Photolysis of Tris(trimethylsilyl)methylsilane in the Presence of 2-Propenol

Bong Hyun Boo[*†§], **Seung Ki Hong**[†], **and Sung Kwon Kang**[†]

[†]*Department of Chemistry, Chungnam National University, Taejon 305-764, Korea*
and [§]*Center for Molecular Science, 373-1 Kusung-dong Yusung-gu, Taejon 305-701, Korea*

UV photolysis of the titled polysilane (Me₃Si)₃SiMe (I) in the presence of a trapping agent of 2-propenol has been performed to investigate the interaction of short-lived silicon species formed from the photolysis of I with 2-propenol. Product studies show that Me(Me₃Si)Si: (II) and (Me₃Si)₃Si·(III) are primarily formed as the major reactive species which saturate their valencies *via* O-H insertion and H-abstraction, respectively. Some products are unstable toward further secondary reaction such as photodissociation and intermolecular reaction. The PM3 semiempirical calculations are performed to deduce the energetics of the photoinduced chemical reactions of I with the substrate.

Introduction

The photochemical fragmentation of permethyloligosilane is of considerable current interest since high molecular weight oligosilanes are used as photoresists in the electronic industry.[1,2] The lithographic technique utilizes photoresists such as oligosilanes for the patterning for electronic circuitry.[3] In 1971, Ishikawa and Kumada have reported a preliminary account of the photochemistry of tris(trimethylsilyl)methylsilane (I).[4] Recently, Davidson and his coworkers[5] have reported that I is decomposed *via* three types of degradation patterns as shown in Scheme 1.

Clear evidence for the photochemical generation of the silylenes and silyl radicals has been obtained in our laboratory *via* trapping with appropriate substrates and has been presented in the literature.[6] Quite recently, Oshita and his coworkers have observed the similar photodissociation patterns in the photolyses of highly branched polysilanes using a low pressure mercury lamp (254 nm).[7] Scheme 2 outlines one of the photolytic results presented in the literature.[7]

We have initiated the photochemical study by photolyzing I by UV (mostly 254 nm) in the presence of 2-propenol to investigate the relative reactivities of photofragments such

$$\text{MeSi(SiMe}_3)_3 \xrightarrow{h\nu} \text{Me(Me}_3\text{Si)Si:}$$

$$\text{II}$$

I   + Me₃SiSiMe₃ (major pathway)
    →Me₂Si: + Me₂Si(SiMe₃)₂ (minor pathway)
    →(Me₃Si)₂MeSi· + ·SiMe₃ (minor pathway)

$$\text{III}$$

Scheme 1.

$$(\text{Me}_3\text{Si})_3\text{SiSi(SiMe}_3)_3 \xrightarrow{h\nu} (\text{Me}_3\text{Si})_4\text{Si} + (\text{Me}_3\text{Si})_2\text{Si:}$$

→Me₃SiSiMe₃ + (Me₃Si)₃Si:

|
Me₃Si
→(Me₃Si)₃Si(Me₃Si)₂Si· →(Me₃Si)₃Si(Me₃Si)₂SiH
→(Me₃Si)₃Si· →Me₃SiH + (Me₃Si)₃SiMe

Scheme 2.

$$2\underset{\underset{\displaystyle \text{OMe}}{|}}{\overset{\overset{\displaystyle \text{H}}{|}}{\text{Me-Si-SiMe}_3}} \xrightarrow{h\nu} \text{Me}_3\text{Si-}\underset{\underset{\displaystyle \text{Me}}{|}}{\overset{\overset{\displaystyle \text{H}}{|}}{\text{Si}}}\text{-O-}\underset{\underset{\displaystyle \text{Me}}{|}}{\overset{\overset{\displaystyle \text{H}}{|}}{\text{Si}}}\text{-SiMe}_3 + \text{MeOMe}$$

Scheme 3.

as silylenes and silyl radicals toward C=C and O-H bonds in 2-propenol, and to clarify that the coupling mechanism (Scheme 3) suggested previously[6] in the photolysis of I in the presence of methanol also operates in this reaction system.

It is found from the product studies that silylene II and radical III interact selectively with only the O-H bond in 2-propenol. Interestingly, the insertion of silylene II into O-H bond in 2-propenol may initiate secondary reactions such as elimination, coupling, and etc..

We have also performed a PM3[8,9] semiempirical study of the thermochemical values of the reaction intermediates and stable products observed or inferred.

Experimental

General Data. ¹H NMR spectra were recorded on a Bruker AC-80 FT and/or Bruker AM-300 FT spectrometer. Gas chromatograph-mass spectra (GC-MS) were recorded on a Shimadzu GCMS-QP1000, and/or on a Hewlett Packard GC/MS spectrometer consisting of a HP 5890 series II gas chromatograph and a HP 5970 series mass selective detector (MSD) operating at an ionization voltage of 70 eV. Flame ionization detector (FID) and thermal conductivity detector (TCD) instruments were employed for analytical gas chromatography. The FID instrument was Varian model 3300. The TCD gas chromatograph was Gow-Mac Series 350. The TCD instrument was also used routinely for separation of reaction mixtures and yield determinations. Yields were based on the amount of unrecovered starting precursor I and were determined with the use of I as an external standard. Chromatographic response factors in the TCD instrument were determined for isolated products or for hydrocarbons with the similar molecular weight as the observed products. All the products were separated by using a 13 ft×1/4″ 20%

Photolysis of (Me₃Si)₃SiMe

Bull. Korean Chem. Soc. **1995**, *Vol. 16, No. 1* **31**

OV-17 on Chromorsorb WHP, 105 ℃.[10]

All chemical shifts are reported in values as measured in parts per million (ppm) down field from tetramethylsilane (TMS). Coupling constants (J) are given in Hz. Signals in the ¹H NMR spectra are described as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

Materials. I was synthesized by the method of Barton.[11] This compound is identified from ¹H NMR, mass, IR, Raman, and UV spectra. The spectral data were reported previously.[6] Fluorescence from I in a cyclohexane solution is observed having a broad maximum at 277-284 nm when this compound is excited at 260 nm.

Photolysis of (Me₃Si)₃SiMe in the presence of 2-propenol. Th photolysis was carried out in two different reaction times of 10 h and 85 h. For the 10 h photolysis, 0.60 g (2.3 mmol) of I, 0.34 g (5.9 mmol) of 2-propenol and 7 ml of cyclohexane were placed in the cylindrical quartz vessel (o.d. 21 mm, length 340 mm). The reaction mixture was thoroughly degassed three times by the freeze-pump-thaw method. The quartz tube was placed in a Rayonet reactor. The sample was irradiated for 10 hours by medium-pressure mercury lamps. Only 14% of the starting material was consumd. The final purification of the products was achieved by gas chromatography. The stable products obtained were Me₃SiSiMe₃ (88%), (Me₃Si)₂SiHMe (5.7%), (Me₃Si)₂SiMe₂ (3.4 %) and 1,1,1,2,4,5,5,5-octamethyltetrasiloxane (VI) (8.8%).[12]

For the second experiment using the 85 h reaction time, 2.0 g (7.6 mmol) of I, 0.97 g (17.0 mmol) of 2-propenol and 7 ml of cyclohexane were placed in the cylindrical quartz vessel. The sample was irradiated for 85 hours. 90% of the starting material was consumed. The stable products obtained were Me₃SiSiMe₃ (62%), 1-methoxy-1,2,2,2-tetramethyl-disilane (IV) (5.9%), (Me₃Si)₂SiHMe (5.1%), (Me₃Si)₂SiMe₂ (4.9%), 1,2,2,2-tetramthyldisilyl-2'-propenyl ether (V) (2.3%), 1,1,1,2,4,5,5,5-octamethyltetrasiloxane (VI) (8.0%), 1-methyl-1-(trimethylsilyl)-1-sila-3-buenyl-2'-propenyl ether (VII) (5.2%) and bis(2-propenyl) ether (trace). 1,2,2,2-tetramethyldisilyl-2'-propenyl ether (V); mass: (M⁺-15) 159 (20), 146 (5.3), 131 (100), 117 (23), 101 (8.9), 99 (6.6), 73 (35), 59 (11), 45 (23), 43 (14), 32 (7.6). 1-Methyl-1-(trimethyl-silyl)-1-sila-3-butenyl-2'-propenyl ether; 300 MHz FT-¹H NMR (CDCl₃): δ −0.22

$$\begin{array}{c} 2 \quad 3 \quad 4 \\ CH_2\text{-}CH\text{=}CH_2 \\ |1 \\ Me\text{-}Si\text{-}SiMe_3 \quad (VII) \\ |1' \quad 2' \quad 3' \\ OCH_2\text{-}CH\text{=}CH_2 \end{array}$$

(s, 3H, SiCH₃), −0.12 (s, 9H, Si(CH₃)₃), 1.37 (d with t, J_{32}=8.1, J_{42}=1.2 Hz, SiCH₂), 3.97 (d with t, 2H, $J_{2'1'}$=5.2 Hz, $J_{3'1'}$=1.5 Hz, OCH₂), 4.69 (d with d with t, 1H, $J_{2'3'_{cis}}$=10.3 Hz, $J_{3'3'}$=2.1, $J_{1'3'}$=1.5 Hz, O-C-C=CH), 4.70 (d with d with t, 1H, $J_{2'3'_{trans}}$=17.1 Hz, $J_{3'3'}$=2.1 Hz, $J_{1'3'}$=1.5 Hz, O-C-C=CH), 4.95 (d with d with t, 1H, $J_{34_{cis}}$=10.2 Hz, J_{44}=1.7 Hz, J_{24}=1.2 Hz, Si-C-C=CH), 5.16 (d with d with t, 1H, $J_{34_{trans}}$=16.8 Hz, J_{24}=1.2 Hz, J_{44}=1.7 Hz, Si-C-C=CH), 5.60 (d with d with t, 1H, J_{23}=8.1 Hz, $J_{43_{trans}}$=16.8 Hz, $J_{43_{cis}}$=10.2 Hz, Si-C-CH=C), 5.81 (d with d with t, 1H, $J_{1'2'}$=5.2 Hz, $J_{3'2'_{trans}}$=17.1 Hz, $J_{3'2'_{cis}}$=10.3 Hz, O-C-CH=C); mass: M⁺ 214 (3.3), 199 (5.5), 173 (100), 157 (19), 147 (7.7), 133 (66), 119 (9.0), 73 (13), 59 (8.2). Bis(2-propenyl) ether; mass: M⁺ 98 (5.7), 84 (71), 83 (18),

Scheme 4.

69 (30), 56 (100), 55 (55), 44 (13), 43 (15), 42 (28), 41 (75), 39 (32), 32 (24). The spectral data for the other compounds have already been reported previously.[6]

Calculation. The calculations were performed using the PM3 methods as implemented in the MOPAC 6.0 package.[8] A microvax computer at the College of Natural Science of Chungnam National University was used for these PM3 calculations.

Results and Discussion

The photofragmentation of I in the presence of 2-propenol is observed with the similar patterns as previously reported.[6] But the primary silylene insertion product is quite unstable under this photolytic condition toward further reactions such as dissociation and intermolecular reactions with the trapping agent or the primary products.

When I was subjected to photolysis in the presence of a 2.2-fold excess of 2-propenol, various products were isolated as shown in Scheme 4.

Interestingly, we have observed bis(2-propenyl) ether as a minor product which might be formed *via* reaction 1.

$$\begin{array}{ccc} H & & H \quad H \\ | & & | \quad | \\ 2Me_3Si\text{-}Si\text{-}R & \rightarrow & Me_3Si\text{-}Si\text{-}O\text{-}Si\text{-}SiMe_3 + ROR + 2.2 \text{ kcal} \quad (1) \\ | & & | \quad | \\ Me & & Me \quad Me \\ R = OCH_2CH\text{=}CH_2 \end{array}$$

Table 1. Thermochemical values derived by the PM3 semiempirical method

Silicon species	ΔH_f^o (kcal/mol)	
	PM3	Experiment
Me(Me₃Si)Si:	0.4	
·SiMe(SiMe₃)₂	−71.9	
MeHSi(SiMe₃)₃	−99.8	
MeO-Si-SiMe₃ (with H, Me)	−124.9	
CH₂=CH-CH₂-O-Si-SiMe₃ (with H, Me)	−105.1	
CH₂=CH-CH₂-O-Si-SiMe₃ (with CH₂-CH-CH=CH₂, Me)	−105.3	
HC≡CH	50.7	54.2[a]
CH₂=CH-CH₂-OH	−31.3	
CH₂=CH-CH₂-O·	8.8	
CH₂-CH-OH (with CH·)	14.5	
CH₂=CH-CH₂-O-CH₂-CH=CH₂	−6.1	
[Me(Me₃Si)HSi]₂O	−206.3	
H₂O	−53.4	−57.8[a]

[a]Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. R.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data, 1985, 14,* Suppl. 1, *(JANAF Thermochemical Tables,* Third Edition).

This indicates that the reaction type of process 1 always occurs when R=-OMe,[6] -OEt,[13] -OCH₂CH=CH₂. As shown in process 1, the reaction is almost thermoneutral and therefore seems to be energetically possible. Note that the energetics reported in this paper is based on the experimental and/or theoretical (if the experimental data are not available) values of the enthalpies of formation given in Table 1.

As shown in Scheme 5, process 1 may be thermally forbidden presumably due to a very large symmetry-imposed barrier, but photochemically allowed *via* the contribution of the reactive excited state to the coupling reaction.

As shown in Scheme 5, reaction 1 may efficiently proceed through a barrierless transition state due to the symmetry-adapted LUMO-LUMO interaction.

Surprisingly we have observed product IV whose formation can be interpreted in terms of orbital symmetry as shown in Scheme 6.

The reaction (process 2) is endothermic by 34.4 kcal, but the reaction can occur *via* absorption of one photon or by an excess internal energy due to a great exothermic process, reaction 3.

$$\text{Me-Si-SiMe}_3 \;(\text{with } H, \text{OCH}_2\text{-CH=CH}_2) \;\rightarrow\; \text{Me-Si-SiMe}_3 + CH\equiv CH - 34.4 \text{ kcal} \quad (2)$$
(with H, OMe)
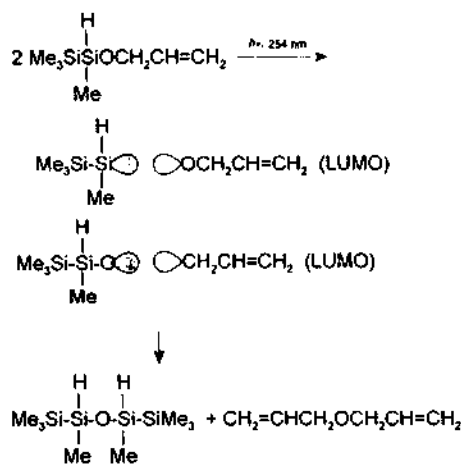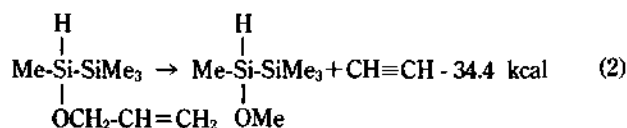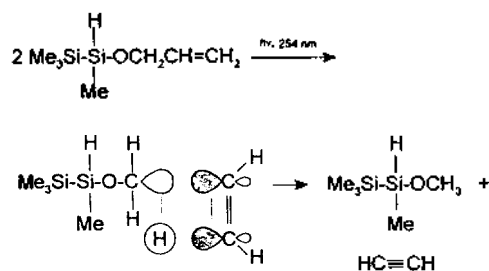
Scheme 5.

Scheme 6.

R = -H or - SiHMe(SiMe₃)

Scheme 7.

$$\text{Me(Me}_3\text{Si)Si: + HOCH}_2\text{-CH=CH}_2 \;\rightarrow$$

$$\text{Me-Si-SiMe}_3 + 74.2 \text{ kcal} \quad (3)$$
(with H, OCH₂-CH=CH₂)
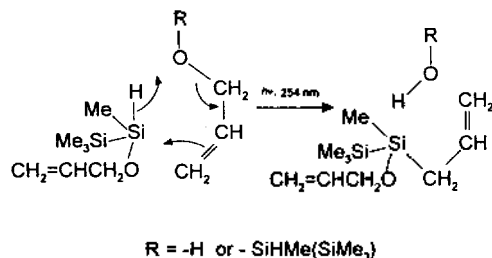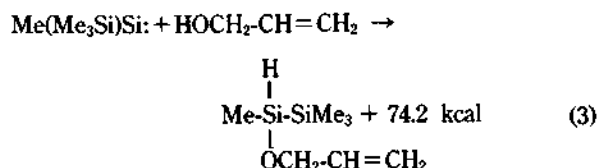
Sych an extrusion of acetylene (process 2) is thermally forbidden but photochemically allowed due probably to the participation of the reactive excited state.

The formation of product VII seems puzzling but may be due to process 4.

$$\text{Me-Si-SiMe}_3 + \text{HOCH}_2\text{-CH=CH}_2 \;\rightarrow$$
(with H, CH₂CH=CH₂)

$$\text{Me-Si-SiMe}_3 + H_2O + 26.7 \text{ kcal} \quad (4)$$
(with OCH₂-CH=CH₂, OCH₂-CH=CH₂)
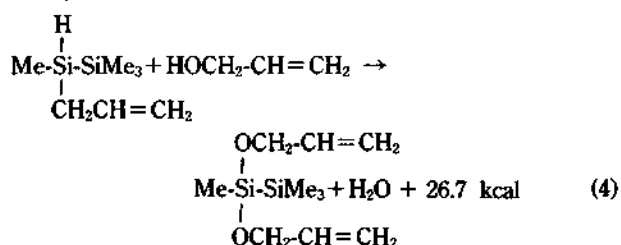
Reaction 4 is energetically favorable *via* an exothermicity of 26.7 kcal. Scheme 7 could explain the formation of VII.

If one of electrons in the C-C π bond in 2-propenol is excited by an UV photon, the bond could easily interact with the silicon center through a 6-membered transition state as shown in Scheme 7. Note that in case of R=-SiHMe(SiMe₃), Scheme 7 indicates that product VII is formed *via* the coupling of a primary product of V.

Finally one can say that a primary product, compound V is quite unstable under this photolytic condition such that V can easily undergo at least three types of reactions as mentioned earlier. As indicated in the experimental section product, V is not observed even in the 10 hr reaction time, indicating that V is easily dissociated or undergoes the intermolecular reactions shortly after its formation.

Acknowledgment. The present studies were supported (in part) by the Basic Science Research Institute Program, Ministry of Education, 1994 Project No. BSRI-94-3432. BHB is grateful to Center for Molecular Science for partial financial support.

References

1. Miller, R. D.; Michl, J. *J. Chem. Rev.* 1989, *89*, 1359.
2. Miller, R. D. In *Silicon Containing Photoresists, Silicon Chemisry*; Corey, J. Y.; Corey, E. R.; Gaspar, P. P., Eds.; Ellis Horwood, Ltd.: Chisester, 1988; Chapter 35.
3. Elliot, D. J. In *Integrated circuit fabrication technology*; McGraw-Hill Book Company: New York, 1982.
4. Ishikawa, M.; Kumada, M. *J. Chem. Soc. Chem. Commun.* 1971, 489.
5. Davidson, I. M. T.; Michl, J.; Simpson, T. *Organometallics* 1991, *10*, 842.
6. Hong, S. K.; Boo, B. H.; Rhee, H. J.; Kang, S. K.; Kim, J. R.; Kwak, Y.-W. *Bull. Korean Chem. Soc.* 1994, *15*, 68.
7. Ohshita, J.; Yoshitomi, T.; Ishikawa, M. *Organometallics* 1994, *13*, 3227.
8. Stewart, J. J. P. *J. Comp. Chem.* 1989, *10*, 221.
9. Coolidge, M. B.; Stewart, J. J. P. *QCPE program No. 455.*
10. The product mixture in all these reaction systems were purified under the same gas chromatographic condition.
11. Barton, T. J., unpublished results. Also the synthetic procedure can be found in: Boo, B. H. *The Chemistry of Silylsilylenes: Generation and Reactions of Trimethylsilylsilylene and Silylsilylene*; Doctoral dissertation: Washington University, St. Louis, 1984.
12. Since one molecule of VI contains two subunits of silylene II, the yield of VI reported here is corrected to be twice larger than the measured yield based on the amount of the unrecovered starting material.
13. The siloxane product has also been observed in the photolysis of I in the presence of ethanol. But the photolysis result is not presented here since the reaction pattern is the same as found in the photolysis experiment employing methanol. But the experimental result can be found in: Hong, S. K. *Generation and Reactivities of Silylenes and Silyl Radicals*; M. S. dissertation, Chungnam National University, Taejon, Apr 1993.

Studies on the Macrocycle-mediated Transport of Divalent Metal Ions in a Supported Liquid Membrane System

Moon Hwan Cho and Sang Chel Shin

Department of Chemistry, Kang Won National University, Chuncheon 200-701, Korea
Received August 17, 1994

Macrocyclic ligands have been studied as cation carriers in a supported liquid membrane system. Cd^{2+} has been transported using nitrogen substituted macrocycles as carriers and several divalent metal ions (M^{2+}=Zn, Co, Ni, Cu, Pb, Mg, Ca, and Sr) have been transported using DBN₃O₂, DBN₂O₂ and PolyNtnoen as carriers in a supported liquid membrane system. Competitive Cd^{2+}-M^{2+} transport studies have also been carried out with the same system. Ligand structure, stability constant, membrane solvent and carrier concentration are also important parameters in the transport of metal ions.

Introduction

It is well known that ions can be transported across liquid membrane.[1] With an ever increasing awareness of our energy demands, energy efficient membrane technology is proving to be a valuable approach in separation processes. The effectiveness of a membrane separation study is determined by the flux of species through the membrane.

Liquid membranes usually produce higher fluxes.[2] There are three types of membranes which are generally employed: bulk liquid membrane,[3] emulsion liquid membrane,[4] and polymer supported liquid membrane.[5] In our previous papers[3,4] we examined the influence of the structural variation within a series of crown ether carriers upon the selectivity and efficiency of the transport of metal ions across the bulk liquid membrane and the emulsion membrane.

Many transport systems for metal ions through a supported liquid membrane (SLM) containing a chelating agent as a carrier have recently been studied.[6] A solid supported liquid membrane, consisting of a microporous polypropylene