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SILYLENE CHEMISTRY
II. A KINETIC STUDY OF THE THERMOLYSIS OF *sym*-DIMETHOXYTETRAMETHYLDISILANE

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SUMMARY

A detailed kinetic study of the thermolysis of *sym*-dimethoxytetramethyldisilane (I) has been carried out. This study provides strong support for our previous proposal that dimethyldimethoxysilane and dimethylsilylene are formed in an unimolecular and rate determining α-elimination step. Further, chemical evidence is reported which, for the first time, clearly and unambiguously demonstrates insertion of silylenes into the silicon–oxygen bond of alkoxysilanes.

INTRODUCTION

The thermolysis of *sym*-dimethoxytetramethyldisilane (I) has been reported[1] to proceed readily at 225° to give dimethyldimethoxysilane and α,ω-dimethoxypermethylpolysilanes (II).

$$\underset{\text{(I)}}{\mathrm{MeO(SiMe_2)_2OMe}} \xrightarrow{225^\circ} \mathrm{Me_2Si(OMe)_2} + \underset{\text{(II)}}{\mathrm{MeO(SiMe_2)_{\mathit{n}}OMe}}$$

Strong support for a mechanism involving α-elimination of dimethylsilylene, followed by a series of silylene insertion reactions, was obtained by chemical trapping,

$$\text{(I)} \xrightarrow{\Delta} \mathrm{Me_2Si(OMe)_2} + \mathrm{Me_2Si\!:}$$

$$\mathrm{Me_2Si\!:} + \mathrm{MeO(SiMe_2)_{\mathit{n}}OMe} \rightarrow \mathrm{MeO(SiMe_2)_{\mathit{n}+1}OMe}$$

where $n = 2, 3$, etc.

mass spectral and preliminary kinetic studies. The observation[1] that the extent of decomposition of (I) was independent of dilution indicated that the rate determining step in this thermolysis was the α-elimination of dimethylsilylene from (I). A more detailed study of the kinetics of the thermolysis of (I) was undertaken in order to substantiate the above mechanistic proposals.

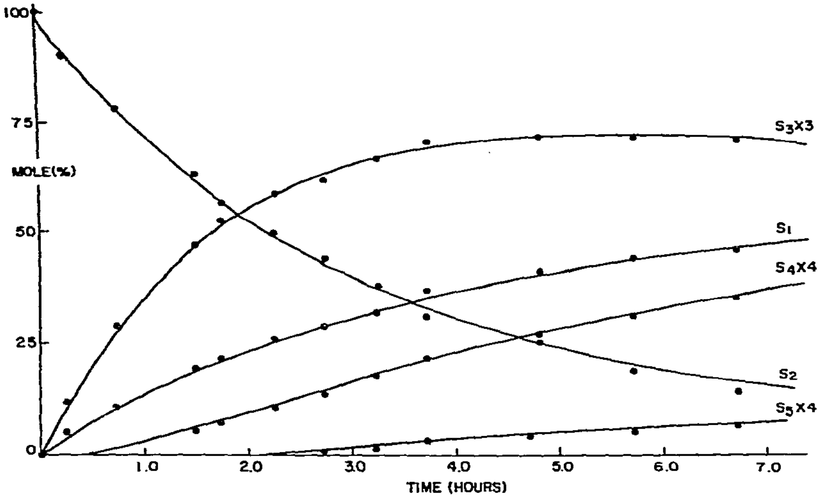


Fig. 1. Kinetic results from the thermolysis of $MeO(SiMe_2)_2OMe(S_2)$ at 220±2°.

RESULTS AND DISCUSSION

The thermolysis of (I) in the presence of benzene (internal standard) was shown to be in good agreement (Fig. 1) with the following kinetic scheme in which step (1) is rate determining.

$$S_2 \xrightarrow{k_1} S_1 + S \tag{1}$$

$$S + S_2 \xrightarrow{k_2} S_3 \tag{2}$$

$$S + S_3 \xrightarrow{k_3} S_4 \tag{3}$$

$$S + S_4 \xrightarrow{k_4} S_5 \tag{4}$$

$$S + S_5 \xrightarrow{k_5} S_6 \tag{5}$$

where $S = Me_2Si$:
$S_n = MeO(SiMe_2)_nOMe, (n = 1\text{–}6)$

The solid lines in Fig. 1 were calculated using numerical integration on a digital computer. The rate constants found by this procedure were:

$$k_1 = 4.7 \times 10^{-5}\ \text{sec}^{-1}$$
$$k_3/k_2 = 0.87 \pm 0.10$$
$$k_4/k_2 = 0.60 \pm 0.10$$
$$k_5/k_2 = 0.5 \pm 0.10$$

The values given for k_4 and k_5 relative to k_2 were determined from competitive studies of the thermolysis of S_2 in the presence of S_4 (see Table 1).

A first order plot for the disappearance of S_2 (see Fig. 2) yields an apparent rate

TABLE 1

COMPETITIVE STUDIES WITH S_2 IN THE PRESENCE OF S_4

Compound	Mole %	
	Calc.	Observed
Starting mole ratio S_2/S_4 = 50/50, time 8 h		
S_1	27.0	25.0
S_2	11.4	11.2
S_3	9.4	9.9
S_4	40.6	41.8
S_5	10.4	11.0
S_6	1.3	1.1
Starting mole ratio S_2/S_4 = 70/30, time 8 h		
S_1	35.7	34.0
S_2	14.1	14.2
S_3	15.3	15.1
S_4	25.8	26.7
S_5	7.9	8.8
S_6	1.3	1.3

constant (8.4×10^{-5} sec^{-1}) which is nearly twice that of k_1. This is as expected, since during the initial portions of the reaction additional S_2 is consumed in step (2)

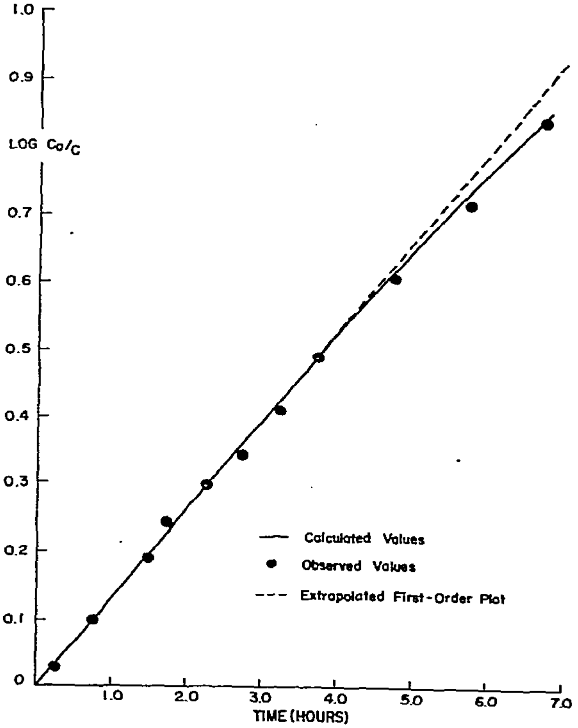


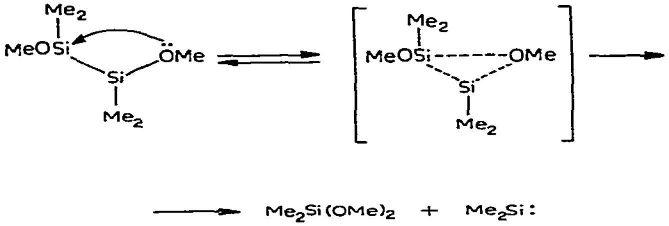
Fig. 2. First-order plot for the thermolysis of $MeO(SiMe_2)_2OMe$ (I) at 220±2°.

at a rate equal to its decomposition in step (1). As the reaction progresses, higher polysilanes (S_3, S_4, etc.) accumulate and compete more favorably for the intermediate silylene (S). Indeed, the decreasing apparent first order rate constants in Fig. 2 (initially 2 k_1, and decreasing toward k_1) is consistent with the model used. Under these thermolysis conditions employed S_3 is thermally stable and thus the reverse of step (3), *i.e.*,

$$S_3 \rightarrow S_2 + S$$

cannot account for the apparent decrease in S_2 consumption.

These kinetic data support our previous proposal[1] that the rate determining step in the thermolysis of (I) is indeed a unimolecular decomposition involving α-elimination.



In the thermolysis of (I), the formation of the series $MeO(SiMe_2)_nOMe$ could be accounted for in terms of insertion* of dimethylsilylene into either silicon–silicon or silicon–oxygen bonds. The possibility of this latter type of insertion has been raised previously[1]. The fact that the relative rates k_2–k_5 are nearly equal tends to favor silicon–oxygen insertion since the number of Si–O bonds is unchanged in all S_n species while the number of Si–Si bonds increases significantly.

Direct chemical evidence has been obtained which, for the first time, demonstrates conclusively the insertion of a silylene into the silicon–oxygen bond of a disilane. When *sym*-tetramethoxydimethyldisilane (III) was heated in the presence of excess *sym*-dimethoxytetramethyldisilane (I) under conditions where the latter is thermally stable, the primary reaction products were methyltrimethoxysilane and the trisilane (IV). The formation of (IV) can be explained by insertion of methylmethoxysilylene into the silicon–oxygen bond of (I).

$$\left.\begin{array}{c} (MeO)_2MeSiSiMe(OMe)_2 \\ (III) \\ + \\ (MeO)Me_2SiSiMe_2(OMe) \\ (I) \end{array}\right\} \xrightarrow{165°} \left\{\begin{array}{c} MeSi(OMe)_3 \\ \\ + \\ (MeO)Me_2SiSiMe_2SiMe(OMe)_2 \\ (IV) \end{array}\right.$$

$$(III) \xrightarrow{\Delta} MeSi(OMe)_3 + Me(MeO)Si:$$

$$Me(MeO)Si: + (I) \xrightarrow{Si-O\ insertion} (IV)$$

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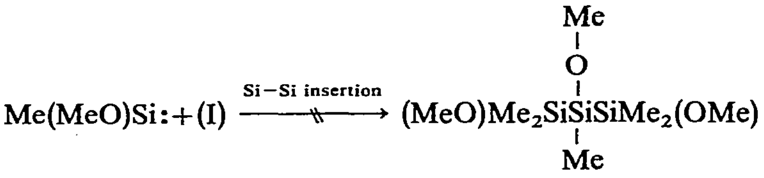
* The insertion of silylenes into a variety of single bonds has been described. For a general review on the preparation and properties of silylenes, see ref. 2.

None of the trisilane (V), which would arise via silylene insertion into the silicon–silicon bond of (I), was observed.



$$\text{Me(MeO)Si:} + \text{(I)} \;\not\xrightarrow{\text{Si}-\text{Si insertion}}\; \text{(MeO)Me}_2\text{Si}\underset{\substack{|\\ \text{Me}}}{\overset{\substack{\text{Me}\\ |\\ \text{O}\\ |}}{\text{Si}}}\text{SiMe}_2\text{(OMe)}$$

(V)

(not observed)

Under the above conditions [165° and excess (I)], only small amounts of dimethyldimethoxysilane and trisilane (VI) were observed.

$$\text{(I)} \xrightarrow{\Delta} \text{Me}_2\text{Si(OMe)}_2 + \text{Me}_2\text{Si:}$$

$$\text{Me}_2\text{Si:} + \text{(I)} \rightarrow \underset{\text{(VI)}}{\text{MeO(SiMe}_2)_3\text{OMe}}$$

The ability of a silylene to insert into a silicon–oxygen bond of an alkoxysilane was also demonstrated in this study. Thus, when (I) was heated in the presence of a large amount of trimethylmethoxysilane, methoxypentamethyldisilane (VII) was produced.

$$\text{(I)} \xrightarrow{\Delta} \text{Me}_2\text{Si(OMe)}_2 + \text{Me}_2\text{Si:}$$

$$\text{Me}_2\text{Si:} + \text{Me}_3\text{SiOMe} \xrightarrow{\text{Si}-\text{O insertion}} \underset{\text{(VII)}}{\text{Me}_3\text{SiSiMe}_2\text{(OMe)}}$$

However, the major reaction path was insertion with the methoxypolysilane, indicating that the silicon–oxygen bond of this monosilane is substantially less reactive than those of the polysilanes. This result agrees with the observations that the reaction,

$$\text{Me}_2\text{Si:} + \text{Me}_2\text{Si(OMe)}_2 \rightarrow \text{(I)}$$

is kinetically unimportant in the thermolysis of (I) (see above kinetic model). Further studies are needed to explain why alkoxypolysilanes are so much more reactive than alkoxymonosilanes toward silylene insertion.

As we have suggested previously[1–4], polysilanes containing a variety of heteroatom substituents (*i.e.*, OR, OSiR_3, halogens, etc.) undergo similar thermolytic decompositions and the intermediacy of silylenes is inferred*. Chemical trapping and kinetic studies supporting silylene formation in such α-elimination reactions are in progress and will be the subject of future publications.

EXPERIMENTAL

General comments

All NMR spectra were obtained with a Varian A-60 spectrometer using tetra-

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* In a recent publication[5], α-elimination reactions of polysilanes with H- and Ph-substituents have been reported, thus extending further the general nature of this reaction.

methylsilane as internal standard and carbon tetrachloride as solvent. Molecular weights were determined with a 90° sector, single focusing mass spectrometer of 12 in. radius (AEI Model MS-12). For quantitative GLPC analyses a F and M Model 720 gas chromatograph was used with helium as the carrier gas. The column was 6′ × 0.25″ stainless steel packed with a copolymer of DOW CORNING® brand silphenylene (25%) and DOW CORNING® KP-5365 Fluid (75%) on 80/100 mesh Chromosorb W (10% by weight silphenylene). Decomposition of the methoxypolysilanes was avoided by using injection port temperatures of < 225°.

Starting materials

The compounds $\mathrm{MeO(SiMe_2)_nOMe}$ ($n = 2$–5) were prepared according to a previously published procedure[6]. The hexasilane ($n = 6$) was prepared by heating an equimolar mixture of the disilane ($n = 2$) and the tetrasilane ($n = 4$) at 220° in a sealed ampoule for 24 h. The pure hexasilane ($n = 6$) was isolated by preparative GLPC. (Found: C, 41.0, 40.9; H, 10.1; mol.wt., 410. $\mathrm{C_{12}H_{36}O_2Si_6}$ calcd.: C, 40.9; H, 10.2%; mol.wt., 410.)

Kinetic studies

Small aliquots (*ca.* 0.2 ml) of a "master" mixture of (I) and benzene (25% by weight) were sealed into dry ampoules and heated in an oven at 220 ± 5°. Periodically a tube was removed, quickly cooled to −78°, and analyzed by GLPC. The area of individual members of the series $\mathrm{MeO(SiMe_2)_nOMe}$ ($n = 1$–6) was obtained by taking the average of at least three chromatograms. Response factors of the reaction products relative to the benzene internal standard were determined in separate experiments. The analytical results are plotted in Fig. 1. Satisfactory mass balances of the series $\mathrm{MeO(SiMe_2)_nOMe}$ ($n = 1$–6) were obtained, accounting for 95–97% of all silicon even at the longer reaction times.

Competitive studies with S_2 in the presence of S_4

These reactions and analyses were carried out using the same general techniques described for the kinetic studies. The calculated and observed results of these competitive studies are given in Table 1.

Thermolysis of sym-tetramethoxydimethyldisilane (III) in the presence of sym-tetramethyldimethoxydisilane (I)

A mixture of 5.0 g (28 mmoles) of (I) and 3.0 g (14 mmoles) of (III) was sealed in an ampoule and heated at 165° for 60 h. Methyltrimethoxysilane and dimethyldimethoxysilane (trace) were removed with the aid of a rotary evaporator. Distillation of the residue gave unreacted (I), a small amount of 1,3-dimethoxyhexamethyltrisilane, and 1.5 g (42.5%) of 1,1,3-trimethoxypentamethyltrisilane (IV), b.p. 80–82° (10 mm) (purity *ca.* 95% by GLPC). An analytical sample was obtained by preparative GLPC. (Found: mol.wt., 252. $\mathrm{C_8H_{24}O_2Si_3}$ calcd.: mol.wt., 252.)

The NMR spectrum of (IV) substantiated the proposed structure showing singlets at τ 6.59 [$\mathrm{Si(OMe)_2}$], 6.69 (SiOMe), 9.81 ($\mathrm{Me_2SiO}$), 9.85 ($\mathrm{SiMe_2}$), and 9.912 ($\mathrm{MeSi{<}^{O}_{O}}$) ppm in the ratio 2/1/2/2/1, respectively.

Thermolysis of (I) in the presence of trimethylmethoxysilane

A mixture of (I) (2.5 g, 48 mmoles) and trimethylmethoxysilane (2.5 g, 240 mmoles) was sealed in an ampoule and heated at 200° for 24 h. Tandem GLPC-mass spectral analyses confirmed the presence of $Me_3SiSiMe_2(OMe)$ (VI). The GLPC area ratio of $Me_3SiSiMe_2(OMe)/MeO(SiMe_2)_nOMe$ ($n = 3$–5) was *ca.* 1/4. Thus, even when present in large amounts, Me_3SiOMe did not compete favorably with the $MeO(SiMe_2)_nOMe$ series for dimethylsilylene. At this temperature (VI) is unchanged in 48 h.

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