Some Aspects of Silicon Radical Chemistry

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1 Introduction and General Considerations

Our present knowledge and understanding of free-radical chemistry is derived almost entirely from the reactions of alkyl and aryl radicals. However, increasing progress is being made in studying the reactions of radicals based on elements other than carbon, especially silicon, which, being the neighbouring element to carbon in Group IV of the Periodic Table, has many features in common with it and may form silyl radicals ($\cdot SiR_3$) analogous to alkyl radicals, and silylenes (SiR_2) analogous to methylene and carbenes.

Recent reviews have surveyed the general chemistry of silicon;[1] the free-radical reactions of the elements of Group IVB, especially silicon;[2] and, more specifically, the chemistry of silylenes.[3] These reviews provide a good comprehensive background to silicon radical chemistry and this Review will attempt to fulfil a complementary rôle, instead of merely reporting further work done since the earlier reviews were published. Accordingly, important areas of the subject, such as the reactions of silyl radicals with olefins and aromatic compounds, well covered elsewhere,[1,2] will be entirely omitted, and this Review will concentrate on a few topics which bring out the distinctive features of silicon radical chemistry and indicate the extent of its potential contribution to an increased understanding of radical reactions in general. Particular emphasis will be placed on kinetic studies, especially in the gas phase, since the quantitative information yielded by these studies, and by other measurements of the energetics of radical reactions, appear to the author to be important at this relatively early stage in the development of the subject.

In order to make a useful contribution to the fundamental understanding of radical chemistry the kineticist must obtain data relating to elementary reactions, either by direct study of the rates of elementary reactions or by finding conditions under which a complex overall mechanism is rate-determined by an elementary reaction. The rates of the elementary reactions (transfer or abstraction, combination, disproportionation, addition, and dissociation) of carbon radicals, particularly simple alkyl radicals, have been widely studied; the Arrhenius activation energies and *A* factors for these reactions provide quantitative information about the relative reactivity of radicals, the strengths of bonds broken and formed in radical reactions, the importance of polar effects, and the structure and configuration of transition states. Direct measurement of the rates of these

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radical reactions requires the availability of a 'clean' radical source, from which radicals may be generated in adequate concentration under mild, controlled conditions without the occurrence of complicating side reactions.

Measurement of the rate of dissociation of molecules into radicals is also relevant, since the energetics of radical formation (*i.e.* dissociation energies of bonds broken to form radicals and heats of formation of radicals) may be deduced from the kinetic data. Since radical concentrations cannot be measured directly in conventional kinetic experiments, the rate of formation of a stable product resulting from the original dissociation into radicals must be measured. It is important to ensure that the sequence of reactions leading to the formation of this product is rate-determined by the initial dissociation, and that the radicals then formed are not also formed in some subsequent step.

It is relatively easy to study kinetically the elementary reactions of simple alkyl radicals, since several excellent clean sources of these radicals are available and since the reactions of the radicals are energetically favourable. On the other hand, it is difficult to measure the rate of thermal dissociation of hydrocarbons and simple organic compounds, since the pyrolysis of these compounds generally proceeds by a radical chain mechanism which is kinetically complex. Although some decompositions may be simplified by the use of radical trapping agents, the difficulties are still substantial.[4]

The basic differences between carbon and silicon are such that the situation described above is essentially reversed in silicon radical chemistry. Clean sources of silicon radicals are less readily available, and some of the most familiar radical reactions, for example hydrogen abstraction, are energetically unfavourable; on the other hand, many silicon compounds may undergo pyrolysis by non-chain sequences from which the rate of initial bond rupture into silyl radicals may readily be obtained. The features of carbon and silicon which give rise to these intriguing differences will now be described in more detail.

Silicon, being a larger atom than carbon, forms weaker bonds to itself, to carbon, and to hydrogen than does carbon; but because of its accessible $3d$ orbitals, or because of its greater electropositivity, it forms stronger bonds than does carbon to electronegative atoms with lone pairs, such as halogens, nitrogen, and oxygen (a detailed discussion of bond strengths in silicon compounds is given in Section 2). Also, silicon does not form stable p_π–p_π double bonds to itself or to other elements. (It may form p_π–d_π bonds, but this contentious question is far from being resolved[5]). These simple differences between carbon and silicon have far-reaching consequences in radical chemistry. Because of the differences in bond strengths, silyl radicals will be poor abstractors of hydrogen from organic substrates, but good abstractors of halogen. The tendency of silicon to form strong bonds to oxygen and to nitrogen also restricts the range of radical sources which may be used with silicon compounds. Thus, abstraction from organic substrates by methyl and trifluoromethyl radicals is readily studied by using the photolysis of acetone or hexafluoroacetone as the radical source, but when the

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[4] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

[5] A. J. Downs, C. J. Adams, and S. Craddock, *Annual Reports*, 1968, **65A**, 215.

substrate is a silicon compound difficulties may arise because of the rapid reaction between silicon hydrides or silyl radicals and ketones to form the strong silicon–oxygen bond. For example, trimethylsilane and hexafluoroacetone react rapidly, even in the dark at low temperature:[6] $Me_3SiH + O{=}C(CF_3)_2 \rightarrow Me_3SiOC(H)(CF_3)_2$. This difficulty does not arise when the substrate is a tetra-alkylsilane (since hydrogen abstraction then gives a silicon-substituted alkyl radical rather than a silyl radical), but when it does it may be circumvented by the use of azomethane or hexafluoroazomethane as the radical source.

The usefulness of silicon-substituted ketones and azo-compounds as sources of silyl radicals is also limited by considerations of bond strength. Thus, although triphenylsilyl radicals may be produced by photolysis of bis(triphenylsilyl) ketone,[7] ketones of the type R_3SiCOR^1 rearrange on photolysis[8] to give a carbene with a silicon–oxygen bond: $R_3SiCOR^1 + h\nu \rightarrow R_3SiO\ddot{C}R^1 \rightarrow$ products. Because of the strength of the silicon–nitrogen bond, silicon-substituted azo-compounds are too stable to be useful as sources of silyl radicals;[9] but silicon–mercury compounds have been used with considerable success in solution:[10,11] $(Me_3Si)_2Hg + h\nu \rightarrow 2{\cdot}Me_3Si{\cdot} + Hg$ although some complications may arise from molecular reactions.[12]

The production of silyl radicals in the gas phase by pyrolysis, photosensitisation, and direct photolysis will be discussed in Sections 2, 3, and 6.

Methylene and carbenes are conveniently produced by the photolysis of the appropriate diazomethanes or ketens, but these compounds are generally unsuitable as sources of silicon-substituted carbenes. For example, trimethylsilyldiazomethane is extremely stable thermally because of the strong silicon–nitrogen bond,[13] while trimethylsilylketen tautomerises:[14] $Me_3Si(H)C{:}C{:}O \rightleftharpoons HC{\vdots}COSiMe_3$. However, silylcarbenes $RMe_2Si\ddot{C}H$ are believed to have been formed in solution by reaction between RMe_2SiCH_2Cl and sodium[15] or butyllithium.[16] There are convenient thermal and photochemical sources of silylenes, discussed in Sections 4 and 6 of this Review, and well covered by an earlier review.[3]

A further consequence of the different bonding characteristics of carbon and silicon is that the pyrolysis of organosilanes proceeds differently from the pyrolysis of hydrocarbons because of the inability of silicon to form p_π–p_π bonds. Pyrolysis of hydrocarbons proceeds by the well-known Rice–Herzfeld mechan-

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[6] A. F. Janzen and C. J. Willis, *Canad. J. Chem.*, 1965, **43**, 3063.
[7] A. G. Brook and G. J. D. Peddle, *J. Organometallic Chem.*, 1966, **5**, 106.
[8] A. G. Brook and J. M. Duff, *J. Amer. Chem. Soc.*, 1967, **89**, 454.
[9] U. Wannegat and C. Krüger, *Z. anorg. Chem.*, 1964, **326**, 304.
[10] C. Eaborn, R. A. Jackson, and R. W. Walsingham, *Chem. Comm.*, 1965, 300; R. A. Jackson, *ibid*, 1966, 827.
[11] C. Eaborn, R. A. Jackson, and R. Pearce, *Chem. Comm.*, 1967, 920.
[12] R. Fields, R. N. Haszeldine, and R. E. Hutton, *J. Chem. Soc.* (*C*), 1967, 2559.
[13] D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Amer. Chem. Soc.*, 1968, **90**, 1080.
[14] L. L. Shchukovskaya, R. I. Pal'chik, and A. N. Lazarev, *Doklady Chem.*, 1965, **164**, 887.
[15] J. W. Connolly, *J. Organometallic Chem.*, 1968, **11**, 429.
[16] I. A. D'yakonov, I. B. Rebinskaya, and G. V. Golodnikov, *Zhur. obshchei. Khim.*, 1965, **35**, 199.

ism, in which slow dissociation of the hydrocarbon molecule into radicals is followed by rapid chain-propagation steps, one of which [reaction (3)] is the dissociation of a large radical into a small radical and an olefin. The mechanism may be illustrated by the simplified version of the complex pyrolysis of ethane,[17] reactions (1)—(4).

$$C_2H_6 \rightarrow 2{\cdot}CH_3 \quad \text{initiation} \tag{1}$$

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5{\cdot} \quad \text{transfer} \tag{2}$$

$$C_2H_5{\cdot} \rightarrow C_2H_4 + H{\cdot} \quad \text{propagation} \tag{3}$$

$$H{\cdot} + C_2H_6 \rightarrow H_2 + C_2H_5{\cdot} \quad \text{propagation} \tag{4}$$

The chain is terminated by various radical combination or disproportionation reactions. Since silicon does not form stable p_π–p_π bonds, the analogous reaction to (3) is energetically unfavourable in the pyrolysis of organosilanes, since the product would be an unstable biradical rather than an olefin-like molecule, and hence a chain reaction would not be propagated and a non-chain sequence should be observed instead. The pyrolysis of hexamethyldisilane at low pressures between 796 K and 828 K has been found to proceed in this way,[18] giving as the main products Me_3SiH and $Me_3SiCH_2Si_2Me_5$ when the initial pressure of hexamethyldisilane was below 1 mm Hg and the extent of decomposition was below 5%. The rate of formation of these products was first-order in hexamethyldisilane, the rate constants† being given by: $\log k = 13{\cdot}5 \pm 1{\cdot}0 - 67{,}300 \pm 2{,}200/2{\cdot}303RT$. The following mechanism was proposed:

$$Me_3SiSiMe_3 \rightarrow 2{\cdot}SiMe_3 \tag{5}$$

$$Me_3Si{\cdot} + Me_3SiSiMe_3 \rightarrow Me_3SiH + Me_3SiSiMe_2\dot{C}H_2 \tag{6}$$

$$Me_3SiSiMe_2\dot{C}H_2 \rightarrow Me_3SiCH_2\dot{S}iMe_2 \tag{7}$$

$${\cdot}SiMe_3 + Me_3SiCH_2\dot{S}iMe_2 \rightarrow Me_3SiCH_2SiMe_2SiMe_3 \tag{8}$$

The product analysis and kinetic features of the reaction are unaffected by the radical rearrangement reaction (7), but it is included because strong evidence for its occurrence is provided by studies of the pyrolysis at higher pressure to be described in Section 5. Steady-state treatment of the above non-chain sequence gives

$$\frac{d[\text{Products}]}{dt} = k_5[Me_3SiSiMe_3]\,.$$

2 Bond Dissociation Energies

The general trends in bond dissociation energies of silicon compounds have been

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†Throughout this Review first order rate constants are in s^{-1} and second order rate constants are in $cm^3\ mol^{-1}\ s^{-1}$, both of which are compatible with S.I. Units. Unless stated otherwise, energies are in kcal mol^{-1} (1 kcal mol^{-1} = 4·18 kJ mol^{-1}) as in the original references.

[17] S. W. Benson, 'Foundations of Chemical Kinetics', McGraw-Hill, New York, 1960, p. 349.

[18] I. M. T. Davidson and I. L. Stephenson, *J. Chem. Soc.* (*A*), 1968, 282.

described in Section 1, and the relevance of these bond dissociation energies to radical chemistry is apparent. Bond dissociation energies and molecular heats of formation are interrelated as shown below for a molecule R_1R_2 with bond dissociation energy $D(R_1\text{–}R_2)$:

$$R_1R_2 \rightarrow R_1\cdot + R_2\cdot \qquad (9)$$
$$\Delta H_9 = D(R_1\text{–}R_2) = \Delta H_f{}^{\circ}(R_1\cdot) + \Delta H_f{}^{\circ}(R_2\cdot) - \Delta H_f{}^{\circ}(R_1R_2)$$

Reliable bond dissociation energies and heats of formation are far from plentiful in silicon chemistry, but some progress has recently been made and the present situation will now be reviewed in some detail.

In a non-chain pyrolysis like that of hexamethyldisilane at low pressure described above, the overall kinetics were determined by the rate of the initial dissociation reaction (5), and hence the overall activation energy may be equated to E_5. Then, $\Delta H_5 = E_5 - E_{-5}$ and if the reverse reaction (− 5), the combination of two trimethylsilyl radicals, is assumed to have an activation energy of zero, $E_5 = \Delta H_5 = D(Me_3Si\text{–}SiMe_3)$ and the activation energy of 67·3 kcal mol^{-1} may be identified with the silicon–silicon bond dissociation energy in hexamethyldisilane. This is a good illustration of the kinetic method of determining bond dissociation energies, which is reliable and relatively direct, provided that the identification of the observed kinetic data with the initial dissociation reaction is correct.[4]

Bond dissociation energies may also be deduced, somewhat less reliably, from electron impact experiments in the mass spectrometer. Under electron impact in the ion source of a mass spectrometer, molecules may dissociate and one of the fragments may become ionized; if the fragment ionized is the one of lower ionization potential, and if it and the other fragment are produced in their ground states from a ground state molecule, then the appearance potential of the ion produced is simply related to the ionization potential of the fragment and the dissociation energy of the bond broken to form it:

$$R_1\text{–}R_2 + e \rightarrow R_1{}^+ + R_2\cdot + 2e$$

The appearance potential is given by $A(R_1{}^+) = D(R_1\text{–}R_2) + \text{I.P.}(R_1)$. Direct determination of the radical ionization potential, $\text{I.P.}(R_1)$, is extremely difficult, and no values are available for silicon radicals. Hence electron impact results alone cannot give bond dissociation energies; the necessary additional information may be (*i*) a bond dissociation energy obtained by the kinetic method, or (*ii*) molecular heats of formation deduced from calorimetric measurements. Recent examples in silicon chemistry are:

(*i*) Electron impact experiments with hexamethyldisilane gave the appearance potential of the trimethylsilyl ion:[19]

$$Me_6Si_2 + e \rightarrow Me_3Si^+ + Me_3Si\cdot + 2e$$
$$A(Me_3Si^+) = 10{\cdot}0\,\text{eV}$$

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[19] I. M. T. Davidson and I. L. Stephenson, *J. Organometallic Chem.*, 1967, **7**, P24.

In conjunction with the kinetically-determined value[18] for $D(\mathrm{Me_3Si{-}SiMe_3})$ of 67 kcal mol^{-1} (2·9 eV), this gives 7·1 eV for the ionization potential of trimethylsilyl. This value may then be used to deduce bond dissociation energies in a series of trimethylsilyl compounds, $\mathrm{Me_3Si{-}R}$, from the appearance potentials of the trimethylsilyl ions from these compounds. Bond dissociation energies for such a series, where R = H, Me, Cl, Br, and I, have been obtained in this way[20] and are given in Table 1.

Table 1 *Bond Dissociation Energies of some Trimethylsilyl Compounds* $\mathrm{Me_3Si{-}X}$

$\mathrm{Me_3Si{-}X}$	$\mathrm{D(Me_3Si{-}X)}$ kcal mol^{-1}
$\mathrm{Me_3Si{-}SiMe_3}$	67 ± 2^a
$\mathrm{Me_3Si{-}Me}$	76 ± 2
$\mathrm{Me_3Si{-}H}$	81 ± 2
$\mathrm{Me_3Si{-}Cl}$	88 ± 2^b
$\mathrm{Me_3Si{-}Br}$	$78{\cdot}5 \pm 2^b$
$\mathrm{Me_3Si{-}I}$	$69 \cdot 2^b$

[a]Determined from gas kinetic experiments; [b]These values are probably too low, see text.

(*ii*) Electron impact studies of silane and disilane[21] gave the following appearance potentials:

$$\mathrm{SiH_4} + e \rightarrow \mathrm{SiH_3^+} + \mathrm{H\cdot} + 2e \qquad (10)$$
$$A_{10}(\mathrm{SiH_3^+}) = 12{\cdot}30\ \mathrm{eV}$$

$$\mathrm{Si_2H_6} + e \rightarrow \mathrm{SiH_3^+} + \mathrm{\cdot SiH_3} + 2e \qquad (11)$$
$$A_{11}(\mathrm{SiH_3^+}) = 11{\cdot}95\ \mathrm{eV}$$

Subtraction of these equations gives an equation for the hypothetical reaction (12):

$$\mathrm{SiH_4} + \mathrm{\cdot SiH_3} \rightarrow \mathrm{Si_2H_6} + \mathrm{H\cdot} \qquad (12)$$
$$\Delta H_{12} = \Delta H_{10} - \Delta H_{11} = A_{10}(\mathrm{SiH_3^+}) - A_{11}(\mathrm{SiH_3^+}) = 0{\cdot}35\ \mathrm{eV} = 8{\cdot}1\ \mathrm{kcal\ mol^{-1}}$$
$$\Delta H_{12} = \Delta H_f^\circ(\mathrm{Si_2H_6}) + \Delta H_f^\circ(\mathrm{H\cdot}) - \Delta H_f^\circ(\mathrm{SiH_4}) - \Delta H_f^\circ(\mathrm{\cdot SiH_3\cdot}).$$

Hence if the heats of formation of silane and disilane are known, the heat of formation of the radical $\mathrm{\cdot SiH_3}$ may be calculated since the heat of formation of the hydrogen atom is well established;[4] the bond dissociation energies $D(\mathrm{H_3Si{-}H})$ and $D(\mathrm{H_3Si{-}SiH_3})$ may then be calculated as in equation (9).

In assessing the reliability of bond dissociation energies obtained from electron impact studies, it is important to remember that in addition to the errors in the appearance potentials themselves, which may be considerable either because of experimental difficulties or because of misinterpretation of the ionization

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[20] S. J. Band, I. M. T. Davidson, and C. A. Lambert, *J. Chem. Soc.* (*A*), 1968, 2068.

[21] P. Potzinger and F. W. Lampe, *J. Phys. Chem.*, 1969, **73**, 3912.

efficiency curves, there may well be errors in the supporting data, be they kinetically determined dissociation energies or calorimetric heats of formation.

The problems associated with the determination of bond dissociation energies in silicon compounds are well illustrated by the above electron impact results for silane and disilane. The heats of formation of these compounds have been measured by Gunn and Green,[22] giving $\Delta H_f^\circ(SiH_4)_g = 7{\cdot}3$ kcal mol^{-1} and $\Delta H_f^\circ(Si_2H_6)_g = 17{\cdot}1$ kcal mol^{-1}. Substitution of these values in equation (12) along with the heat of formation of the hydrogen atom and the value of 8·1 kcal mol^{-1} for ΔH_{12} from the appearance potentials, gives $\Delta H_f^\circ(H_3Si\cdot) = 53{\cdot}8$ kcal mol^{-1}. Hence, $D(H_3Si{-}H) = 98{\cdot}6$ kcal mol^{-1} and $D(H_3Si{-}SiH_3) = 90{\cdot}5$ kcal mol^{-1}. The value for the silicon–hydrogen dissociation energy in silane appears to be rather high in view of the values in Table 1, but even if it is correct, there appears to be no reason why the silicon–silicon dissociation energy in disilane should be as high as 90·5 kcal mol^{-1} when it is only 67 kcal mol^{-1} in hexamethyldisilane; the difference between the bond dissociation energies in silane and disilane should almost certainly be greater than 8·1 kcal, and since this small difference is directly derived from the appearance potentials, it is these which are suspect in this case rather than the heats of formation. Similar shortcomings have become apparent in the appearance potentials and derived dissociation energies in the trimethylsilyl halides (Table 1), which will be discussed later.

The kinetic method of determining dissociation energies has recently been applied to trimethylsilane,[23] where both the silicon–hydrogen and the silicon–methyl dissociation energies could be obtained. Pyrolysis of trimethylsilane between 943 K and 1031 K up to 10% decomposition gave methane and hydrogen in the approximate ratio of 5 : 1 and several products containing two silicon atoms. The rates of formation of methane and hydrogen were measured, and each was found to be first-order in trimethylsilane, the rate constants being given by:

$$\log k_{CH_4} = 16{\cdot}1 \pm 0{\cdot}5 - 76{,}500 \pm 500/2{\cdot}303RT$$
$$\log k_{H_2} = 15{\cdot}8 \pm 0{\cdot}5 - 80{,}300 \pm 500/2{\cdot}303RT$$

Both A factors have the high values characteristic of unimolecular dissociations into monoradicals, and the activation energies are extremely close to those expected from the electron impact values in Table 1. Consequently, there is good kinetic evidence that methane and hydrogen were each formed in radical non-chain mechanisms, rate-determined by the initial dissociations, as in hexamethyldisilane,[18] and the activation energies may be identified with the appropriate dissociation energies in trimethylsilane. The reactions forming methane and hydrogen are set out [(13)—(16)].

$$Me_3SiH \rightarrow Me_2\dot{S}iH + Me\cdot \qquad (13)$$

$$Me_3SiH \rightarrow Me_3Si\cdot + H\cdot \qquad (14)$$

$$Me\cdot + Me_3SiH \rightarrow CH_4 + \cdot CH_2SiMe_2H \qquad (15)$$

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[22] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, 1961, **65**, 779.
[23] I. M. T. Davidson and C. A. Lambert, *Chem. Comm.*, 1969, 1276.

$$H\cdot + Me_3SiH \rightarrow H_2 + \cdot CH_2SiMe_2H \qquad (16)$$

There are no subsequent reactions in which methyl radicals or hydrogen atoms are formed. The radical formed in reactions (15) and (16) was said to be $\cdot CH_2SiMe_2H$ rather than $Me_3Si\cdot$, because at these high temperatures the greater availability of the hydrogens attached to carbon should outweigh the difference between the carbon–hydrogen and carbon–silicon bond strengths (see Table 2). The subsequent reactions, and the products resulting from them, will be discussed in Section 3.

Bond Dissociation Energies – Conclusions.—The appearance potentials of trimethylsilyl ions from hexamethyldisilane, tetramethylsilane, and trimethylsilane, have been measured by significantly different techniques with closely concordant results.[20,24,25] In conjunction with the kinetically-determined value of 67 kcal mol^{-1} for $D(Me_3Si\text{–}SiMe_3)$, these appearance potential measurements give 81 kcal mol^{-1} for $D(Me_3Si\text{–}H)$ and 76 kcal mol^{-1} for $D(Me_3Si\text{–}Me)$; the kinetic experiments with trimethylsilane[23] gave 80·3 kcal mol^{-1} for $D(Me_3Si\text{–}H)$ and 76·5 kcal mol^{-1} for $D(HMe_2Si\text{–}Me)$. Bond dissociation energies in these compounds thus appear to be very well established, but the position regarding their heats of formation is unsatisfactory, since the literature contains many conflicting and mutually inconsistent values.[25,26] These arise because the traditional calorimetric methods used so successfully to obtain the heats of combustion (and hence the heats of formation) of hydrocarbons do not give accurate results for silicon compounds because of the involatility of silica, the formation of solid films over uncombusted material, and a tendency to detonation. Consequently, early thermochemical values of heats of formation of silicon compounds must be viewed with considerable reserve. The modern techniques of rotating bomb calorimetry and fluorine bomb calorimetry should allow much more reliable heats of combustion of silicon compounds to be measured in future, and progress is also possible by measuring the heats of less troublesome reactions than combustion. For example, the heats of hydrolysis of several organosilicon compounds have been measured, leading to apparently reliable heats of formation.[27,28]

Potzinger and Lampe have recently critically reviewed the heats of formation of alkyl silanes and have proposed a new series of self-consistent values.[25] They applied Allen's bond interaction scheme,[29] using as their basic information the heats of formation of silane and disilane[22] and various appearance potentials

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[24] J. A. Connor, G. Finney, G. J. Leigh, R. N. Haszeldine, P. J. Robinson, R. D. Sedgwick, and R. F. Simmons, *Chem. Comm.*, 1966, 178.

[25] P. Potzinger and F. W. Lampe, *J. Phys. Chem.*, 1970, **74**, 719.

[26] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279, and references therein.

[27] A. E. Beezer and C. T. Mortimer, *J. Chem. Soc.* (*A*), 1966, 514.

[28] J. C. Baldwin, M. F Lappert, J. B. Pedley, and J. A. Treverton, *J. Chem. Soc.* (*A*), 1967, 1980.

[29] T. L. Allen, *J. Chem. Phys.*, 1959, **31**, 1039.

from the compounds in question, which they had measured by the retarding potential difference technique.[21,25,30] They obtained a value of 9 kcal mol^{-1} for the heat of formation of the trimethylsilyl radical, which in conjunction with the well-established heat of formation of trimethylchlorosilane (from its heat of hydrolysis[27] and its heat of combustion[31]) gave 123 kcal mol^{-1} for D(Me$_3$Si–Cl). This is much greater than the value quoted in Table 1, and Potzinger and Lampe suggested that the appearance potential of the trimethylsilyl ion from trimethylchlorosilane obtained by Band, Davidson, and Lambert[20] was lowered by a substantial contribution from ion-pair formation: $Me_3SiCl + e \rightarrow Me_3Si^+ + Cl^- + e$, which requires less energy because the electron affinity of chlorine is exothermic. This is a perfectly reasonable suggestion which may also explain the wide divergence in the values of this appearance potential found by other workers using techniques of different sensitivity,[20,24,32] and the silicon–halogen dissociation energies in Table 1 are probably too low, although the error in the iodide at least may well be small. Nevertheless, the true values may not be so high as Potzinger and Lampe's estimate of D(Me$_3$Si–Cl) might suggest, since there is in turn some doubt about the absolute values of the heats of formation of alkyl silanes, and hence of the trimethylsilyl radical, which they proposed; it has already been noted that their appearance potentials for the formation of the SiH_3^+ ion from silane and disilane seem to be incorrect, which diminishes confidence in the reliability of the appearance potentials which they used in calculating heats of formation.

The present situation, therefore, is that reliable bond dissociation energies are known for hexamethyldisilane, tetramethylsilane, and trimethylsilane, but reliable heats of formation are not; on the other hand, reliable heats of formation of Me_3SiX, where X is Cl, Br, OH, SBu^n, NHMe, and NMe_2 are known, largely from heats of hydrolysis,[27,28] but accurate bond dissociation energies are not. There is some hope that these deficiencies may be remedied soon by the wider application of modern calorimetric techniques to the measurement of heats of formation, and of kinetic methods to the determination of dissociation energies, giving a body of data capable of being checked for mutual consistency.

3 Some Further Pyrolysis Studies of Organosilicon Compounds

Few detailed kinetic studies of the pyrolysis of organosilanes have been reported other than those of hexamethyldisilane[18] and trimethylsilane.[23] The latter study clearly indicated that the silicon–hydrogen bond in trimethylsilane is stronger than the silicon–methyl bond, but Marès and Chvalovsky[33] concluded that trialkylsilanes were less stable thermally than tetra-alkylsilanes. They measured the rates of pyrolysis of $MeEt_2SiH$, Et_3SiH, Pr_3SiH, and Bu^i_3SiH, and activation energies ranging from 24 to 41 kcal mol^{-1} can be calculated from their results. These low activation energies were probably due to homogeneous chain reactions

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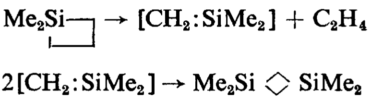
[30] P. Potzinger and F. W. Lampe, *J. Phys. Chem.*, 1970, **74**, 587.
[31] S. N. Hajiev and M. J. Agarunov, *J. Organometallic Chem.*, 1970, **22**, 305.
[32] G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Amer. Chem. Soc.*, 1965, **85**, 23.
[33] F. Marès and V. Chvalovsky, *J. Organometallic Chem.*, 1966, **6**, 327.

resulting from the splitting off of small alkyl radicals from the large alkyl groups present, a possibility which was not open to trimethylsilane.

An interesting investigation of the pyrolysis of 1,1-dimethyl-1-silacyclobutane between 673 K and 733 K has been reported by Flowers and Gusel'nikov.[34] Up to 50% decomposition, the products were ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane, formed in a first-order reaction with rate constants given by $\log k = 15{\cdot}80 \pm 0{\cdot}20 - 63{,}800 \pm 500/2{\cdot}303RT$. The formation of these products indicated the presence of the 'double-bonded' short-lived intermediate, $[CH_2{:}SiMe_2]$ which dimerised to give the disilacyclobutane:



The existence of $[CH_2{:}SiMe_2]$ was verified by the addition of trapping agents. When water vapour was added Me_3SiOH was formed, while added ammonia gave Me_3SiNH_2.

In the pyrolysis of trimethylsilane,[23] 1,1,3,3-tetramethyl-1,3-disilacyclobutane was a product, as were the trimethyl- and dimethyl-disilacyclobutanes. The other silicon-containing products were the disilanes $Si_2H_mMe_{(6-m)}$ where $m = 0,1,2$, and the disilamethylenes $CH_2Si_2H_nMe_{(6-n)}$ where $n = 1,2$. These straight chain products were obviously formed by combination reactions of the radicals produced in reactions (13) to (16), but the formation of the three disilacyclobutanes implies the prior formation of the double-bonded intermediates, $[CH_2{:}SiMe_2]$ and $CH_2{:}SiMeH$. It was proposed that these were formed in radical disproportionation reactions, [(17)—(19)].

$$\cdot CH_2SiMe_2H + H\ \ iMe_2 \rightarrow Me_3SiH + [CH_2{:}SiMeH] \qquad (17)$$

$$\cdot CH_2SiMe_2H + Me_3Si\cdot \rightarrow Me_3SiH + [CH_2{:}SiMe_2] \qquad (18)$$

$$\cdot CH_2SiMe_2H + \cdot CH_2SiMe_2H \rightarrow Me_3SiH + [CH_2{:}SiMe_2] \qquad (19)$$

The kinetic evidence that methane and hydrogen were formed by a non-chain mechanism precluded the possibility of radical dissociations:

$$\cdot CH_2SiMe_2H \nrightarrow Me\cdot + [CH_2{:}SiMeH]$$
$$\cdot CH_2SiMe_2H \nrightarrow H\cdot + [CH_2{:}SiMe_2]$$

Formation of $[CH_2{:}SiMe_2]$ has also been postulated by Fritz and his co-workers in the pyrolysis of tetramethylsilane.[35] They have pyrolysed a number of silicon compounds in a recycled flow system,[36] making no attempt to measure reaction rates, but directing considerable skill and care to the identification of products. They have given particular attention to the pyrolysis of tetramethyl-

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[34] M. C. Flowers and L. E. Gusel'nikov, *J. Chem Soc* (*B*), 1968, 419.

[35] G. Fritz and B. Raabe, *Z. anorg. Chem.*, 1959, **299**, 232; G. Fritz and J. Grobe, *ibid.*, 1962, **315**, 157; G. Fritz, D. Kummer, and G. Sonntag, *ibid.*, 1966, **342**, 113.

[36] G. Fritz, *Z. anorg. Chem.*, 1953, **273**, 275; G. Fritz and D. Ksinsik, *ibid.*, 1963, **322**, 46; G. Fritz, H. J. Buhl, and D. Kummer, *ibid.*, 1964, **327**, 165.

silane, where they have identified more than forty products.[35] The product composition depends upon the reaction time, which makes it difficult to draw close comparisons between their results and the kinetic experiments at low percentage decomposition. Good evidence for the presence of $[CH_2{:}SiMe_2]$ was provided by the presence among the products of $Me_2Si\Diamond SiMe_2$ and of the six-membered heterocyclic compound $(CH_2SiMe_2)_3$. It may have been formed by radical disproportionation, as in the pyrolysis of trimethylsilane, for example

$$\cdot CH_2SiMe_3 + Me_3Si\cdot \rightarrow Me_4Si + [CH_2{:}SiMe_2]$$

Disproportionation may thus be a more important reaction of silyl radicals than has previously been supposed,[2] and direct studies of combination to disproportionation ratios are needed.

The detailed kinetic investigations of the pyrolysis of silane[37] and disilane[38] are best considered in Section 4.

4 Silylenes

There is a progressive increase in the stability of the MR_2 radical relative to the MR_3 radical down Group IVB, and hence it is not surprising that silylene intermediates are important in silicon chemistry. Silylenes undergo similar reactions to carbenes and their chemistry has been thoroughly reviewed recently.[3] They insert rapidly into silicon–hydrogen bonds and into bonds between silicon and an atom with lone pairs (halogens, oxygen, and nitrogen), probably by initial attack by the silylene radical at the electron-rich atom. They also insert into hydrogen, probably[38] with an activation energy of about 8 kcal mol^{-1}, but do not insert into silicon–carbon, carbon–hydrogen, or carbon–carbon bonds even at elevated temperatures.[3,43] Pyrolysis of certain silicon compounds yields silylenes rather than silyl radicals, and it has been suggested that the selective insertion characteristics of silylenes described above are important in determining which silicon compounds give silylenes on pyrolysis, a silylene only being formed when the molecule formed along with it contains a bond into which the silylenes could readily insert. The formation of silylenes[3] from Si_2H_6, Si_2X_6 (X = halogen), and $(MeO)Me_2SiSiMe_2(OMe)$, but not from Si_2Me_6, which gives trimethylsilyl radicals on pyrolysis,[18] rather than $SiMe_2$ and $SiMe_4$, has been rationalized in this way.[39]

In those cases where silylenes are formed the original compound will also contain a bond into which silylenes will readily insert, and hence a simple non-chain mechanism will describe the main course of reaction. A good example[38,40] is the pyrolysis of disilane itself, [reactions (20)—(22)].

$$Si_2H_6 \rightarrow SiH_4 + SiH_2 \qquad (20)$$

$$Si_2H_6 + SiH_2 \rightarrow Si_3H_8 \qquad (21)$$

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[37] J. H. Purnell and R. Walsh, *Proc. Royal Soc.*, 1966, **A293**, 543.

[38] M. Bowrey and J. H. Purnell, *J. Amer. Chem. Soc.*, 1970, **92**, 2594; M. Bowrey, Ph.D. Thesis, University of Wales, 1969.

[39] I. M. T. Davidson, *J. Organometallic Chem.*, 1970, **24**, 97.

[40] E. M. Tebben and M. A. Ring, *Inorg. Chem.*, 1969, **8**, 1787.

$$Si_3H_8 + SiH_2 \rightarrow Si_4H_{10} \text{ (2 isomers)} \qquad (22)$$

Some solid polymer of approximate formula $(SiH_2)_n$ is also formed at the walls of the reaction vessel, where it partially decomposes to give hydrogen.[43] The kinetic investigation of this pyrolysis by Bowrey and Purnell[38] was particularly detailed; they obtained evidence for the very rapid and temperature-independent insertion of SiH_2 into silicon–hydrogen bonds in SiH_4 and in $MeSiH_3$ and for the non-insertion of SiH_2 into silicon–carbon bonds. Their kinetic data for the rate of formation of pyrolysis products between 556 K and 612 K up to 5% decomposition gave first-order rate constants, with an activation energy of 49·5 kcal mol^{-1}. Since a non-chain sequence was followed, this activation energy may be identified with E_{20}, and since the reverse reaction has no activation energy, $E_{20} = \Delta H_{20}$. Substitution of the heats of formation of silane and disilane in reaction (20) then gave 59·2 kcal mol^{-1} for the heat of formation of the silylene radical, SiH_2. This value is close to that obtained by similar reasoning from the results of Purnell and Walsh[37] on the pyrolysis of silane, which had an activation energy of 55·4 kcal mol^{-1}.

Although singlet silylenes are more selective than singlet methylene in their insertion reactions, methylene shows some discrimination in favour of silicon–hydrogen bonds, since it inserts into the silicon–hydrogen bonds of methylsilane 8·9 times faster than into the carbon–hydrogen bonds.[41] Methylene also inserts rapidly into silane, but some abstraction takes place as well:[42]

$$SiH_4 + :CH_2 \rightarrow \cdot SiH_3 + \cdot CH_3$$

5 Rearrangements

Although radical non-chain reactions are important in the pyrolysis of silicon compounds when either silyl or silylene radicals are formed, chain reactions are not unknown. The possible occurrence of chain mechanisms in the pyrolysis of higher trialkylsilanes than trimethylsilane has been discussed in Section 3, and a chain reaction may also be propagated by a radical rearrangement, as in the pyrolysis of hexamethyldisilane at high pressure.[43] Under these conditions the decomposition proceeds quite differently from the low-pressure pyrolysis described in Section 2, giving the isomeric $Me_3SiCH_2SiMe_2H$ as the main product with some trimethylsilane. The pyrolysis follows this course in a gas-phase flow system[43] at approximately atmospheric pressure at 873 K and in sealed tubes at several atmospheres[44] between 673 K and 723 K. The ratio of isomer to trimethylsilane was found to be 4:1, indicating a short chain length.[45] A gas kinetic study[46] of the early stages of this rearrangement gave a rate of formation of products which was three-halves order in hexamethyldisilane, with an activation

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[41] C. J. Mazac and J. W. Simons, *J. Amer. Chem. Soc.*, 1968, **90**, 2484.
[42] J. W. Simons and C. J. Mazac, *Canad. J. Chem.*, 1967, **45**, 1717.
[43] K. Shiina and M. Kumada, *J. Org. Chem.*, 1958, **23**, 139.
[44] H. Sakurai, A. Hosomi, and M. Kumada, *Chem. Comm.*, 1968, 930.
[45] H. Sakurai, R. Koh, A. Hosomi, and M. Kumada, *Bull. Chem. Soc. Japan*, **1966, 39,** 2050.
[46] C. Eaborn and J. M. Simmie, *Chem. Comm.*, 1968, 1426.

energy of 60 kcal mol^{-1}. These findings may be explained, and reconciled with the low-pressure results, by the following mechanism:

$$\mathrm{Me_3SiSiMe_3 \rightarrow 2{\cdot}SiMe_3} \tag{5}$$

$$\mathrm{Me_3Si{\cdot} + Me_3SiSiMe_3 \rightarrow Me_3SiH + Me_3SiSiMe_2\dot{C}H_2} \tag{6}$$

$$\mathrm{Me_3SiSiMe_2\dot{C}H_2 \rightarrow Me_3SiCH_2\dot{S}iMe_2} \tag{7}$$

$$\left.\begin{array}{l} \mathrm{Me_3SiCH_2SiMe_2 + Me_3SiSiMe_3 \rightarrow Me_3SiCH_2SiMe_2H +} \\ \qquad\qquad\qquad\qquad\qquad\qquad \mathrm{Me_3SiSiMe_2\dot{C}H_2} \quad (23) \\ \qquad \mathrm{2(Me_3SiCH_2\dot{S}iMe_2) \rightarrow (Me_3SiCH_2SiMe_2)_2} \quad (24) \end{array}\right\} \text{at high pressure}$$

$$\left.\mathrm{Me_3Si{\cdot} + Me_3SiCH_2\dot{S}iMe_2 \rightarrow Me_3SiCH_2SiMe_2SiMe_3}\right\} \text{at low pressure} \tag{8}$$

Steady-state treatment of the high-pressure chain sequence gives:

$$\frac{\mathrm{d[Products]}}{\mathrm{d}t} = \left(\frac{k_5 k_{23}^2}{2k_{24}}\right)^{\frac{1}{2}} [\mathrm{Me_3SiSiMe_3}]^{1\frac{1}{2}}\,.$$

If the value of 67 kcal mol^{-1} for E_5 (from the low-pressure results[18]) and reasonable estimates of E_{23} and E_{24} are substituted into this complex expression, the activation energy for the chain reaction leading to the rearranged product may be calculated to be 61 kcal mol^{-1}, in good agreement with the experimental value[46] of 60 kcal mol^{-1}.

The radical formed in reaction (6) may also be generated in the liquid phase at lower temperatures by decomposing organic peroxides in hexamethyldisilane;[45] at 353 K the rearrangement reaction (7) does not occur, nor does it occur in solution[47] at 402 K, thus indicating that reaction (7) has an appreciable activation energy. The pyrolysis of chloromethylpentamethyldisilane proceeds similarly to hexamethyldisilane, thus illustrating the preferential abstraction of chlorine rather than hydrogen from organic substrates by silyl radicals (Scheme 1).[48]

$$\mathrm{Me_3SiSiMe_2CH_2Cl \rightarrow Me_3Si{\cdot} + {\cdot}SiMe_2CH_2Cl}$$
$$\mathrm{R_3Si{\cdot} + Me_3SiSiMe_2CH_2Cl \rightarrow R_3SiCl + Me_3SiSiMe_2\dot{C}H_2}$$
$$\mathrm{Me_3SiSiMe_2\dot{C}H_2 \rightarrow Me_3SiCH_2\dot{S}iMe_2}$$
$$\mathrm{Me_3SiCH_2\dot{S}iMe_2 + Me_3SiSiMe_2CH_2Cl \rightarrow Me_3SiCH_2SiMe_2Cl + Me_3SiSiMe_2\dot{C}H_2}$$

Scheme 1

The rearrangement reaction (7) presumably proceeds through a three-centre transition state in which a silicon–silicon bond is broken while a stronger silicon–carbon bond is formed, the reaction thus being exothermic. Other rearrangements of silicon molecules and radicals have not been investigated in the same detail, but the indications are that other factors besides these simple thermodynamic considerations are important. For example, rearrangements of α-silyl alkyl radicals are not observed, even when they are thermodynamically favourable, and

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[47] H. Sakurai, T. Kishida, A. Hosomi, and M. Kumada, *J. Organometallic Chem.*, 1967, **8**, 65.
[48] M. Kumada, J. I. Nakajima, M. Ishikama, and Y. Yamamoto, *J. Org. Chem* , 1958, **23**, 292.

this has been ascribed to stabilisation of these radicals by p_π–d_π bonding.[49,50] Examples of this 'non-rearrangement' are:

$$\cdot\mathrm{CH_2SiMe_2H} \not\longrightarrow \mathrm{Me_3Si}\cdot \qquad \text{(ref. 23)}$$

$$\cdot\mathrm{CH_2SiPh_3} \not\longrightarrow \mathrm{Ph_2\dot{S}iCH_2Ph} \qquad \text{(ref. 50)}$$

$$\cdot\mathrm{CH_2SiMe_2R} \begin{array}{l} \not\longrightarrow \mathrm{Me_2\dot{S}iCH_2R} \\ \not\longrightarrow \mathrm{RMe\dot{S}iEt} \end{array} \Bigg\} \qquad \text{(ref. 51)}$$

6 Photochemical Decomposition of Silanes

Silicon hydrides and alkylsilanes, like paraffins, do not absorb in the near u.v., but may be dissociated by mercury photosensitisation. The photosensitised reaction between $\mathrm{SiH_4}$ and ethylene has been interpreted in terms of the initial formation of $\cdot\mathrm{SiH_3}$ radicals,[52] but the mercury-photosensitised decomposition of $\mathrm{SiH_4}$ alone was found to be complex.[53] However, Gunning and his coworkers[54] have shown that if methylsilanes containing at least one hydrogen attached to silicon are subjected to mercury photosensitisation, selective silicon–hydrogen bond cleavage occurs, giving a clean source of substituted silyl radicals which initiate a simple non-chain sequence, as shown for trimethylsilane in reactions (25)—(28). Small quantities of higher silanes were also formed. This non-chain mechanism was obeyed up to at least 673 K, the only significant effect of temperature being that proportionately more $\cdot\mathrm{CH_2SiMe_2H}$ was formed at higher temperatures, consistent with the preferential formation of this radical in the pyrolysis of trimethylsilane[23] around 1000 K. Some rearrangement of hexamethyldisilane was also observed.

$$\mathrm{Me_3SiH} + \mathrm{Hg}^* \rightarrow \mathrm{Me_3Si}\cdot + \mathrm{H}\cdot + \mathrm{Hg} \tag{25}$$

$$\mathrm{H}\cdot + \mathrm{Me_3SiH} \rightarrow \mathrm{H_2} + \mathrm{Me_3Si}\cdot \tag{26}$$

$$\mathrm{H}\cdot + \mathrm{H}\cdot + \mathrm{M} \rightarrow \mathrm{H_2} + \mathrm{M} \tag{27}$$

$$2\mathrm{Me_3Si}\cdot \rightarrow \mathrm{Me_3SiSiMe_3} \tag{28}$$

Similarly, dimethylsilane gave $\mathrm{H_2}$ and $\mathrm{(Me_2SiH)_2}$, while methylsilane gave $\mathrm{H_2}$ and $\mathrm{(MeSiH_2)_2}$ as the main products of photosensitization.[54] Although the main course of these reactions was determined by silyl radical reactions like (25) to (28), some silylene formation may also have occurred with dimethylsilane and methylsilane, for example: $\mathrm{Me_2SiH_2} + \mathrm{Hg}^* \rightarrow \mathrm{Me_2Si} + \mathrm{H_2} + \mathrm{Hg}$.

Added nitric oxide profoundly affected these reactions; disilanes and polysilanes were no longer formed, the main products being more hydrogen, nitrogen,

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[49] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, **91**, 6161.

[50] J. W. Wilt, O. Kolewe, and J. F. Kraemer, *J. Amer. Chem. Soc.*, 1969, **91**, 2624.

[51] K. Yamamoto, K. Nakamishi, and M. Kumada, *J. Organometallic Chem.*, 1967, **7**, 197.

[52] D. G. White and E. G. Rochow, *J. Amer. Chem. Soc.*, 1954, **70**, 3897.

[53] H. Niki and G. J. Mains, *J. Phys. Chem.*, 1964, **68**, 304.

[54] M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.* 1965, **87**, 179.

and a disiloxane. A chain reaction was proposed (Scheme 2). The strong tendency

$$\begin{aligned} MeR_2\dot{S}i + NO &\rightarrow MeR_2SiON \\ 2MeR_2SiON &\rightarrow MeR_2SiON{=}NOSiR_2Me \\ MeR_2SiON{=}NOSiR_2Me &\rightarrow 2MeR_2SiO\cdot + N_2 \\ MeR_2SiO\cdot + MeR_2SiH &\rightarrow MeR_2SiOSiR_2Me + H \\ H\cdot + MeR_2SiH &\rightarrow H_2 + MeR_2Si\cdot \end{aligned}$$

Scheme 2

for the formation of silicon–oxygen bonds is again responsible for inversion of the behaviour to be expected by analogy with carbon chemistry; nitric oxide, a well-known inhibitor of chain reactions in hydrocarbons, has here initiated chain reactions in hitherto non-chain systems.

More recently, Gunning and his co-workers[55] have turned their attention to direct photolysis in the far u.v., and have conducted a very detailed study of the photolysis of methylsilane at 1470 Å and 1236 Å. Eight primary steps were distinguished, including the formation of silyl and substituted silyl radicals, but the main primary reactions were the formation of silylenes or similar intermediates:

$$\begin{aligned} MeSiH_3 + h\nu &\rightarrow MeSiH^* + H_2 \\ &\rightarrow CH_2SiH_2^* + H_2 \\ &\rightarrow SiH_2 + \cdot CH_3 + H\cdot \\ &\quad (^* - \text{'hot' species}) \end{aligned}$$

In comparing the pyrolytic and photolytic behaviour of methylsilanes, it may be significant to note that the efficiency of direct photolysis of the methylsilanes decreased in the order, $MeSiH_3 > Me_2SiH_2 > Me_3SiH$, which corresponds to the difficulty in forming silylene intermediates thermally.[39]

Photosensitization as a Radical Source.—The clean production of trimethylsilyl radicals by photosensitization of trimethylsilane may be used to measure the rate of combination of these radicals by the rotating sector technique.[56] However, mercury-photosensitised dissociation of silicon hydrides is clearly an unsuitable way of producing substituted silyl radicals for hydrogen abstraction studies, since the product of abstraction would be indistinguishable from the radical source: $R_3Si\cdot + R^1H \rightarrow R_3SiH + R^1$. As noted in Section 1, there are also thermodynamic obstacles to the study of hydrogen abstraction from organic substrates by silyl radicals. Consider for instance the reaction between trimethylsilyl radicals and methane, reaction (29). The activation energy for reaction (– 29) is

$$Me_3Si\cdot + CH_4 \rightleftharpoons Me_3SiH + \cdot CH_3 \qquad (29)$$
$$\Delta H_{29} = D(H_3C\text{–}H) - D(Me_3Si\text{–}H) = 104 - 80 = 24 \text{ kcal mol}^{-1}$$

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[55] O. P. Strausz, K. Obi, and W. K. Duholke, *J. Amer. Chem. Soc.*, 1968, **90,** 1359; K. Obi, A. Clement, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1969, **91,** 1622.

[56] P. Cadman, G. M. Tilsley, and A. F. Trotman-Dickenson, personal communication.

between 7 and 8 kcal mol^{-1} (see Table 2), and hence the activation energy E_{29} is between 31 and 32 kcal mol^{-1}. These difficulties may have been overcome in a preliminary study[57] of reaction (29) in which the trimethylsilyl radicals were generated by mercury-photosensitisation of trimethylchlorosilane between 670 K and 770 K. At these temperatures the mercury chloride formed was volatile and was condensed outside the reaction zone. An activation energy of about 29 kcal mol^{-1}, in moderate agreement with the expected value, was obtained.

7 Reactions of Alkyl Radicals with Silicon Compounds

Whilst the difficulties associated with measuring the rates of abstraction reactions by silyl radicals are formidable, the reverse abstractions by alkyl radicals from silanes are exothermic and should be easily studied by conventional methods. The most recent results for transfer reactions in which methyl, trifluoromethyl, and ethyl radicals abstract hydrogen from silicon componds are collected in Table 2.

Transfer reactions of methyl radicals to give methane are expected to have values of log *A* between 11·0 and 12·0. All of the reactions of methyl radicals in Table 2 have *A* factors within this range, except for most of the reactions with halogenosilanes reported by Kerr, Slater, and Young.[58,59] These authors have subsequently suggested[60] that all of their earlier results, which included those giving high *A* factors, should be considered to be suspect, but since their *A* factor for abstraction from trimethylsilane is not higher than that found later by other workers they may prove to have been too widely self-critical. Nevertheless, further work on transfer reactions involving halogenosilanes is clearly necessary.

The most general formulation of a transfer reaction is (30). The activation

$$\text{R}\cdot + \text{SX} \rightarrow \text{RX} + \text{S}\cdot \qquad (30)$$

energy is determined partly by the endothermicity, given simply by $\Delta H_{30} = D(\text{S–X}) - D(\text{R–X})$, and partly by polar factors associated with the interaction between R· and SX. In Table 2 a good illustration of the importance of polar effects is provided by the work of Bell and Zucker[61] on the reactions between trifluoromethyl radicals and methylfluorosilanes, $\text{Me}_n\text{SiF}_{(4-n)}$, where $n = 1, 2, 3$, or 4. The activation energy is lowest for Me_4Si and highest for MeSiF_3, and this trend was correlated with the chemical shift of the proton magnetic resonance in these compounds. Me_4Si has the highest electron density round its protons, while the protons in MeSiF_3 are the least negative; a strong polar effect then arises because the trifluoromethyl radical is electrophilic.

8 Radical Reactions of Silicon Compounds with Halogens and Halides

Many reactions under this heading have been studied, and have been well

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[57] I. M. T. Davidson and J. M. Edwards, unpublished results.

[58] J. A. Kerr, D. H. Slater, and J. C. Young, *J. Chem. Soc.* (*A*), 1966, 104.

[59] J. A. Kerr, D. H. Slater, and J. C. Young, *J. Chem. Soc.* (*A*), 1967, 134.

[60] J. A. Kerr, A. Stephens, and J. C. Young, *Internat. J. Chem. Kinetics*, 1969, **1**, 339.

[61] T. N. Bell and U. F. Zucker, *J. Phys. Chem.*, 1970, **74**, 979.

Table 2 *Rate Data for the Transfer Reactions* $R\cdot + SH \rightarrow RH + S\cdot$

R	SH	*Bond Broken*	*log* A	E kcal mol^{-1}
CH_3	SiH_4	Si–H	11·82 ± 0·09	6·89 ± 0·16[a]
CH_3	SiH_4	Si–H	11·80 ± 0·32	6·99 ± 0·56[b]
CH_3	SiD_4	Si–D	11·98 ± 0·32	8·19 ± 0·65[b]
CH_3	Si_2H_6	Si–H	11·96 ± 0·18	5·63 ± 0·32[b]
CH_3	Si_2D_6	Si–D	12·19 ± 0·21	6·96 ± 0·35[b]
CH_3	$PhSiD_3$	Si–D	11·99 ± 0·18	8·03 ± 0·31[b]
CH_3	$PhSiD_3$	C–H	10·03 ± 0·77	5·87 ± 1·32[b]
CH_3	$HSiF_3$	Si–H	12·4	8·7[c]
CH_3	$HSiCl_3$	Si–H	13·4	8·5[d]
CH_3	$HSiMeCl_2$	Si–H	11·8	7·2[d]
CH_3	$MeSiCl_3$	C–H	12·9	11·5[d]
CH_3	Me_2SiCl_2	C–H	13·2	11·6[c]
CH_3	Me_3SiCl	C–H	13·4	11·5[c]
CH_3	Me_3SiH	Si–H	11·1	7·0[c]
CH_3	Me_3SiH	Si–H	11·34	7·83[a]
CH_3	Me_3SiH	Si–H C–H	11·42 ± 0·10	7·92 ± 0·18[a]
CH_3	Me_4Si	C–H	11·53 ± 0·20	10·30 ± 0·40[a]
CH_3	Me_4Si	C–H	12·60 ± 0·19	11·00 ± 0·34[e]
CH_3	Me_4Si	C–H	11·57 ± 0·18	10·23 ± 0·36[f]
CD_3	Me_4Si	C–H	11·86 ± 0·06	10·36 ± 0·12[f]
C_2H_5	Me_4Si	C–H	11·91 ± 0·22	11·40 ± 0·48[f]
CF_3	$HSiCl_3$	Si–H	12·13	6·85[g]
CF_3	$MeSiF_3$	C–H	11·98 ± 0·04	11·71 ± 0·09[h]
CF_3	Me_2SiF_2	C–H	12·27 ± 0·06	10·53 ± 0·12[h]
CF_3	Me_3SiF	C–H	12·43 ± 0·05	9·48 ± 0·09[h]
CF_3	Me_4Si	C–H	11·91 ± 0·09	7·29 ± 0·14[h]
CF_3	Me_4Si	C–H	11·90 ± 0·05	7·23 ± 0·09[f]

[a] E. R. Morris and J. C. J. Thynne, *J. Phys. Chem.*, 1969, **73**, 3294; [b] O. P. Strausz, E. Jakubowski, H. S. Sandhu, and H. E. Gunning, *J. Chem. Phys.*, 1969, **51**, 552; [c] ref. 59; [d] ref. 58; [e] A. U. Chaudry and B. G. Gowenlock, *J. Organometallic Chem.*, 1969, **16**, 221; [f] ref. 60; [g] T. N. Bell and B. B. Johnson, *Austral. J. Chem.*, 1967, **20**, 1545; [h] ref. 61.

reviewed by Jackson.[3] This discussion will be confined to the relatively few quantitative kinetic studies in the gas phase and in solution.

The photoreduction of alkyl halides to alkanes by silicon hydrides was first observed in the liquid phase by Haszeldine and Young,[62] who proposed a radical chain mechanism with the propagation steps shown in reactions (31) and (32).

$$R_3Si\cdot + R^1X \rightarrow R^1 + R_3SiX \qquad (31)$$

$$R^1 + R_3SiH \rightarrow R^1H + R_3Si\cdot \qquad (32)$$

Since silicon forms stronger bonds to halogens and weaker bonds to hydrogen

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[62] R. N. Haszeldine and J. C. Young, *J. Chem. Soc.*, 1960, 4503.

than does carbon, both these steps are exothermic. The gas-phase reaction between alkyl halides and trichlorosilane proceeds similarly,[63] and relative rates have been measured for various halides.[64,65] The reaction was initiated by irradiation with a medium-pressure mercury lamp, which probably dissociated the alkyl halide, although some photodissociation of the trichlorosilane may also have occurred. Reasonable reaction steps are shown [(33)—(37)] The chain

$$RX + h\nu \rightarrow R\cdot + X\cdot \tag{33}$$

$$R\cdot + HSiCl_3 \rightarrow RH + \cdot SiCl_3 \tag{34}$$

$$\cdot SiCl_3 + RX \rightarrow R\cdot + XSiCl_3 \tag{35}$$

$$X\cdot + HSiCl_3 \rightarrow HX + \cdot SiCl_3 \tag{36}$$

$$R\cdot + HX \rightarrow RH + X\cdot \tag{37}$$

sequence could be (33), (34), (35) or (33), (36), (35), (37). In either case, if the chain is reasonably long, the formation of the alkane RH will be rate-determined by reaction (35). By competitive experiments in which the relative rate of formation of the alkanes R^1H and R^2H from the halides R^1X and R^2X were measured, the relative rate data in Table 3 were obtained. These results were found to fit the Polanyi equation.

Table 3 *Relative Rates of the Reaction* $\cdot SiCl_3 + RX \rightarrow XSiCl_3 + R\cdot$

RX	$\frac{A(RX)}{A(MeCl)}$	E(MeCl)–E(RX) kcal mol^{-1}
MeCl	1·0	0[a]
Pr^{n}Cl	1·26	1·10[b]
EtCl	0·94	1·12[a]
Bu^{n}Cl	1·32	1·26[a]
Bu^{i}Cl	1·14	1·32[a]
Me_3CCH_2Cl	0·93	1·46[a]
Pr^{i}Cl	1·65	1·88[a]
Bu^{s}Cl	1·82	1·99[a]
CCl_4	11·5	2·00[b]
cyclo–C_5H_9Cl	0·52	2·55[b]
Bu^{t}Cl	1·60	3·25[a]
MeBr	0·27	5·395[a]
EtBr	0·34	6·38[a]
Pr^{i}Br	0·53	7·045[a]
Bu^{t}Br	0·64	7·93[a]

[a]Ref. 64; [b]Ref. 65

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[63] J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and J. C. Young, *Chem. Comm.*, 1966, 157.

[64] J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and J. C. Young, *J. Chem. Soc.* (*A*), 1968, 510.

[65] P. Cadman, G. M. Tilsley, and A. F. Trotman-Dickenson, *J. Chem. Soc.* (*A*), 1969, 1370.

Liquid-phase studies of this type of reaction have been continued by Cooper and by Nagai and his co-workers. Cooper reacted the series of silanes $Me_nCl_{(3-n)}SiH$ ($n = 0$, 1, 2, and 3) with n-chlorohexane and chlorocyclohexane, with initiation by mercury-photosensitisation.[66] As all of the experiments were at 298 K, Arrhenius parameters could not be obtained, but relative rate measurements for the competitive reaction of each silane with the two chlorohexanes revealed that the reactivity of the silyl radicals decreased in the order, $Me_3Si\cdot > Me_2ClSi\cdot > MeCl_2Si\cdot > Cl_3Si\cdot$. This order was explained in terms of increasing delocalisation of the unpaired electron. Nagai *et al* found that alkyl bromides were more rapidly reduced than alkyl chlorides, in agreement with the gas-phase results. The relative rate of reduction of alkyl iodides, however, was extremely low, and this was said to be due to the endothermicity of the step corresponding to reaction (31) in the chain sequences:[67]

$$R_3Si\cdot + R^1I \rightarrow R_3SiI + R^1 \qquad (38)$$

Nagai and his co-workers have also observed the halogen–halogen exchange reaction:[68]

$$R_3SiI + R^1X \rightarrow R_3SiX + R^1I \; (X = Cl, Br)$$

and have suggested that it too is a radical chain reaction having as one of its propagation steps the reverse of reaction (38), which would thus, according to their earlier explanation, be exothermic.

$$R_3SiI + h\nu \rightarrow R_3Si\cdot + I\cdot \qquad (39)$$

$$R_3Si\cdot + R^1X \rightarrow R_3SiX + R^1 \qquad (31)$$

$$R^1 + R_3SiI \rightarrow R_3Si\cdot + R^1I \qquad (-\,38)$$

Although these suggestions are neat and self-consistent, they require that the silicon–iodine bond should be weaker than the carbon–iodine bond for reaction (38) to be endothermic and reaction (– 38) to be exothermic, and indeed for reaction (– 38) to occur instead of hydrogen abstraction by the alkyl radical R^1. There appears to be little doubt, however, that the silicon–iodine bond is significantly stronger than the carbon–iodine bond, whatever the exact dissociation energy of the former may be, and an alternative explanation should therefore be sought for these results. So far as the halogen–halogen exchange reaction is concerned, there seems to be no strong evidence from the rate or product composition that it is a chain reaction, although it undoubtedly is a radical reaction. The non-chain sequence shown in Scheme 3, consistent with the known behaviour of iodides on photolysis,[69] may well account more satisfactorily for the observed results.

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[66] D. Cooper, *J. Organometallic Chem.*, 1967, **10**, 447.

[67] Y. Nagai, I. Shiojima, K. Nishiyama, and H. Matsumoto, *J. Syn. Org. Chem. Japan*, 1968, **26**, 999.

[68] Y. Nagai, H. Muramatsa, M-A. Ohtsuki, and H. Matsumoto, *J. Organometallic Chem.*, 1969, **17**, P19.

[69] Ref. 17, p. 398.

$$\begin{gathered}
R_3SiI + h\nu \rightarrow R_3Si\cdot + I\cdot \\
R_3Si\cdot + I\cdot \rightarrow R_3SiI \\
R_3Si\cdot + R^1X \rightarrow R_3SiX + R^1 \\
2I\cdot \rightarrow I_2 \\
R^1 + I_2 \rightarrow R^1I + I\cdot \\
R^1 + I\cdot \rightarrow R^1I
\end{gathered}$$

Scheme 3

Similarly, although the reduction of silicon hydrides by alkyl iodides is a chain reaction, the low rate is probably not due to the propagation step (38) being endothermic, but to the low effective rate of initiation of the chain sequence because of the reactions outlined in Scheme 4, which cause photolyses of alkyl iodides to have low quantum yields:[69]

$$\begin{gathered}
RI + h\nu \rightarrow R\cdot + I\cdot \\
R\cdot + I\cdot \rightarrow RI \\
2I\cdot \rightarrow I_2 \\
R\cdot + I_2 \rightarrow RI + I\cdot
\end{gathered}$$

Scheme 4

The gas-phase photobromination of trichlorosilane has been investigated[70] between 291 K and 313 K. Above 275 mm Hg a homogeneous chain mechanism, reactions (40)—(43), is believed to operate. In chain reactions of this type which

$$Br_2 + h\nu \rightarrow 2Br\cdot \tag{40}$$

$$Br\cdot + HSiCl_3 \rightarrow \cdot SiCl_3 + HBr \tag{41}$$

$$\cdot SiCl_3 + Br_2 \rightarrow BrSiCl_3 + Br\cdot \tag{42}$$

$$2Br\cdot + M \rightarrow Br_2 + M \tag{43}$$

are initiated by the dissociation and recombination of a halogen, rate parameters for the first propagation step may be deduced from the overall rate and the equilibrium data for the dissociation of the halogen. The activation energy E_{41} was calculated to be 5·9 kcal mol^{-1} in this way. At lower pressures a heterogeneous mechanism showing great sensitivity to surface conditions and to traces of oxygen predominated.

The photobromination of trimethylsilane to give trimethylsilylbromide showed many features in common with the trichlorosilane reaction, including sensitivity to surface conditions, impurities, and daylight.[71] It probably proceeded by a similar radical chain mechanism, but the reaction was too rapid for any kinetic results to be obtained in a conventional static system, even by competitive experiments. This enhanced reactivity of trimethylsilane compared to trichlorosilane may reflect the greater reactivity of trimethylsilyl radicals compared to trichlorosilyl radicals found by Cooper.[66]

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[70] B. L. Mahoney, *Diss. Abs.*, 1967, 4347-B.

[71] I. M. T. Davidson and P. P. Ellis, unpublished work.

Some photobromination studies of ethyltrichlorosilane and higher alkyltrichlorosilanes have been reported, but these proceed by the normal chain mechanism involving silicon-substituted alkyl radicals with the unpaired electron on carbon. The results furnished further evidence for the stabilisation of α-silyl alkyl radicals noted in Section 5.[72]

Hexamethyldisilane reacts less rapidly with halogens than trimethylsilane, and the thermal iodination of hexamethyldisilane has been studied[73] in the gas phase between 458 K and 523 K. A homogeneous reaction, first-order in hexamethyldisilane and one-half-order in iodine, gave trimethylsilyl iodide as the only product; a simple chain mechanism consistent with these findings is outlined, [reactions (44)—(46)].

$$I_2 + M \rightleftharpoons 2I\cdot + M \tag{44}$$

$$I\cdot + Me_3SiSiMe_3 \rightarrow Me_3SiI + Me_3Si\cdot \tag{45}$$

$$Me_3Si\cdot + I_2 \rightarrow Me_3SiI + I\cdot \tag{46}$$

$-\dfrac{d[Me_6Si_2]}{dt} = k_{45}K_{44}^{\frac{1}{2}}\,[Me_6Si_2]\,[I_2]^{\frac{1}{2}}$, where K_{44} is the equilibrium constant for the thermal dissociation of iodine. Hence, $\log k_{45} = 11{\cdot}23 \pm 0{\cdot}50 - 8{,}100 \pm 1{,}100/2{\cdot}303RT$. The differences between this mechanism and the well-known mechanism for the iodination of hydrocarbons[74] are due to the differences in bond dissociation energies to carbon and silicon. Reaction (46) is similar to the reaction of alkyl radicals with iodine, but is more exothermic because the silicon–iodine bond is stronger than carbon–iodine bonds in alkyl iodides. The reverse reaction (− 46) is therefore unimportant, whereas it is appreciable for alkyl iodides.[75] The radical displacement reaction (45) offers an energetically favourable alternative to hydrogen abstraction, the route followed in the iodination of hydrocarbons, because the silicon–silicon bond is somewhat weaker than the silicon–iodine bond.

9 Structure of Silicon Radicals

Spectroscopic studies of the structure of some silylenes, especially SiF_2, have been reviewed by Atwell and Weyenberg.[3] Subsequently the i.r. spectrum of $SiCl_2$ in a low temperature matrix has been reported,[76] the radical being generated by photolysis of H_2SiCl_2 in the far u.v. By the same technique, the i.r. spectra of $\cdot SiCl_3$ from $HSiCl_3$[77] and of $\cdot SiF_3$ from $HSiF_3$[78] have been obtained. However, most of the presently available information on the structure of silyl radicals is derived from e.s.r. studies.

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[72] K. W. Michael, H. M. Bank, and J. L. Speier, *J. Org. Chem.*, 1969, **34**, 2832.

[73] S. J. Band and I. M. T. Davidson, *Trans. Faraday Soc.*, 1970, **66**, 406.

[74] J. H. Knox and R. G. Musgrave, *Trans. Faraday Soc.*, 1967, **63**, 2201, and references therein.

[75] R. K. Boyd, G. W. Downs, J. S. Gow, and C. Horrex, *J. Phys. Chem.*, 1963, **67**, 719.

[76] M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, 1968, **49**, 1938.

[77] M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, 1968, **49**, 3130.

[78] D. E. Milligan, M. E. Jacox, and W. A. Guillory, *J. Chem. Phys.*, 1968, **49**, 5330

In an early investigation of the radical produced by irradiation of SiH_4 in an argon matrix at 4·2 K with u.v. light, an e.s.r. spectrum consisting of a quartet of lines was attributed to the $\cdot SiH_3$ radical.[79] Morehouse, Christiansen, and Gordy conducted a more detailed investigation,[80] in which the $\cdot SiH_3$ radical was produced in a krypton matrix at 4·2 K by γ-irradiation of SiH_4. Features believed to arise from hyperfine coupling with ^{29}Si were observed, from which the orbital of the unpaired electron was deduced to have 22% *s*-character, and the $\cdot SiH_3$ radical was said to be extremely non-planar, with a bond angle of 110·6°. However, similar experiments in a xenon matrix, which should have given essentially the same results as those in krypton, gave a lower value for the ^{29}Si hyperfine coupling, indicating a less bent configuration for the $\cdot SiH_3$ radical.[81] Recently, Sharp and Symons have γ-irradiated solid $MeSiH_3$ and Me_3SiH at 77 K, obtaining the radicals $Me\dot{S}iH_2$ and $Me_3Si\cdot$ respectively.[82] Their results agreed well with those for $\cdot SiH_3$ in xenon, and they concluded that the spin density at silicon and the bond angles in the silyl radicals were unchanged along the series $\cdot SiH_3$ to $\cdot SiMe_3$. The bond angle in all of these radicals was calculated to be 113—114°. The same authors conducted similar experiments with Me_3SiCl, forming $\cdot CH_2SiMe_2Cl$ and probably also $Me_2\dot{S}iCl$.

E.s.r. spectra of several silicon-containing radicals in the liquid phase have been observed by Krusic and Kochi[49,83] and by Hudson and his collaborators.[84,85] A static system was used by both groups, in which a solution of di-t-butyl peroxide in the appropriate silane was irradiated by u.v. light in the cavity of the e.s.r. spectrometer. The t-butoxyl radical thus formed abstracted hydrogen to give the silicon-containing radical: $Me_3CO\cdot + Me_3SiH \rightarrow Me_3Si\cdot + Me_3COH$. The silyl radicals $Me_3Si\cdot$, $Me_2\dot{S}iH$, $Me\dot{S}iH_2$, and $H_3Si\cdot$ were formed from the corresponding silanes, and their e.s.r. spectra showed the same features as the spectra in the solid state.[83,85] Although some flattening of the radicals with increasing methyl substitution was suggested,[85] the results are consistent with the more recent conclusion[82] that the shape of the radicals is unaffected by replacing hydrogen with methyl, and this interpretation thus appears to offer the best rationalisation of all of the available data.

The non-planarity of silyl radicals has been predicted theoretically,[86] and good chemical evidence is available from studies of optically active silyl radicals, which are found to undergo reactions with substantial retention of configuration. Thus, α-naphthylphenylmethylsilyl radicals, generated in solution by peroxide[87] or by photolysis,[88] abstracted chlorine from carbon tetrachloride to give a product

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[79] E. L. Cochran, 4th Internat. Symposium, Free Radical Stabn., Nat. Bureau Stds., 1959.

[80] R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, 1966, **45**, 1751.

[81] G. S. Jackel and W. Gordy, *Phys. Rev.*, 1968, **176**, 443.

[82] J. H. Sharp and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 3068.

[83] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, **91**, 3938.

[84] A. Hudson and H. A. Hussain, *Mol. Phys.*, 1969, **16**, 199; A. Hudson and H. A. Hussain, *J. Chem. Soc.* (*B*), 1969, 793.

[85] S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc.* (*A*), 1970, 348.

[86] L. Pauling, *J. Chem. Phys.*, 1969, **51**, 2767.

[87] H. Sakurai, M. Murakami, and M. Kumada, *J. Amer. Chem. Soc.*, 1969, **91**, 519.

[88] A. G. Brook and J. M. Duff, *J. Amer. Chem. Soc.*, 1969, **91**, 2118.

which was up to 85% optically pure in the experiments initiated by peroxide and up to 64% optically pure in the photolytic experiments.

The e.s.r. spectra of some more complex silyl radicals, including $Et_3Si\cdot$, $Me_3Si\dot{Si}Me_2$, $Me_3SiCH_2\dot{Si}Me_2$, and $(Me_3Si)_3Si\cdot$ have been obtained by the same technique of abstraction by t-butoxyl radicals,[85] as have the e.s.r. spectra of some silicon-containing alkyl radicals,[49] including $Me_3Si\dot{C}H_2$, $Et_3Si\dot{C}HCH_3$, $Et_3SiCH_2\dot{C}H_2$, $Me_3SiSiMe_2\dot{C}H_2$, $Me_3SiOSiMe_2\dot{C}H_2$, and $(MeO)_3SiO\dot{C}H_2$. The radical $Me_3Si\dot{C}H_2$ was readily formed from Me_4Si, in contrast to the behaviour of neopentane which did not give a detectable concentration of $Me_3C\dot{C}H_2$ by this method. The difference was attributed to stabilisation of the α-silyl radical by delocalisation of the unpaired electron.[49] The previously noted (Section 5) inability of this type of radical to undergo rearrangement reactions provides supporting evidence for its relatively high stability.

The formation of the secondary radical $Et_3Si\dot{C}HCH_3$ from Et_4Si was to be expected, but the concomitant formation of the primary radical $Et_3SiCH_2\dot{C}H_2$ is unprecedented, and has been explained in terms of hyperconjugative stabilisation:[49]

$$Et_3SiCH_2CH_2\cdot \rightleftharpoons Et_3\dot{Si} \quad CH_2{:}CH_2$$

Similar factors may account for the formation[54] of $(EtO)_2Si(H)O\dot{C}HCH_3$ from $(EtO)_3SiH$ instead of $(EtO)_3Si\cdot$; the analogous carbon compound, $(EtO)_3CH$ gives $(EtO)_3\dot{C}$.

Clearly, much insight into the chemistry of silicon-containing radicals, as well as into their structure, may be expected from further e.s.r. studies.