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THE PYROLYSIS OF ORGANOMETALLIC COMPOUNDS IV*. KINETIC STUDIES OF THE DECOMPOSITION OF TETRAMETHYLSILANE

R. P. CLIFFORD**, B. G. GOWENLOCK, C. A. F. JOHNSON AND J. STEVENSON***
Department of Chemistry, Heriot–Watt University, Edinburgh (Great Britain)

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SUMMARY

The pyrolysis of tetramethylsilane has been investigated in a flow system at 810–980°K and 0.1–30 mm. In reaction vessels seasoned by pyrolysis of tetramethylsilane the decomposition is independent of surface to volume ratio and the first-order rate constants may be represented by the equation:

$$\log_{10}k(\mathrm{sec}^{-1}) = (14.30 \pm 0.23) - (67600 \pm 800)/(2.303R \cdot T)$$

The major products formed are methane, ethane, trimethylsilane, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, hexamethyldisilane, and 2,2,4,4-tetramethyl-2,4-disilapentane. A reaction scheme is proposed which invokes the existence of a silicon–carbon π-bonded intermediate.

In a reaction vessel seasoned by the pyrolysis of tetramethyltin, the decomposition of tetramethylsilane is heterogeneous, and certain products are obtained which indicate that rapid surface initiated rearrangement reactions are taking place.

INTRODUCTION

Until comparatively recently there have been few kinetic studies of the decompositions of organosilanes. The only previous direct kinetic study of the pyrolysis of tetramethylsilane was carried out over thirty years ago by Helm and Mack[1]. Fritz[2] has used the pyrolysis of tetramethylsilane as a preparative technique for a wide range of carbosilanes, including many ring compounds. Fritz used a recycling flow technique with high degrees of decomposition. No kinetic parameters were measured. Recently Hase and Simons[3] have investigated the insertion of a single methylene into the silicon–hydrogen bond in trimethylsilane to produce chemically activated tetramethylsilane. By the application of RRKM theory Hase and Simons have predicted that reaction (1) would have:

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* Part III see ref. 36.

** Department of Chemistry, University of Hull, England.

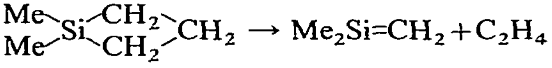
*** Department of Chemistry, University of Western Ontario, London, Ontario, Canada.

$$\log_{10} A_1(\mathrm{sec}^{-1}) = 15.0\text{–}15.5\,.$$

$$\mathrm{Me_4Si \rightarrow Me_3Si^{\bullet} + Me^{\bullet}} \qquad (1)$$

The production of a methyl radical as in (1) is now accepted as the initiation step in the thermal decompositions of all Group IV tetramethyl compounds. The pyrolysis of neopentane has been studied in detail[4–7], while that of tetramethyllead has been the subject of a recent communication[8]. The pyrolyses of tetramethylgermanium and -tin compounds were studied[9,10] before the advent of modern analytical techniques and the mechanisms proposed for their decompositions are unacceptable on modern kinetic and thermochemical grounds. The pyrolyses of methylsilane[11], trimethylsilane[12], and hexamethyldisilane[13–15] have also been investigated.

If the pyrolyses of organosilicon compounds are compared with those for hydrocarbons, it is usually presumed[12] that Rice–Herzfeld mechanisms will not apply to the former case because of the absence of stable compounds containing carbon–silicon double bonds[16,17]. Two of us[18] have suggested that bond dissociation energy considerations could imply greater stabilities for $\gt C{=}Si\lt$ structures than previously accepted. Kinetic evidence for the participation of a π-bonded carbon–silicon compound is provided by a study[19] of the pyrolysis of 1,1-dimethyl-1-silacyclobutane. A consideration of the pre-exponential factor in the Arrhenius equation showed that the initial decomposition was:



$$\mathrm{Me_2Si(CH_2)_3 \rightarrow Me_2Si{=}CH_2 + C_2H_4}$$

followed by dimerisation of the double bonded species to produce 1,1,3,3-tetramethyl-1,3-disilacyclobutane. If this proposal is valid alkylsilyl halides should eliminate hydrogen halides as do alkyl halides. It has been shown, however, that trimethylsilyl iodide does not decompose[20] under analogous conditions to tert-butyl iodide[21].

$$\mathrm{Me_3MI \rightarrow Me_2M{=}CH_2 + HI\ (M = C,\ Si)}$$

Our present study was to determine the Arrhenius parameters for the unimolecular decomposition of tetramethylsilane, and to clarify the position with regard to silicon–carbon π-bonded compounds in gas phase reactions.

EXPERIMENTAL

Tetramethylsilane was supplied by British Drug Houses Co. Ltd. (NMR reference material) and subjected to repeated distillation *in vacuo*. Analysis by gas–liquid chromatography showed no detectable impurities. Carbon dioxide was obtained by vacuum sublimation of the solid. Mono-, di- and trimethylsilanes were prepared by the reduction of the appropriate methylchlorosilanes. Hexamethyldisilane was prepared by the action of potassium metal on trimethylchlorosilane[22]. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane was prepared by the action of magnesium metal on (chloromethyl)dimethylchlorosilane[23]. Methane, ethane, ethylene, propane, and n-butane were supplied by the Matheson Co. Ltd.

The flow system was designed so that the tetramethylsilane could be passed through the reaction vessel either by itself, or in the presence of added carbon dioxide. Four silica reaction vessels of similar design were used. The 30 mm diameter cylindrical

TABLE 1

Vessel	Packing	Surface[a]	Volume/cm^3	Surface/vol/cm^{-1}
A	None	TMS	176	2.3
B	Silica tubes	TMS	181	2.7
C	Silica wool	TMS	181	17.6
D	None	TMT	170	2.2

[a] TMS, tetramethylsilane; TMT, tetramethyltin.

vessel had a narrow thermocouple pocket along the axis of the vessel. The reactant entered at 90° to this tube; the combination of these factors with the absence of a calming length prevents channelling in the reaction vessel, and thus the gas is homogeneously dispersed over all cross-sections of the vessel. The reaction vessel parameters are summarised in Table 1. The surfaces of vessels A, B, and C were seasoned by the pyrolysis of tetramethylsilane. Prior to its use in this investigation, vessel D had been used to study the thermal decompositions of tetramethyltin and hexamethylditin. As a result a grey coating had been formed on the surface. Analysis of the coating indicated that it contained tin and carbon. It was also shown that the tin could not be removed by treatment with gaseous chlorine. It is therefore possible that the material contains a carbide of tin.

The reaction vessels were housed in an electrically heated furnace, the temperature being maintained constant to within ±0.5°K by an AEI Sunvic RT2 controller. The rate of flow of reactant was determined by lengths of capillary placed before and after the reaction vessel. Condensable products were collected in traps at 195 and 112°K. Non-condensable products were transferred into a gas burette/Töpler system by a single jet mercury circulating pump. Products were analysed using an F and M model 720 gas chromatograph, fitted with a katharometer detector. Permanent gases were analysed by temperature programmed GSC on a 2 m molecular sieve type 5A column[26]; condensable products were determined on a 2 m silicone rubber column and on a 2 m squalane column.

RESULTS

The pyrolysis of tetramethylsilane was studied at 810–980°K, and 0.1–30 mm, with contact times of 0.5–10.0 sec, and extents of decomposition of 0.05–28.0%. Rate constants were calculated on the assumed first order decomposition of the tetramethylsilane. Assuming plug flow, contact times were calculated by dividing the volume of the reaction vessel by the rate of flow of tetramethylsilane and carrier gas. The extent of decomposition was estimated from the amount of methane and ethane produced. This estimate was considered to be valid since the primary fission is, (2):

$$Me_4Si \rightarrow Me_3Si^{\bullet} + Me^{\bullet} \qquad (2)$$

The rate constants determined in this way were the same whether tetramethylsilane flowed alone or with added carbon dioxide. This implies that under our conditions (2) is in the limiting first order region.

In a new reaction vessel, the initial values of k_2 were high and irreproducible, but after several pyrolyses the values of k_2 became lower and reproducible. We assume that reaction vessel 'seasoning', a common phenomenon in gas-phase organic and organometalic decompositions, had taken place. In Table 2 are shown the Arrhenius parameters obtained using the different reaction vessels. Subjecting all the results obtained in vessels A, B and C to a standard least mean squares treatment leads to the following expression for reaction (2):

$$\log_{10} k_2\ (\text{sec}^{-1}) = (14.3 \pm 0.23) - (67600 \pm 800)/(2.303R \cdot T)$$

Small amounts of hydrogen and ethylene were found in the non-condensable gases in addition to methane and ethane. A number of liquid products were also detected. The yields of these are summarised in Table 3. The propane and n-butane yields varied, but consideration of the very small yields (10^{-8} mole) of these two products implies no special significance. The yield of the tetramethyldisilapentane is affected by surface to volume ratio, being high in vessel C (10–11 %) and low in vessel A (5–8 %). The yield of trimethylsilane varied from 0.75 to 0.95 of the yield of the tetramethyl-

TABLE 2

Vessel	E (kcal/mole)	$\log_{10} A$ (sec^{-1})
A	67.4	14.3
B	68.7	14.6
C	67.1	14.3
D	37.0	7.0

TABLE 3

Product	Mole % of liquid products
Propane	0.6–0.9
n-Butane	0.3–0.5
Trimethylsilane	35
Hexamethyldisilane	15
1,1,3,3-Tetramethyl-1,3-disilacyclobutane	36–43
2,2,4,4-Tetramethyl-2,4-disilapentane	5–11

TABLE 4

Temperature (°K)	Trimethylsilane/2 × TMDSCB[a]	
	Vessel A	Vessel C
849	0.48	
887	0.46	0.44
894	0.44	0.42
915	0.41	0.38

[a] TMDSCB 1,1,3,3-tetramethyl-1,3-disilacyclobutane.

disilacyclobutane, this variation being a function both of temperature and of surface to volume ratio. In Table 4 is shown the ratio of trimethylsilane to the number of $Me_2Si{=}CH_2$ units (twice the yield of the disilacyclobutane). No solid products were detected in the 195°K trap, although a white involatile solid was formed at the exit of all the reaction vessels.

The gaseous products formed in vessel D were the same as those produced in the other three vessels, but the liquid products contained a number of methyl and ethyl silanes. Typical yields are shown in Table 5.

TABLE 5

Product	Mole % of liquid products
$MeSiH_3$	3
Me_2SiH_2	10
Me_3SiH	30
Me_3SiEt	35
Me_2SiEt_2	12
$MeSiEt_3$	2
$SiEt_4$	1
$(Me_3Si)_2$	5
$(Me_3Si)_2O$	2

DISCUSSION

The decomposition of tetramethylsilane is independent of the surface in reaction vessels seasoned by several pyrolyses of tetramethylsilane and the first order rate constants obey the expression:

$$\log_{10} k_3\ (\mathrm{sec}^{-1}) = (14.3 \pm 0.23) - (67600 \pm 800)/(2.303 R \cdot T)$$

The activation energy (67.6 kcal/mole) is lower than $D(Me_3Si{-}Me) = 76$ kcal/mole derived by Davidson *et al.*[24] but closer to the value of 70.7 kcal/mole obtained by Baldwin *et al.*[25]. If the true value for $D(Me_3Si{-}Me)$ is greater than our activation energy, then since heterogeneous decomposition is necessarily excluded by the constancy of our rate constants and Arrhenius parameters in vessels A, B and C, it is suggested that a chain mechanism could play a part in the decomposition. The primary fission (3) is followed by the abstraction of a hydrogen atom by the methyl radical (4).

$$Me_4Si \rightarrow Me_3Si^{\bullet} + Me^{\bullet} \qquad (3)$$

$$Me^{\bullet} + Me_4Si \rightarrow CH_4 + Me_3SiCH_2^{\bullet} \qquad (4)$$

Reaction (4), the main route to methane, has recently been the subject of independent investigations[26,27,28] and obeys the rate expression:

$$\log_{10} k_4\ (\mathrm{cm}^3 \cdot \mathrm{mole}^{-1} \cdot \mathrm{sec}^{-1}) = 11.5 - 10230/(2.303 R \cdot T)$$

The presence of small amounts of hydrogen in the reaction products indicates a contribution from a radical decomposition mechanism. The homogeneous gas-phase reaction (5) is unlikely to occur since Kerr *et al.*[27] have deduced that $D(Me_3SiCH_2{-}H) = 97$ kcal/mole.

$$\mathrm{Me_4Si \rightarrow Me_3SiCH_2^{\bullet} + H^{\bullet}} \tag{5}$$

As the yield of hydrogen is not increased in reaction vessel C, which has the highest surface to volume ratio, a heterogeneous reaction (5) must be excluded. Thus the only route to hydrogen is decomposition of the trimethylsilyl radical (6), followed by the abstraction reaction (7), an explanation which is analogous to the Rice–Herzfeld mechanism in hydrocarbon decompositions.

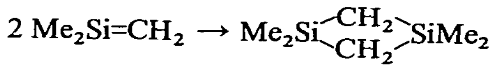
$$\mathrm{Me_3Si^{\bullet} \rightarrow Me_2Si{=}CH_2 + H^{\bullet}} \tag{6}$$

$$\mathrm{H^{\bullet} + Me_4Si \rightarrow H_2 + Me_3SiCH_2^{\bullet}} \tag{7}$$

If the trimethylsilylmethyl radical can decompose by (8) we have a possible explanation for the lowering of the experimental activation energy, measured from methyl radical production, compared with $D(\mathrm{Me_3Si{-}Me})$.

$$\mathrm{Me_3SiCH_2^{\bullet} \rightarrow Me_2Si{=}CH_2 + Me^{\bullet}} \tag{8}$$

Production of $\mathrm{Me_2Si{=}CH_2}$ is further implied by the formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (9).



$$\mathrm{2\,Me_2Si{=}CH_2 \rightarrow Me_2Si\!\begin{smallmatrix}\diagup CH_2 \diagdown\\ \diagdown CH_2 \diagup\end{smallmatrix}\!SiMe_2} \tag{9}$$

Hexamethyldisilane and 2,2,4,4-tetramethyl-2,4-disilapentane are produced in the radical recombination reactions (10) and (11).

$$\mathrm{2\,Me_3Si^{\bullet} \rightarrow Me_3SiSiMe_3} \tag{10}$$

$$\mathrm{Me_3Si^{\bullet} + Me_3SiCH_2^{\bullet} \rightarrow Me_3SiCH_2SiMe_3} \tag{11}$$

Production of small amounts of propane, n-butane and ethylene implies the presence of ethyl radicals.

$$\mathrm{2\,C_2H_5^{\bullet} \rightarrow n\text{-}C_4H_{10}} \tag{12}$$

$$\mathrm{2\,C_2H_5^{\bullet} \rightarrow C_2H_4 + C_2H_6} \tag{13}$$

$$\mathrm{C_2H_5^{\bullet} + CH_3^{\bullet} \rightarrow C_3H_8} \tag{14}$$

$$\mathrm{C_2H_5^{\bullet} + CH_3^{\bullet} \rightarrow CH_4 + C_2H_4} \tag{15}$$

$$\mathrm{2\,CH_3^{\bullet} \rightarrow C_2H_6} \tag{16}$$

Ethyl radical formation could occur via (17) and (18), although thermochemical considerations indicate that $D(\mathrm{Me_3Si{-}Et}) = 74$ kcal/mole. We consider that, in view of the short contact times used here, we would detect some ethyltrimethylsilane if reaction (17) occurred. A second source of the ethyl radical (19) has no equivalent in hydrocarbon decompositions.

$$\mathrm{Me_3SiCH_2^{\bullet} + CH_3^{\bullet} \rightarrow Me_3SiEt} \tag{17}$$

$$\mathrm{Me_3SiEt \rightarrow Me_3Si^{\bullet} + Et^{\bullet}} \tag{18}$$

$$\mathrm{Me_3SiCH_2^{\bullet} + CH_3^{\bullet} \rightarrow Me_3Si^{\bullet} + Et^{\bullet}} \tag{19}$$

A similar reaction has recently been proposed[8] in the pyrolysis of tetramethyllead. It may be thought of as the resultant of (17) and (18) in which the heat of formation of the C–C bond is available for rapid redistribution into the weaker Si–C bond.

Possible reactions of the trimethylsilyl radical are:

$$2\,Me_3Si^\cdot \rightarrow Me_3SiSiMe_3 \tag{10}$$

$$2\,Me_3Si^\cdot \rightarrow Me_3SiH + Me_2Si{=}CH_2 \tag{20}$$

$$Me_3Si^\cdot + Me_4Si \rightarrow Me_3SiH + Me_3SiCH_2^\cdot \tag{21}$$

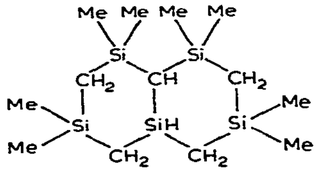
$$Me_3Si^\cdot \rightarrow Me_2Si{=}CH_2 + H^\cdot \tag{6}$$

$$Me_3Si^\cdot + Me_3SiCH_2^\cdot \rightarrow Me_3SiCH_2SiMe_3 \tag{11}$$

$$Me^\cdot + Me_3Si^\cdot \rightarrow CH_4 + Me_2Si{=}CH_2 \tag{22}$$

Assuming that (21) is negligible due to its endothermic character (18 kcal/mole), our product analyses imply that, at 900°K, $k_{20}/k_{10} = 1.2$. Cadman *et al.*[29] have shown that, at 300°K, $k_{20}/k_{10} \leqslant 10^{-3}$. A variation of this magnitude requires that (20) has an activation energy of 6–7 kcal/mole, assuming that $E_{10} = 0$.

The elemental balance for pyrolyses in vessels A, B and C is $C_{4.1}H_{13}Si$, compared to $C_4H_{12}Si$ in tetramethylsilane. This imbalance, the white solid deposited at the exit of the reaction vessel, and the irreproducibility of the first order rate constant in clean reaction vessels are indicative of small quantities of undetected higher products. In his investigation of the extensive and repetitive pyrolysis of tetramethylsilane Fritz[30] obtained products of the type $Me_3Si(CH_2SiMe_2)_nMe$, where $n = 4$–8 and:



On inspection we see that these are built up primarily of $Me_2Si{=}CH_2$ units. Since we are postulating the formation of $Me_2Si{=}CH_2$ as an intermediate, it seems possible that, in addition to forming 1,1,3,3-tetramethyl-1,3-disilacyclobutane, it may also form higher products, either similar to those of Fritz, or polymeric. Such products would remain undetected in our system, and if produced would make the elemental balance closer to that of tetramethylsilane.

Of the reactions producing the $Me_2Si{=}CH_2$ species, (6) is of minor importance as is indicated by the small yields of molecular hydrogen. If (20) is the major source of trimethylsilane, then it is also a major source of $Me_2Si{=}CH_2$. Disproportionation reactions similar to reaction (20) have recently been reported by Davidson and Lambert[31] in the pyrolysis of trimethylsilane, in order to explain the various disilacyclobutanes produced in their system. Our results indicate a disproportionation/combination ratio of 1.2 for the trimethylsilyl radical at 900°K. This compares with the value[32] of 4.6 for the analogous tert-butyl radical at 373°K.

There is however an excess of the Me_2SiCH_2 species over the yield of trimethylsilane. This could be accounted for if cross-disproportionation with a methyl radical occurs, reaction (22). The other reaction capable of producing the π-bonded species is reaction (8), although Davidson and Lambert[31] concluded that reactions of this type do not occur in the pyrolysis of trimethylsilane, only the disproportionation reactions being important.

The minimum stabilisation of the Si=C double bond may be estimated on the basis of our activation energy for the disproportionation reaction (20) and values of D(C–H) and D(Si–H). It amounts to 17 kcal/mole. If the reverse of reaction (20) has an activation energy the above quantity is necessarily increased. The stabilisation of the π-bond in Si=C must however be greater than 17 kcal/mole if reaction (8) is to occur as a homogeneous gas-phase reaction, for this requires an activation energy of (76 – stabilisation energy) kcal/mole. The π-bond energy of Me_2SiCH_2 has been estimated by Walsh[33] as lying between 30 and 42 kcal/mole. The energy of the π-bond in the analogous isobutene is about 60 kcal/mole. If we assume that the only radical disproportionation reaction that occurs is reaction (20) then, at the highest temperatures used in this study, an upper limit of 11% of the yield of methyl radicals may arise from reaction (8). At the lower temperatures this fraction is smaller, and will have the overall effect of lowering our activation energy compared to the true Si–C bond dissociation energy.

Throughout these mechanistic considerations we return repeatedly to the conclusion that π-stabilised Me_2SiCH_2 is an important intermediate, and in this way our data reinforce the conclusions of Flowers and Gusel'nikov[19] for the pyrolysis of 1,1-dimethyl-1-silacyclobutane. Some comment is required concerning the general belief that π-stabilised Si=C bonds do not exist. This is based upon (*a*) Seyferth and Stone's theoretical considerations[16] and (*b*) failure to prepare such compounds by conventional synthetic methods. It is however apparent that the methods of gas kinetics have on previous occasions[34,35] been utilised to prepare materials which a similar combination of theory and practice declared to be non-existent. The general feature which links these phenomena is that the materials concerned should be stable in the gas-phase and labile in the condensed phase or in conventional solvents. It is appropriate to make reference to *p*-quinodimethanes[34], and primary and secondary *C*-nitrosoalkanes[35], both of which were prepared as by-products from gas-kinetic investigations.

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