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Review

Some examples of the contribution of gas-kinetic studies to the understanding of organosilicon reaction mechanisms *

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Abstract

Several cases in which gas kinetic studies have elucidated mechanistic problems in organosilicon chemistry are described and discussed, in the hope of encouraging wider use of simple gas kinetic techniques.

Introduction

It is a particular privilege and pleasure to have been asked to contribute to an issue of this Journal honouring Colin Eaborn, because I owe him an incalculable debt. When I embarked on my academic career here, thirty years ago, he not only encouraged me to apply my training in gas kinetics to problems in organosilicon chemistry, but he very generously shared his own hard-won resources with me to enable my research to get under way in what was then a small and under-funded Department. Our early collaboration established the theme of all of my subsequent research, to use gas kinetic studies to elucidate reaction mechanisms and to obtain quantitative information about the reactivity of organosilicon molecules and intermediates. Carrying out experiments in the gas phase offers freedom from solvent effects, with the prospect of studying the reactions, especially unimolecular reactions, of isolated molecules and intermediates. Such experiments have grown in importance over the years with the growth of interest in the reactions of organosilicon intermediates in the gas phase; examples from our own work are discussed below. If these constitute a useful contribution to progress in understanding reactivity in organosilicon chemistry, much of the credit for that belongs to Colin Eaborn.

Discussion

Our first co-operative study was the thermal decomposition of 2-chloroethyltrichlorosilane [1,2]. It had long been known that 2-chloroethylsilanes were exception-

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* Dedicated to Professor Colin Eaborn in recognition of his outstanding achievements in organosilicon chemistry, and in warm appreciation of his encouragement and friendship over many years.

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Table 1

Arrhenius parameters for elimination of ethene from 2-chloroethylsilanes

Compound	log *A* (s^{-1})	*E* (kJ mol^{-1})	*k* (s^{-1}) (400 °C)
$ClCH_2CH_2SiCl_3$	11.08 ± 0.23	188 ± 3	3.08×10^{-4}
$ClCH_2CH_2SiCl_2Et$	12.12 ± 0.56	193 ± 8	1.38×10^{-3}
$ClCH_2CH_2SiClEt_2$	11.88 ± 0.26	172 ± 4	3.39×10^{-3}
$ClCH_2CH_2SiEt_3$	11.07 ± 0.35	164 ± 4	2.19×10^{-2}
$ClCH_2CH_2SiMe_3$	10.98 ± 0.20	157 ± 3	6.22 ± 10^{-2}

ally reactive and thermally labile, eliminating ethene on heating [3], but the mechanism of that elimination was unclear. By measuring the kinetics of decomposition and of formation of products in the pyrolysis of 2-chloroethyltrichlorosilane in a static system between 356 and 417 °C at initial pressures between 12 and 138 mmHg, with and without added nitrogen oxide, NO, as a test for radical chain reactions, we showed [2] that the main decomposition pathway was the formation of ethene and silicon(IV) chloride in a first-order reaction with kinetics unaffected by added NO, thus constituting good evidence for the unimolecular reaction (1).

$$ClCH_2CH_2SiCl_3 \rightarrow C_2H_4 + SiCl_4 \qquad (1)$$

Minor pathways were dehydrochlorination, reaction (2), and dehydrosilylation, reaction (3).

$$ClCH_2CH_2SiCl_3 \rightarrow CH_2{=}CHSiCl_3 + HCl \qquad (2)$$

$$ClCH_2CH_2SiCl_3 \rightarrow CH_2{=}CHCl + HSiCl_3 \qquad (3)$$

These studies were extended to other 2-chloroethylsilanes [4], where dehydrosilylation was not observed. The kinetic results for ethene elimination are summarized in Table 1. We concluded that unimolecular elimination of ethene proceeded through a four-centre transition state with appreciable polar character, as envisaged by Maccoll for the gas-phase dehydrohalogenation of alkyl halides [5], and in keeping with Benson's semi-ion pair model [6]. The rate constants in Table 1 cover a range of ca. 200, implying some development of positive charge on silicon in the transition state, but with the latter less polar then in alkyl halide pyrolyses, which show considerably larger substituent effects [5].

Subsequent work on the pyrolysis of ethyltrichlorosilane and ethyltrimethylsilane [7] gave evidence to suggest that the dehydrosilylation reaction (3) occurred by a radical chain sequence, reactions (4) and (5).

$$ClCH_2CH_2SiCl_3 + {}^{\cdot}SiCl_3 \rightarrow HSiCl_3 + {}^{\cdot}ClC_2H_3SiCl_3 \qquad (4)$$

$${}^{\cdot}ClC_2H_3SiCl_3 \rightarrow CH_2{=}CHCl + {}^{\cdot}SiCl_3 \qquad (5)$$

It also appeared [7] that trichlorosilyl radicals were significantly less efficient in chlorine-abstraction than are alkylsilyl radicals [8]; there have been few kinetic studies of these reactions in the gas phase [9], and further work on the effect of substituents could be quite illuminating.

2-Silyl substituent effects are of continuing interest, as exemplified by a kinetic study of the gas-phase elimination of ethanoic acid from 2-substituted ethyl ethanoates [10]. Accelerating effects relative to H = 1.0 at 327 °C were $SiMe_3$ = 125,

$SiMe_2Ph = 144$, and $SiEt_3 = 179$. Another recent example is the investigation of the stability of 2-silicon-substituted alkyl radicals by two different gas-phase methods. Using the iodination method of estimating carbon–hydrogen bond dissociation energies [11], Walsh deduced that a 2-trimethylsilyl substituent stabilised an alkyl radical by 13 ± 4 kJ mol^{-1} [12]. We obtained an almost identical result by comparing the activation energies for the low-pressure pyrolysis of $Me_3SiCH_2CH_2CMe_3$ and $CH_3CH_2CMe_3$ under conditions rate-determined by the rupture of the weak Me_3C–carbon bond [13].

An excellent example of the intriguing complexity of radical reactions in organosilicon chemistry, and of the role of gas kinetics in quantitatively elucidating complex radical mechanisms, is provided by the pyrolysis of hexamethyldisilane. The main initial step in the pyrolysis is undoubtedly rupture of the silicon–silicon bond, reaction (6), but the subsequent course of the pyrolysis depends strongly on

$$Me_3SiSiMe_3 \rightarrow 2\ Me_3Si^{\cdot} \qquad (6)$$

the experimental conditions. At relatively high pressure, in a flow system [14] or in sealed tubes [15], the predominant process was isomerisation, reaction (7), with some formation of trimethylsilane. Pyrolysis under these conditions is clean enough to be a satisfactory way of synthesising the isomer I.

$$Me_3SiSiMe_3 \rightarrow \underset{(I)}{Me_3SiCH_2SiMe_2H} \qquad (7)$$

At low pressure, however, isomerisation was a minor process. The main product was trimethylsilane, while other minor products besides I were 1,1,3,3-tetramethyl-1,3-disilacyclobutane and tetramethylsilane; formation of all of these products was reduced to differing extents by added *m*-xylene which, having readily abstracted benzylic hydrogen, acts like toluene as a radical trap [16].

A unified mechanism to account quantitatively for all of the foregoing features may be developed from the results of three separate gas kinetic studies in different laboratories under substantially different conditions. The kinetics of the isomerisation were studied in a static system between 444 and 507 ° C, with initial pressures of hexamethyldisilane between 10 and 125 mmHg [17]. Under these conditions, the main product was the isomer I; a typical product analysis was: I 92.2%; trimethylsilane 5.4%; tetramethylsilane 1.6%; methane 0.5%. Formation of I was found to be three-halves order in hexamethyldisilane, with rate constants given by:

$$k\ (cm^{3/2}\ mol^{-1/2}\ s^{-1}) = 10^{16.65 \pm 0.70} \exp[-(251 \pm 8)/RT]$$

The rate of formation of I was unaffected by changes in surface-to-volume ratio or by added argon or benzene, but was reduced by added toluene. These results are entirely consistent with the radical chain mechanism for isomerisation of hexamethyldisilane previously proposed [14,15], shown in Scheme 1.The key step in the isomerisation is the unimolecular radical rearrangement reaction (9), envisaged as proceeding via a three-centre transition state; the silicon–carbon bond being stronger than silicon–silicon, the reaction is exothermic. Reaction (11) is the main termination step, leading to three-halves order kinetics because the rearranged radical is the most abundant.

Steady-state treatment of the above reaction sequence gives: $d[I]/dt = (k_6 k_{10}^2/k_{11})^{1/2}[Me_6Si_2]^{3/2}$, whence the observed activation energy, $E = (E_6 + 2E_{10} - E_{11})/2$.

Scheme 1. Radical reactions for the isomerisation of Si_2Me_6.

$$\mathrm{Me_3SiSiMe_3 \rightarrow 2\ Me_3Si^{\cdot}} \qquad (6)$$

$$\mathrm{Me_3Si^{\cdot} + Me_3SiSiMe_3 \rightarrow Me_3SiH + Me_5Si_2\dot{C}H_2} \qquad (8)$$

$$\mathrm{Me_5Si_2\dot{C}H_2 \rightarrow Me_3SiCH_2\dot{Si}Me_2} \qquad (9)$$

$$\mathrm{Me_3SiCH_2\dot{Si}Me_2 + Me_3SiSiMe_3 \rightarrow Me_3SiCH_2SiMe_2H + Me_5Si_2\dot{C}H_2} \qquad (10)$$

$$\mathrm{2\ Me_3SiCH_2\dot{Si}Me_2 \rightarrow (Me_3SiCH_2SiMe_2)_2} \qquad (11)$$

The pyrolysis of low pressures of hexamethyldisilane was studied in a batch flow system between 497 and 600 °C (a higher temperature range than the previous study [17] because reaction times were much shorter) in a carrier gas of dried de-oxygenated dinitrogen above atmospheric pressure, with partial pressures of hexamethyldisilane corresponding to the low concentration range of 1.4×10^{-9} to 5.5×10^{-7} mol cm^{-3}; excess *m*-xylene was added in some experiments [16,18]. As noted above, pyrolysis in the absence of *m*-xylene gave trimethylsilane as the main product, with smaller quantities of I, tetramethylsilane, and 1,1,3,3-tetramethyl-1,3-disilacyclobutane; a little methane was also formed at high temperature. The kinetic order and Arrhenius parameters for formation of all of the silicon-containing products were measured; tetramethylsilane was formed in a clean first order reaction with $\log A = 13.7 \pm 0.7$ and $E = 282 \pm 12$ kJ mol^{-1}, but formation of the other products was kinetically complex, with orders between 1 and 2. Kinetic parameters for the formation of trimethylsilane and the disilacyclobutane were the same (implying a common route to these products), but different from those for I. The effect of adding *m*-xylene was to suppress completely the formation of the disilacyclobutane and reduce the rates of formation of trimethylsilane and I, with no effect on the kinetics of formation of tetramethylsilane. The kinetic behaviour was simplified, with an order of 1 for the formation of trimethylsilane and 1.5 for I. These results, in the absence of *m*-xylene, may be explained by the same sequence as before, reactions (6), (8)–(11), plus the additional reactions shown in Scheme 2. At these low pressures, reaction (12) competes with reaction (10); reactions (8), (9) and (12) make up the main chain propagation sequence, forming trimethylsilane and dimethylsilaethene, $Me_2Si{=}CH_2$, which dimerises by reaction (13) to form the disilacyclobutane, the product concomitant kinetically with trimethylsilane. Because of the increased concentration of $Me_3Si\cdot$ radicals, the termination reactions (14) and (15) compete with reaction (11), causing the observed fractional orders.

In the presence of excess *m*-xylene (denoted by RH), the radical reactions are those shown in Scheme 3. The suppression of the formation of the disilacyclobutane by excess *m*-xylene shows that reaction (18) completely outweighs reaction (12). Formation of the isomerisation product I then proceeds by the chain sequence, reactions (17), (9), (18), with clean three-halves order kinetics because there is now only one significant termination step, reaction (19). However, with the suppression

Scheme 2. Additional reactions in the low-pressure pyrolysis of Si_2Me_6.

$$\mathrm{Me_3SiCH_2\dot{Si}Me_2 \rightarrow Me_3Si^{\cdot} + Me_2Si{=}CH_2} \qquad (12)$$

$$\mathrm{2\ Me_2Si{=}CH_2 \rightarrow Me_2\underset{\smile}{\overset{\frown}{Si\ Si}}Me_2} \qquad (13)$$

$$\mathrm{2\ Me_3Si^{\cdot} \rightarrow Me_3SiSiMe_3} \qquad (14)$$

$$\mathrm{Me_3Si^{\cdot} + Me_3SiCH_2\dot{Si}Me_2 \rightarrow Me_3SiCH_2Si_2Me_5} \qquad (15)$$

Scheme 3. Pyrolysis of Si_2Me_6 in excess *m*-xylene (RH).

$$Me_3SiSiMe_3 \rightarrow 2\ Me_3Si^{\bullet} \tag{6}$$

$$Me_3Si^{\bullet} + RH \rightarrow Me_3SiH + R^{\bullet} \tag{16}$$

$$R^{\bullet} + Me_3SiSiMe_3 \rightleftharpoons RH + Me_5Si_2\dot{C}H_2 \tag{17}$$

$$Me_5Si_2\dot{C}H_2 \rightarrow Me_3SiCH_2\dot{S}iMe_2 \tag{9}$$

$$Me_3SiCH_2\dot{S}iMe_2 + RH \rightarrow Me_3SiCH_2SiMe_2H + R^{\bullet} \tag{18}$$

$$2\ R^{\bullet} \rightarrow R_2 \tag{19}$$

of reaction (12), formation of trimethylsilane is a non-chain process rate-determined by reaction (6). Measurement of first-order rate constants for the formation of trimethylsilane in the presence of excess *m*-xylene thus gave Arrhenius parameters for reaction (6): $\log A_6 = 17.2 \pm 0.3$ and $E_6 = 337 \pm 4$ kJ mol^{-1}. The activation energy equals the silicon–silicon bond dissociation energy in hexamethyldisilane, and the above value of 337 kJ mol^{-1} is generally accepted as the best measure of it [11]. Earlier kinetic attempts to measure this key thermochemical quantity were vitiated by the previously unsuspected complexity of the pyrolysis mechanism [19].

Tetramethylsilane, the only product formed in a clean first-order reaction unaffected by added *m*-xylene, was probably produced in a minor primary reaction, namely elimination of dimethylsilylene by reaction (20).

$$Me_3SiSiMe_3 \rightarrow Me_2Si{:} + Me_4Si \tag{20}$$

Although this is a minor reaction in the pyrolysis of hexamethyldisilane, the corresponding reaction (21) is well known to be much faster than silicon–silicon bond rupture in the pyrolysis of pentamethyldisilane.

$$Me_3SiSiMe_2H \rightarrow Me_2Si{:} + Me_3SiH \tag{21}$$

This is a neat example of the interplay between thermodynamic and kinetic factors [20]. The silylene elimination reactions (20) and (21), with tight three-centre transition states, have much smaller A factors than dissociation reactions such as (6); consequently, silylene elimination would only be faster than dissociation into silyl radicals if the former process had much the lower activation energy. For reactions (20) and (21), each of these activation energies is related to the endothermicity and the activation energy for the reverse process by $E_{20} = \Delta H_{20} + E_{-20}$ and $E_{21} = \Delta H_{21} + E_{-21}$. Silylenes are well known to insert rapidly into silicon–hydrogen bonds (reaction (-21)), but not into silicon–carbon (reaction (-20)); hence, although $\Delta H_{20} \simeq \Delta H_{21}$, $E_{-20} \gg E_{-21}$ and thus $E_{20} > E_{21}$. The size of these effects is enough to tilt the balance between the two modes of primary reaction in these two cases. Since E_{-21} is close to zero, E_{-20} may be estimated to be ≤ 80 kJ mol^{-2}, from the activation energies of reactions (20) and (21) [21].

With regard to the main radical reactions in the pyrolysis of hexamethyldisilane, it appeared from reasonable estimates of Arrhenius parameters for these reactions that the foregoing ideas could account for the dependence of product composition on conditions [17,18], but it would obviously be desirable to measure these Arrhenius parameters directly. Considerable progress towards that goal has been achieved by using mercury-photosensitisation to generate the $Me_3SiSiMe_2\dot{C}H_2$ radical from hexamethyldisilane at different temperatures and pressures [22]. Mercury-photo-

Table 2

Arrhenius parameters for radical reactions in the pyrolysis of Si_2Me_6

Reaction	log A [a]	E (kJ mol^{-1})
$Me_3SiSiMe_2\dot{C}H_2 \xrightarrow{9} Me_3SiCH_2\dot{S}iMe_2$	12.3 ± 0.4	90 ± 5
$Me_3SiCH_2\dot{S}iMe_2 + Me_6Si_2 \xrightarrow{10} Me_3SiCH_2SiMe_2H + Me_5Si_2\dot{C}H_2$	10.4 ± 0.4	75 ± 5
$Me_3SiCH_2\dot{S}iMe_2 \xrightarrow{12} Me_3Si^{\cdot} + Me_2Si{=}CH_2$	15.0 ± 0.4	191 ± 5

[a] First-order A factors in s^{-1} and second order in dm^3 mol^{-1} s^{-1}.

sensitisation was used to great effect to study radical reactions in methylsilanes by Gunning, Strausz and co-workers, over twenty years ago [23]; it is surprising that their excellent work has not been more widely emulated. The primary process with hexamethyldisilane is reaction (22):

$$Me_3SiSiMe_3 + Hg^{\star} \rightarrow Me_3SiSiMe_2\dot{C}H_2 + H^{\cdot} + Hg \qquad (22)$$

At low temperatures, between 70 and 196 °C, the only subsequent reactions were a displacement reaction between hexamethyldisilane and hydrogen atoms, the radical rearrangement reaction (9) and various radical combination reactions. Arrhenius parameters were deduced for reaction (9) from the yields of the products of these combination reactions. Higher temperatures, 220 to 475 °C, with 5 mmHg of hexamethyldisilane, provided good conditions for the occurrence of the abstraction reaction (10), enabling Arrhenius parameters for that reaction to be measured by conventional means from the relative amounts of I and the product of reaction (11). Finally, reducing the pressure of hexamethyldisilane to 0.2 mmHg and increasing the temperature range (400 to 507 °C) made the radical dissociation reaction (12) predominant. Arrhenius parameters for it were then deduced from the product yields. Arrhenius parameters obtained in this work [22] are summarized in Table 2.

Additivity calculations showed that the high A factor for the abstraction reaction (10) arises from a high entropy change [22]. The activation energies in Table 2 may be used to show the mutual consistency of the kinetic studies at high [17] and low [18] pressure. Taking $E_6 = 337 \pm 4$ from the low pressure study, $E_{10} = 75 \pm 5$ from Table 2, and $E_{11} = 0$ for a radical combination reaction, we calculate the activation energy for isomerisation from $E = (E_6 + 2E_{10} - E_{11})/2$. Thus $E = \{(337 \pm 4) + 2(75 \pm 5) - 0\}/2 = 244 \pm 9$ kJ mol^{-1}, in good agreement with the experimental value [17] of 251 ± 8 kJ mol^{-1}.

The Arrhenius parameters in Table 2 also allow quantitative estimates to be made of the course of the pyrolysis under different conditions. For instance, the extent to which the isomerisation product I is formed depends directly on the competition between reactions (10) and (12); the condition for, say, 90% of the $Me_3SiCH_2\dot{S}iMe_2$ radicals to be converted to I is therefore $k_{10}[Me_6Si_2]/k_{12} = 0.9$. At 400 °C, that condition would be fulfilled with $[Me_6Si_2] = 3.6 \times 10^{-5}$ mol dm^{-3} (1.5 mmHg), while at 500 °C, $[Me_6Si_2] = 5.2 \times 10^{-4}$ mol dm^{-3} (25 mmHg). A higher concentration is required at higher temperature because $E_{12} > E_{10}$.

This highly satisfactory quantitative model for the pyrolysis of hexamethyldisilane should now be worth extending to permethylated polysilanes in view of the substantial current interest in these compounds as precursors to silicon–carbon fibres and silicon carbide ceramics. Formation of silicon–carbon bonds from silicon–silicon bonds undoubtedly occurs by radical sequences, such as those in Scheme 1 (an analogous sequence of reactions with similar kinetic parameters has been shown to be involved in the thermal ring-expansion of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane to 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane [24]). Radicals are the main intermediates because silaalkenes, from reaction (12), are only important at low pressure, while silylenes, from reaction (20), do not participate in subsequent reactions to any extent; although Me_2Si: would insert rapidly into the silicon–hydrogen bond of I, that reaction would be very rapidly reversible at the temperatures involved [21].

In the case of the simplest permethylated polysilane, octamethyltrisilane, primary silylene formation by reaction (23) would be expected to be faster than reaction (20), because silylenes are known to insert more readily into silicon–silicon bonds {reaction (−23)} than into silicon–carbon {reaction (−20)} [25].

$$Me_3SiSiMe_2SiMe_3 \rightarrow Me_3SiSiMe_3 + Me_2Si: \qquad (23)$$

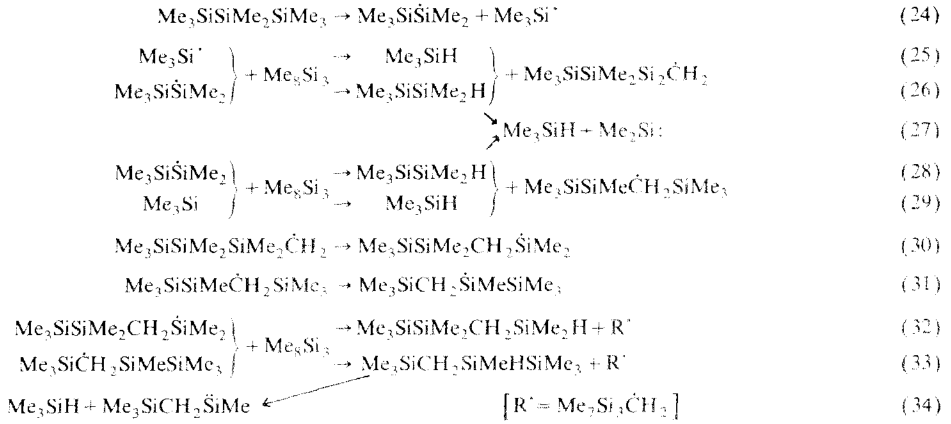
Furthermore, silylene-forming reactions would affect the outcome of the radical sequences analogous to Scheme 1, as shown in Scheme 4. Scheme 4 is strictly analogous to Scheme 1, but more complex because two different radicals are formed in the initiation reaction (24), and two isomeric carbon-centred radicals may be formed in the first abstraction reactions (25/26) and (28/29), leading to two parallel chain cycles involving reactions (30), (32) and (31), (33). One factor affecting the relative amounts of products from these cycles would be the rapid decomposition of some products by silylene elimination, reactions (27) and (34). These silylenes would probably ultimately form polymeric products by heterogeneous reactions. Octamethyltrisilane would therefore be expected to undergo more degradation to lower methylsilanes and polymeric products than does hexamethyldisilane, with reaction (32) as the main route to an isomerisation product, but it would be very timely to test these suggestions in kinetic experiments analogous to those on hexamethyldisilane [17,18], especially as there are many other possible interesting reactions besides those in Scheme 4. For instance, radical rearrangement might occur by four- or five-centre reactions as well as by the three-centre reactions (30) and (31).

Part of the intriguing complexity of the hexamethyldisilane pyrolysis arose from the simultaneous presence of different intermediates, radicals, silylenes, and silaalkenes. This feature is common to many other pyrolyses in organosilicon chemistry, including the pyrolysis of allyltrimethylsilane, which is another instructive example of the contribution that gas kinetic experiments can make to the elucidation of mechanism. As in the case of hexamethyldisilane, different products of pyrolysis of allyltrimethylsilane have been reported by different workers. In pyrolyses above 600 °C, Bailey and Kaufmann [26] detected 1,1,3,3-tetramethyl-1,3-disilacyclobutane, which they took to be evidence for the formation of dimethylsilaethene by a six-centre retroene elimination of propene, reaction (35). However, Sakurai, Hosomi and Kumada [27] found the major products of flow pyrolysis at 500 °C to be

$$Me_3SiCH_2CH{=}CH_2 \rightarrow Me_2Si{=}CH_2 + CH_3CH{=}CH_2 \qquad (35)$$

trimethylsilane, tetramethylsilane and vinyltrimethylsilane. Formation of vinyltrimethylsilane is intriguing, and a direct unimolecular elimination of methylene was

Scheme 4. Probable reactions in the pyrolysis of $\mathrm{Si_3Me_8}$.



$$\mathrm{Me_3SiSiMe_2SiMe_3 \rightarrow Me_3Si\dot{S}iMe_2 + Me_3Si^{\cdot}} \tag{24}$$

$$\left.\begin{array}{c}\mathrm{Me_3Si^{\cdot}}\\ \mathrm{Me_3Si\dot{S}iMe_2}\end{array}\right\} + \mathrm{Me_8Si_3}\begin{array}{l}\rightarrow \mathrm{Me_3SiH}\\ \rightarrow \mathrm{Me_3SiSiMe_2H}\end{array}\left.\vphantom{\begin{array}{c}x\\x\end{array}}\right\} + \mathrm{Me_3SiSiMe_2Si_2\dot{C}H_2} \qquad (25),\ (26)$$

$$\searrow\!\nearrow\ \mathrm{Me_3SiH + Me_2Si{:}} \tag{27}$$

$$\left.\begin{array}{c}\mathrm{Me_3Si\dot{S}iMe_2}\\ \mathrm{Me_3Si}\end{array}\right\} + \mathrm{Me_8Si_3}\begin{array}{l}\rightarrow \mathrm{Me_3SiSiMe_2H}\\ \rightarrow \mathrm{Me_3SiH}\end{array}\left.\vphantom{\begin{array}{c}x\\x\end{array}}\right\} + \mathrm{Me_3SiSiMe\dot{C}H_2SiMe_3} \qquad (28),\ (29)$$

$$\mathrm{Me_3SiSiMe_2SiMe_2\dot{C}H_2 \rightarrow Me_3SiSiMe_2CH_2\dot{S}iMe_2} \tag{30}$$

$$\mathrm{Me_3SiSiMe\dot{C}H_2SiMe_3 \rightarrow Me_3SiCH_2\dot{S}iMeSiMe_3} \tag{31}$$

$$\left.\begin{array}{c}\mathrm{Me_3SiSiMe_2CH_2\dot{S}iMe_2}\\ \mathrm{Me_3Si\dot{C}H_2SiMeSiMe_3}\end{array}\right\} + \mathrm{Me_8Si_3}\begin{array}{l}\rightarrow \mathrm{Me_3SiSiMe_2CH_2SiMe_2H + R^{\cdot}}\\ \rightarrow \mathrm{Me_3SiCH_2SiMeHSiMe_3 + R^{\cdot}}\end{array} \qquad (32),\ (33)$$

$$\mathrm{Me_3SiH + Me_3SiCH_2\ddot{S}iMe} \leftarrow \qquad [\mathrm{R^{\cdot} = Me_7Si_3\dot{C}H_2}] \tag{34}$$

suggested. Jones and co-workers [28] obtained similar results, but suggested on the basis of labelling experiments that vinyltrimethylsilane was formed by a radical rearrangement initiated by silicon–methyl bond rupture. In view of the difficulties with both of these explanations on energetic grounds, and of the conflicting evidence on the product composition, we undertook a gas kinetic investigation of this pyrolysis. In a preliminary study by low pressure pyrolysis, between 580 and 730 °C, with initial pressures of allyltrimethylsilane of 0.2 mmHg, the main products were propene and trimethylsilane, with small quantities of the disilacyclobutane but very little vinyltrimethylsilane. However, vinyltrimethylsilane was observed in sealed tube experiments at 550 °C, increasing as the pressure of allyltrimethylsilane was increased, until by 30 mmHg it was a major product [29]. These experiments indicated that the retroene reaction (35) and silicon–allyl bond rupture, reaction (36), were occurring simultaneously and that formation of vinyltrimethylsilane,

$$\mathrm{Me_3SiCH_2CH = CH_2 \rightarrow Me_3Si. + (CH_2CHCH_2).} \tag{36}$$

being strongly pressure-dependent, was a bimolecular process. The radicals produced in reaction (36) form trimethylsilane and propene by abstraction, making it difficult to obtain separate kinetic data for reactions (35) and (36), because propene is a common product and silaalkenes react with radicals. This problem was solved in a more detailed study [30] by carrying out pyrolyses in the presence of chloromethane, which efficiently traps trimethylsilyl radicals to form trimethylchlorosilane [9], but does not react with dimethylsilaethene. Under low pressure conditions, to favour the unimolecular primary reactions over bimolecular reactions, $(k_{35} + k_{36})$ was measured between 590 and 670 °C from the rate of formation of propene, k_{36} from the rate of formation of trimethylchlorosilane, and k_{35} by difference. The resulting Arrhenius parameters are summarized in Table 3. The Arrhenius parameters for reaction (35) are similar to those for an analogous retroene elimination of propene in hydrocarbon chemistry [31], while the Arrhenius parameters for reaction (36) conform to expectations for the rupture of a silicon–allyl bond. Isolating the primary processes at low pressure revealed that reaction (35) is indeed the main initial reaction, as originally suggested [26], but obscured in later work [27,28] by the complexity of the secondary reactions.

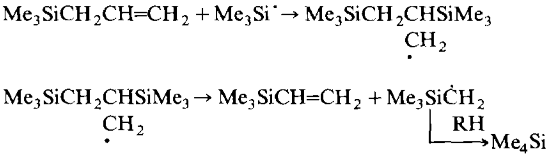
Table 3

Primary reactions in the pyrolysis of allyltrimethylsilane

Reaction	log A	E (kJ mol^{-1})	k (s^{-1}) (630 °C)
$Me_3SiCH_2CH{=}CH_2 \xrightarrow{35} Me_2Si{=}CH_2 + CH_3CH{=}CH_2$	11.6 ± 0.5	230 ± 8	2.0×10^{-2}
$Me_3SiCH_2CH{=}CH_2 \xrightarrow{36} Me_3Si^{\bullet} + (CH_2CHCH_2)^{\bullet}$	15.6 ± 0.5	305 ± 8	8.5×10^{-3}

As well as resolving confusion over the nature of the primary reactions, this kinetic study solved the problem of the origin of the vinyltrimethylsilane by showing that it was not a primary product, but was formed in secondary bimolecular reactions. A reasonable reaction sequence accounting for the formation of both vinyltrimethylsilane and tetramethylsilane is shown in Scheme 5. Reaction (37) is the internal addition of trimethylsilyl radicals to allyltrimethylsilane; terminal addition would also occur (indeed, it is the favoured process), but would be reversible. The radical dissociation reaction (38) has as its driving force the formation of the π-bond in vinyltrimethylsilane; tetramethylsilane results from the hydrogen-abstraction reaction (39).

Scheme 5. Formation of vinyltrimethylsilane and tetramethylsilane



$$Me_3SiCH_2CH{=}CH_2 + Me_3Si^{\bullet} \rightarrow Me_3SiCH_2\underset{\underset{\bullet}{CH_2}}{CH}SiMe_3 \qquad (37)$$

$$Me_3SiCH_2\underset{\underset{\bullet}{CH_2}}{CH}SiMe_3 \rightarrow Me_3SiCH{=}CH_2 + Me_3Si\dot{C}H_2 \qquad (38)$$

$$Me_3Si\dot{C}H_2 \xrightarrow{RH} Me_4Si \qquad (39)$$

Gas kinetic experiments and calculations have also proved to be helpful in clearing up confusion over the isomerisation of hydridosilaalkenes to silylenes, exemplified by reaction (40). It is well known that silacyclobutanes decompose

$$HMeSi{=}CH_2 \rightarrow Me_2Si: \qquad (40)$$

unimolecularly in the gas phase to ethene and a silaalkene, and that the latter forms a cyclic adduct with butadiene [32], but when Conlin generated $HMeSi{=}CH_2$ by pyrolysis of 1-methylsilacyclobutane at 650 °C in the presence of butadiene, he obtained only dimethylsilacyclopentenes, the adducts of Me_2Si: to butadiene [33]. Pyrolysis products in the absence of butadiene were also consistent with Me_2Si: being the only intermediate present. He concluded that reaction (40) went rapidly to completion under these conditions. His results appeared to conflict with those of Barton and co-workers, who successfully trapped $HMeSi{=}CH_2$ generated from a different precursor at lower temperature [34], and with theoretical estimates, which predicted that reaction (40) would be approximately thermoneutral, with a barrier to isomerisation in either direction of ca. 170 kJ mol^{-1} [35]. We have carried out gas kinetic studies to try to resolve these problems. We estimated that ΔS_{40} should also be zero [36]; hence, reaction (40) should not go to completion but to a state of equilibrium equally accessible from either side and with an equilibrium constant close to unity. We therefore generated Me_2Si: from two different disilane precursors over an extended temperature range (447 to 651 °C), with and without added butadiene [36]. We also undertook similar experiments starting with 1-methylsilacyclobutane, the precursor to HMeSi=CH_2 [37]. In the presence of butadiene, we found that both precursors gave only the silacyclopentenes, exactly as found by Conlin, but we were able to the show by simple kinetic estimates [36], subsequently refined by computer-assisted modelling [37], that this result does not in fact imply that reaction (40) goes to completion. Butadiene trapping gives a misleading impression, mainly because the rate constant for addition of Me_2Si: to butadiene is greater than the rate constant for addition of HMeSi=CH_2, but also because the adduct of Me_2Si: is more thermally stable than the adduct of HMeSi=CH_2. These kinetic considerations are of crucial importance in interpreting these pyrolyses, and enabled us to show that all of the experimental results starting from either type of precursor, with and without added butadiene, were consistent with reaction (40) being fully reversible, as predicted theoretically.

It should be clear from the foregoing examples that kinetic measurements can help very substantially in clarifying mechanistic problems in organosilicon chemistry. The experimental techniques we have developed require only simple apparatus and, with the aid of inexpensive microcomputers for data collection and analysis, enable kinetic studies to be reformed rapidly with only small quantities of material [21,38]. Any laboratory equipped to undertake simple flash vacuum pyrolysis experiments could very profitably expand into kinetic studies with only a modest outlay of money and effort, and it is to be hoped that this paper will encourage more to do so.

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