylsilene dimer⁶⁹ seems more reasonable than the earlier suggestions of Roark and Peddle,⁷⁰ and Gaspar's mechanism⁷¹ for the rearrangement of $(\text{Me}_3\text{Si})_2\text{Si}$ seems quite plausible.

Concluding Remarks

Substantial progress has been made in recent years in establishing a quantitative picture of bond strengths in silicon compounds. What is now of urgent need is for more reliable and extensive heat of formation data to reduce the heavy reliance placed on Steele's determination of $\Delta H_f^\circ(\text{Me}_4\text{Si})$. Nevertheless, although much remains to be done, we can expect that thermochemical information will have an increasing impact in the fields of silicon chemistry in general and organosilicon reaction mechanisms in particular.

I thank Howard Purnell who kindled my interest in silanes, Sidney Benson whose inspiration lies behind so much of this work, and Alan Doncaster for much fruitful discussion during the course of it. I also thank the U.K. Science Research Council for Financial support.

(52) E. Bastian, P. Potzinger, A. Ritter, H.-P. Schuchmann, C. von Sonntag, and G. Weddle, *Ber. Bunsenges. Phys. Chem.*, **84**, 56 (1980).

(53) L. Gammie, C. Sandorfy, and O. P. Strausz, *J. Phys. Chem.*, **83**, 3075 (1979).

(54) T. H. Richardson and J. W. Simons, *Int. J. Chem. Kinet.*, **10**, 1055 (1978), and references cited therein.

(55) S. P. Lodge and R. Walsh, unpublished calculations.

(56) The complexity of the thermal decomposition of methylsilanes, which can show both molecular and radical processes,⁵⁷ makes isolation of the bond rupture rate constant difficult. This appears to have been achieved only in the case of tetramethylsilane.¹⁷

(57) (a) P. S. Neudorfl and O. P. Strausz, *J. Phys. Chem.*, **82**, 241 (1978); (b) I. M. T. Davidson and M. A. Ring, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1520 (1980).

(58) T. J. Barton, G. Marquardt, and J. A. Kilgus, *J. Organometal. Chem.*, **85**, 317 (1975).

(59) (a) For dimethylcyclobutane, $\log k/\text{s}^{-1} = 15.68-61.0 \text{ kcal mol}^{-1}/\theta$; P. C. Rotoli, M.Sc. Thesis, University of Rochester, 1963. (b) For 1,1-dimethylsilacyclobutane, $\log k/\text{s}^{-1} = 15.64-62.6 \text{ kcal mol}^{-1}/\theta$; M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, **419**, 1396 (1968).

(60) D. Seyferth, D. C. Annarelli, S. C. Vick, and D. Duncan, *J. Organometal. Chem.*, **201**, 179 (1980), and references therein.

(61) W. E. Falconer, T. F. Hunter, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, **609** (1961).

(62) Assumed equal to that for cyclopropane.^{4b}

(63) For a differing view, see M. S. Gordon, *J. Am. Chem. Soc.*, **102**, 7419 (1980).

(64) If the rate data of ref 60 were to apply to the gas phase, then a strain energy of ca. 50 kcal mol⁻¹ would be implied for hexamethylsilirane.

(65) (a) M. S. Gordon, *Chem. Phys. Lett.*, **54**, 9 (1978); (b) H. F. Shaeffer III, *Acc. Chem. Res.*, **12**, 287 (1979).

(66) R. T. Conlin and D. L. Wood, *J. Am. Chem. Soc.*, **103**, 1843 (1981).

(67) For a recent review of silylene chemistry, see P. P. Gaspar in "Reactive Intermediates", Vol. 2, M. Jones, Jr., and R. A. Moss, Eds., Wiley, New York, 1981.

(68) W. D. Wulff, W. F. Goure, and T. J. Barton, *J. Am. Chem. Soc.*, **100**, 6236 (1978).

(69) R. T. Conlin and P. P. Gaspar, *J. Am. Chem. Soc.*, **98**, 868 (1976).

(70) D. N. Roark and G. J. D. Peddle, *J. Am. Chem. Soc.*, **94**, 5837 (1972).

(71) Y. S. Chen, B. H. Cohen, and P. P. Gaspar, *J. Organometal. Chem.*, **195**, C1 (1980).