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## Laser-powered homogeneous pyrolysis of 1,1-dimethyl-1-silacyclobutane in the presence of some common monomers

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### Abstract

Laser-induced homogeneous pyrolysis of 1,1-dimethyl-1-silacyclobutane yields 1,1,3,3-tetramethyl-1,3-disilacyclobutane and ethene as major products. In the presence of vinyl acetate, allyl methyl ether, acrolein, methyl vinyl ether, methyl acrylate or methyl methacrylate, the intermediate dimethylsilene is trapped by these monomers, or by products of their thermal decomposition, to yield both volatile and viscous or solid organosilicon compounds. The mode of formation of these products is discussed. Ethoxytrimethylsilane is judged to arise from addition of trimethylsilanol to ethene, and this was confirmed in independent thermal initiation of this reaction. Dimethylsilene is suggested to react with unsaturated methyl ethers to yield methoxytrimethylsilane and to undergo copolymerization with methyl acrylate.

### Introduction

Thermolysis of silacyclobutanes  $R^1R^2\text{SiCH}_2\text{CH}_2\text{CH}_2$  in the gas-phase yields ethene and transient silenes  $R^1R^2\text{Si}=\text{CH}_2$  [1,2]. Variation of the reaction conditions and substituents at silicon affect the fate of silenes and the complexity of reaction owing to the operation of other modes of fragmentation. Reactions occurring alongside the 2 + 2 cycloreversion are (i) dehydrochlorination when  $R^1, R^2 = \text{halogen}$  [3–5], and (ii) cleavage into silylene and  $C_3$  unsaturates when  $R^1,$

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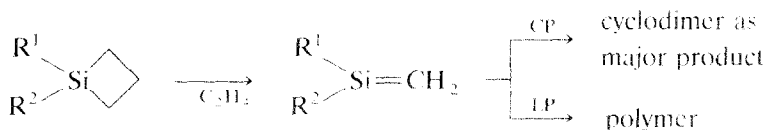
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$R^2 = H$  [6]. Isomerization of silenes has been shown to be a minor pathway for  $CH_2=CH(R)Si(CH_3)CH_2CH_2$  [7–9] and a rather important one for  $R^1, R^2 = H$  [6]. The decomposition scheme inferred for silacyclobutanes possessing hydrogen(s) at silicon is quite complicated. 1-Methyl-1-silacyclobutane decomposes to yield ethene and methylsilene, which is rapidly isomerizing into dimethylsilylene [10]. Silacyclobutane follows the pathway involving formation of silene, rearranged silene, and parent silylene [6], or alternatively (and more likely) that involving a 1,2-hydrogen shift in the parent silacyclobutane to give n-propylsilylene, which subsequently loses  $\text{:SiH}_2$  [11]. Evidence for these mechanisms is based on trapping experiments. In the absence of traps, the silenes generated from hydridosilacyclobutanes take part in cyclodimerization [10], insertion into the Si–H bond [10], decomposition [12], and polymerization [13]. The relative importance of these routes has been little studied. It is known that more silene insertion into the Si–H bond during low-pressure pyrolysis of 1-methyl-1-silacyclobutane occurs at lower temperatures [10], that more cyclodimerization of dimethylsilene can be achieved in conventional heat-induced than in multiphoton IR-induced decomposition of 1,1-dimethyl-1-silacyclobutane [14], that more polymerization in low-pressure pyrolysis of 1,1-dimethyl-1-silacyclobutane occurs with shorter distances between hot and cold sites [15], and that more isomerization of 2-methyl-2-silabuta-1,3-diene during the decomposition of 1-methyl-1-vinyl-1-silacyclobutane occurs at higher temperatures [7].

Our studies of laser-powered homogeneous pyrolysis (LP) of silacyclobutanes with  $R^1, R^2 = CH_3, H$  [16] and  $CH_3, CH_2=CH$  [17], as well as that of 4-silaspiro[3.4]octane [18], revealed that the intermediate silenes generated in a surfaceless reactor undergo exclusively polymerization. The same silenes generated in conventional (hot-wall) thermolysis (CP) are known [7–10, 19] to undergo mainly cyclodimerization (Scheme 1).

Whether the difference in the fate of these and other silenes under the two sets of conditions is the result of elimination of hot-wall effect and/or high peak temperatures in LP [20–22] or is associated with the nature of the substituents on silicon is to be established. Interest in LP of silacyclobutanes also arises from the possibility of carrying out the gas-phase copolymerization of reactive silenes with common monomers. In spite of the fact that bimolecular reactions of silenes with various trapping reagents have been studied very intensively [1,2], their mechanisms are not clearly established, and information on reactions of silenes with oxygenated olefins is almost totally lacking.

Following our previous paper on IR laser-powered decomposition of silane in the presence of some common monomers [23], we decided to investigate the course of the LP of 1,1-dimethyl-1-silacyclobutane (DMSCB) and the ability of thermally generated dimethylsilene to react with methyl acrylate (MA), methyl methacrylate



( $R^1, R^2 = Me, H; Me, Vi; (CH_3)_3$ )

Scheme 1

(MMA), acrolein (AC), allyl methyl ether (AME), methyl vinyl ether (MVE) and vinyl acetate (VA).

## Experimental

Experiments were carried out with a continuous-wave CO<sub>2</sub> laser operated on the P(20) line of the 00°1 → 10°0 transition. The laser beam was focussed (Ge lens, focal length 10 cm) on the middle of the glass tube (10 cm × 3.6 cm ID) reactor equipped with two NaCl windows, a sleeve with rubber septum and a stopcock for the connection to a standard vacuum-line. The mixtures of DMSCB, sulphur hexafluoride (used as sensitizer) and monomer (trapping reagent) were irradiated at a laser output of 10 W (incident radiation density ~ 30 W cm<sup>-2</sup>) for chosen times and the IR spectrum then recorded. Absorption bands of DMSCB (710 cm<sup>-1</sup>), MA (1650 cm<sup>-1</sup>), AC (2800 cm<sup>-1</sup>), AME (1203 cm<sup>-1</sup>), MMA (1660 cm<sup>-1</sup>), MVE (1457 cm<sup>-1</sup>) and VA (1656 cm<sup>-1</sup>) were used for the determination of change in concentration of these compounds. Gaseous products, ethene (3140 cm<sup>-1</sup>), acetone (1712 cm<sup>-1</sup>), ethyne (710 cm<sup>-1</sup>) and carbon monoxide (2140 cm<sup>-1</sup>) were identified from their infrared spectra. Subsequently, helium was expanded into the reactor and samples of the gaseous mixtures were withdrawn through the septum by syringe and analysed by use of a gas chromatograph linked to a mass spectrometer (Shimadzu, model QP 1000, column packed with silicone elastomer SE-30 or Porapak P, programmed temperature) and of an IR spectrometer (Perkin-Elmer model 621). Gaseous products were identified by comparison of their mass spectra and retention times with those of authentic samples. The IR spectra of the deposit on NaCl windows were recorded after evacuation of the reactor. Irradiation conditions and the products formed in the irradiated DMSCB-SF<sub>6</sub>-monomer systems are shown in Table 1.

Scanning electron microscopy of some deposits was carried out with a Tesla BS 350 microscope. The deposits were produced on aluminium sheets placed in the reactor before irradiation.

Samples of polymeric deposits were analysed on a HP 1090 M (Hewlett-Packard) liquid chromatograph using a tandem of two columns PLgel 50A and 500A (Polymer Laboratories, Shropshire, UK) under the following conditions: tetrahydrofuran as the mobile phase (flow rate 1.0 ml min<sup>-1</sup>), diode array and refractive index detectors in tandem for detection of both polymer samples and calibration standards. The molecular weight calibration curve for the column set-up was determined by use of polystyrene standards (Polymer Standards Service).

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the deposit obtained upon the irradiation of mixture DMSCB-SF<sub>6</sub>-MA were recorded on a Bruker AM 400 spectrometer at 400.13 resp. 100.61 MHz in deuteriochloroform at 300 K.

MA, AC, VA, MMA and sulphur hexafluoride (all Fluka) were commercial samples and were distilled prior to use. MVE and AME were prepared as reported previously [23]. DMSCB and trimethylsilanol were obtained by the methods described in refs. 24 and 25, respectively.

## Results and discussion

Irradiation at the IR frequency of the  $\nu_3$  mode of SF<sub>6</sub> ensures rapid heating of DMSCB-SF<sub>6</sub>-monomer mixtures and results in the formation of several gaseous

products and deposits of viscous or solid material on the reactor walls. Along with the thermal decomposition of DMSCB into transient dimethylsilene (DMS), that of monomers can also take place.

It is therefore appropriate to judge first which reactions of monomers or of products of their thermal decomposition with DMS can take place in the irradiated mixtures. Compounds containing C=C or C=O double bonds are reactive towards DMS [1,2]. Olefins undergo addition to  $\text{Me}_2\text{Si}=\text{CH}_2$  to give only other 1,1-dimethyl-1-silacyclobutanes, whose fate is the same as that of DMSCB. Carbonyl-containing compounds react with DMS by nucleophilic attack and ensuing [2 + 2]- or [2 + 4]-cycloaddition, and enolizable ones undergo the ene reaction. The products of these reactions are [2 + 4]-cycloadducts, or dimethylsilanone  $\text{Me}_2\text{Si}=\text{O}$  along with olefins.

The mean effective temperature of the irradiated mixtures can be estimated [26] as between 700–800 K. In this temperature range the decomposition of DMSCB [7] is significantly faster than that of MA and MMA [26]. The main reactions occurring in the mixtures of MA and MMA should therefore be those of  $\text{Me}_2\text{Si}=\text{CH}_2$  with MA and MMA, with those with products of MA and MMA decompositions (methacrolein, acrolein, formaldehyde) less important. Arrhenius parameters reported [27] for thermal decomposition of AME into  $\text{CH}_2\text{O}$  and propene suggest, on the other hand, that this decomposition will occur alongside that of DMSCB. This implies that DMS can react with both AME and  $\text{CH}_2\text{O}$ . As for MVE, LP of this ether affords [28] propanal and ethanal along with hydrocarbons. DMS can thus undergo reactions with MVE and these two aldehydes. AC is known [29] to decompose to ethene and CO, which suggests that new compounds can be formed by addition of AC to  $\text{Me}_2\text{Si}=\text{CH}_2$ . Thermal decomposition of VA had not previously been reported, but we have shown under the irradiation conditions used that VA yields mostly acetone.

The main volatile products observed after the irradiation of DMSCB– $\text{SF}_6$ –monomer mixtures are shown in Table 1 and Fig. 1. It is apparent that the decomposition of the monomer certainly takes place in mixtures of VA and MVE. The absence of the products of monomer decomposition in other cases does not, however, imply that monomers do not decompose, since the products could be used up in subsequent reactions.

1,1,3,3-Tetramethyl-1,3-disilacyclobutane (TMDSCB) was observed in all cases, its yield being higher the lower the contents of the monomer in the initial mixture. In irradiation of DMSCB and  $\text{SF}_6$  in the absence of monomer (Fig. 1a) the cyclodimer is a major product. This finding is important, and implies that laser conditions do not favor polymerization of intermediary DMS. The exclusive polymerization of  $\text{Me}_2\text{Si}=\text{CH}_2$ ,  $\text{MeHSi}=\text{CH}_2$  and  $(\text{CH}_3)_2\text{Si}=\text{CH}_2$  observed previously in LP of silacyclobutanes  $\text{R}_1\text{R}_2\text{SiCH}_2\text{CH}_2\text{CH}_2$  (Scheme 1) [16–18] thus suggests that not only the reaction conditions (perhaps the absence of surface effect) but also the nature of the substituents on silicon are important in determining which pathway will be preferred for the disappearance of the silene.

Some identified gaseous products can be accounted for in terms of known bimolecular reactions [1,2] of silenes with carbonyl compounds. Such reactions in the irradiated mixtures appear to be complex, since their only primary products are  $(\text{CH}_3)_3\text{SiOC}(\text{CH}_3)=\text{CH}_2$  (mass fragmentation ( $m/z$ , relative intensity): 130 ( $M$ , 19), 115 ( $M - 15$ , 67), 75 (100), 73 (41), 47 (13), 45 (39), 43 (25)), formed via the

Table 1  
LPD of DMSCB in the presence of monomers

Monomer	Pressure (kPa)		DMSCB	monomer		Molar. % SF <sub>6</sub>	Conversion (%)		Irradiation time (s)	Gaseous products
	SF <sub>6</sub>	DMSCB		DMSCB	monomer		DMSCB	monomer		
MA	0.9-2.3	0.9-3.2	1.1-3.5	1.1-3.5	0.17-0.50	100	29-54	100-1620	C <sub>2</sub> H <sub>4</sub> , TMDSCB, Me <sub>3</sub> SiOEt, (Me <sub>3</sub> Si) <sub>2</sub> O, (Me <sub>3</sub> SiO) <sub>3</sub> , C <sub>3</sub> H <sub>6</sub> , C <sub>4</sub> H <sub>8</sub> , C <sub>2</sub> H <sub>2</sub>	
VA	1.3-5.3	1.3	2.7-5.3	2.7-5.3	0.25	70-100	70-100	70-900	C <sub>2</sub> H <sub>4</sub> , TMDSCB, Me <sub>3</sub> SiOH, Me <sub>3</sub> SiOEt Me <sub>3</sub> SiOCMe=CH <sub>2</sub> , Me <sub>3</sub> SiOCOMe, MeCOMe <sup>a</sup> , CO, C <sub>2</sub> H <sub>2</sub> , (Me <sub>3</sub> Si) <sub>2</sub> O	
AME	1.3-4.0	1.3-2.6	2.6-5.3	2.6-5.3	0.25-0.33	66-86	58-74	75-300	C <sub>2</sub> H <sub>4</sub> , TMDSCB, Me <sub>3</sub> SiOMe, CO, C <sub>2</sub> H <sub>2</sub> (Me <sub>3</sub> Si) <sub>2</sub> O, Me <sub>3</sub> SiOMe <sub>2</sub> SiOMe	
AC	0.8-1.3	1.3-1.5	2.9-3.2	2.9-3.2	0.15-0.23	70-100	35-37	50-900	C <sub>2</sub> H <sub>4</sub> , Me <sub>3</sub> SiOEt, (Me <sub>3</sub> Si) <sub>2</sub> O, (Me <sub>2</sub> SiO) <sub>2</sub> , (Me <sub>2</sub> SiO) <sub>4</sub> , Me <sub>2</sub> SiOCH=CHCH <sub>2</sub> CH <sub>2</sub>	
MVE	1.3	1.3	2.6	2.6	0.25	27-62	40-55	30-780	C <sub>2</sub> H <sub>4</sub> , TMDSCB, Me <sub>3</sub> SiOMe, Me <sub>3</sub> SiOEt, (Me <sub>3</sub> Si) <sub>2</sub> O, C <sub>2</sub> H <sub>2</sub> , CO, EtCHO <sup>a</sup>	
MMA	1.3	1.3	2.6	2.6	0.25	100	45	360	C <sub>2</sub> H <sub>4</sub> , Me <sub>3</sub> SiOEt, (Me <sub>3</sub> Si) <sub>2</sub> O, C <sub>2</sub> H <sub>2</sub>	
-	0.4-2.8	1.6-2.8	-	-	0.2-0.5	61-100	-	55-1440	C <sub>2</sub> H <sub>4</sub> , TMDSCB, Me <sub>3</sub> SiOEt, (Me <sub>3</sub> Si) <sub>2</sub> O	

<sup>a</sup> Product of monomer decomposition.

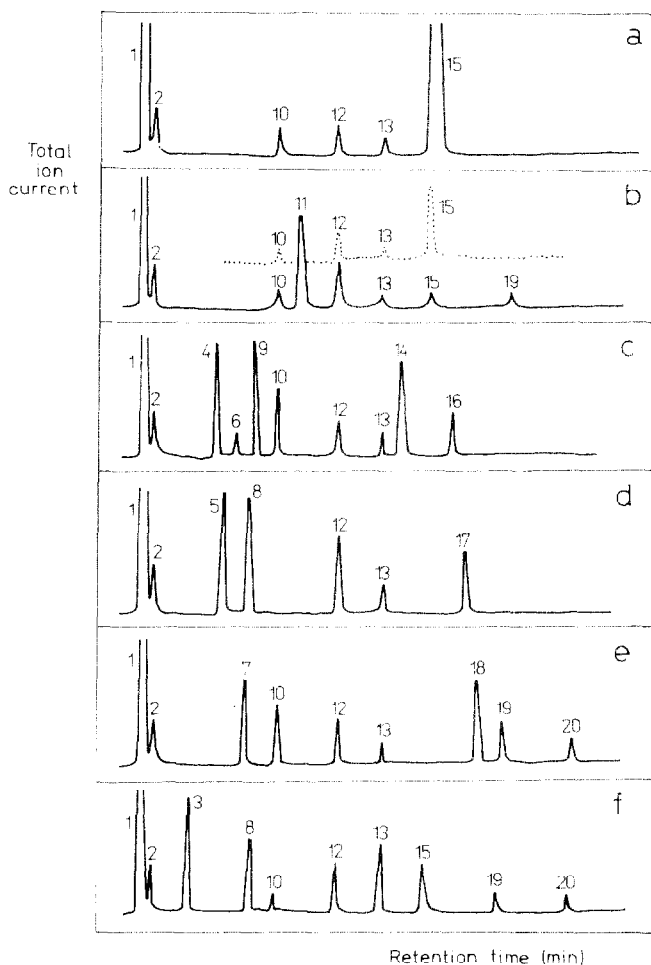
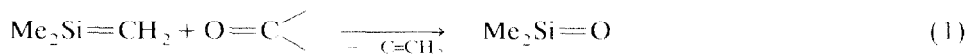


Fig. 1. GC/MS traces of the mixtures obtained upon laser irradiation of DMSCB (1.3 kPa)— $\text{SF}_6$  (1.3 kPa)—monomer (2.7 kPa) after disappearance of 90–100 and 50% of the DMSCB and the monomer respectively. (a) monomer absent; (b)–(f) relate, in the given order, to MA, VA, AME, AC and MVE. Dotted line refers to DMSCB (2.6 kPa)— $\text{SF}_6$  (1.3 kPa)—MA (1.3 kPa). Conditions: column, 3 m, packed with SE-30 silicon elastomer, temperature 10–150°C programmed over 20 min. Peak identification: 1,  $\text{SF}_6$ ; 2,  $\text{C}_2\text{H}_2$ ; 3, MVE +  $\text{CH}_3\text{CH}_2\text{CHO}$ ; 4,  $\text{CH}_3\text{COCH}_3$ ; 5, AME; 6,  $(\text{CH}_3)_3\text{SiOH}$ ; 7, AC; 8,  $(\text{CH}_3)_3\text{SiOCH}_3$ ; 9, VA; 10,  $(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$ ; 11, MA; 12, DMSCB; 13,  $[(\text{CH}_3)_2\text{Si}]_2\text{O}$ ; 14,  $(\text{CH}_3)_3\text{SiOC}(\text{CH}_3)=\text{CH}_2$ ; 15, TMDCB; 16,  $(\text{CH}_3)_3\text{SiOCOCH}_3$ ; 17,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{OCH}_3$ ; 18,  $(\text{CH}_3)_2\text{SiOCH}=\text{CHCH}_2\text{CH}_3$ ; 19,  $[(\text{CH}_3)_2\text{SiO}]_3$ ; 20,  $[(\text{CH}_3)_2\text{SiO}]_4$ .

addition [30] of acetone (product of VA decomposition) to DMS, and 1,1-dimethyl-1-sila-2-oxa-3-cyclohexene ( $m/z$ , relative intensity: 128 ( $M$ , 36), 113 ( $M - 15$ , 100), 111 (35), 85 (25), 75 (35) 72 (13), 59 (27), 45 (43), 43 (44), 39 (20), 29 (20), 27 (26)), the formation of which can be attributed to [31] a direct [2 + 4]-cycloaddition of AC to DMS.

Intermediate formation of dimethylsilanone  $(\text{CH}_3)_2\text{Si}=\text{O}$  via addition of carbonyl compounds to DMS (eq. 1):



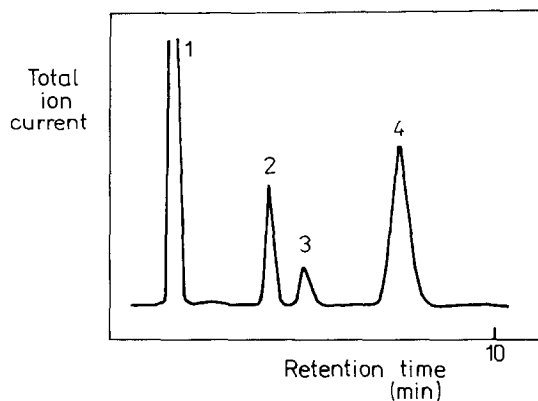
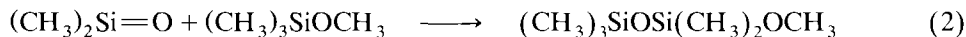


Fig. 2. GC/MS trace of the mixture obtained after laser irradiation of  $C_2H_4$  (6.7 kPa)— $SF_6$  (4 kPa)— $(CH_3)_3SiOH$  (1.3 kPa) with 10 W laser output for 5 min. Conditions: column, 3 m, packed with SE-30 silicon elastomer, temperature  $30^\circ C$ , injector temperature  $40^\circ C$ . Peak identification: 1,  $SF_6 + C_2H_4$ ; 2,  $(CH_3)_3SiOH$ ; 3,  $(CH_3)_3SiOC_2H_5$ ; 4  $[(CH_3)_3Si]_2O$ .

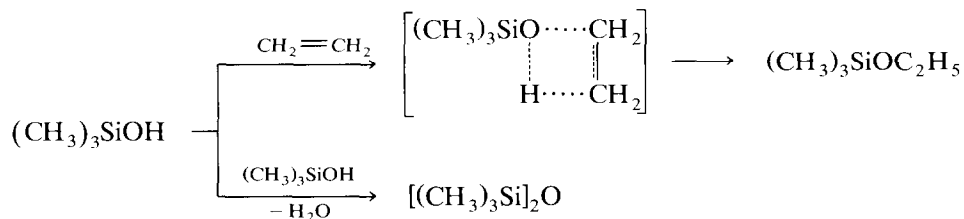
is followed by its cyclooligomerization: both trimer and tetramer  $(Me_2SiO)_n$  ( $n = 3, 4$ ) were identified in the gas phase. Another possible reaction of the silanone is addition to methoxytrimethylsilane, which was also detected among the volatile products. Silanones are known [2] to undergo addition of oxygen nucleophiles, and the assumed reaction of  $Me_2Si=O$  and  $Me_3SiOMe$  leading to the observed methoxypentamethyldisiloxane ( $m/z$ , intensity: 163 ( $M - 15$ , 100), 133 (98), 129 (23), 73 (20), 59 (31)) is an example of such an addition (eq. 2):



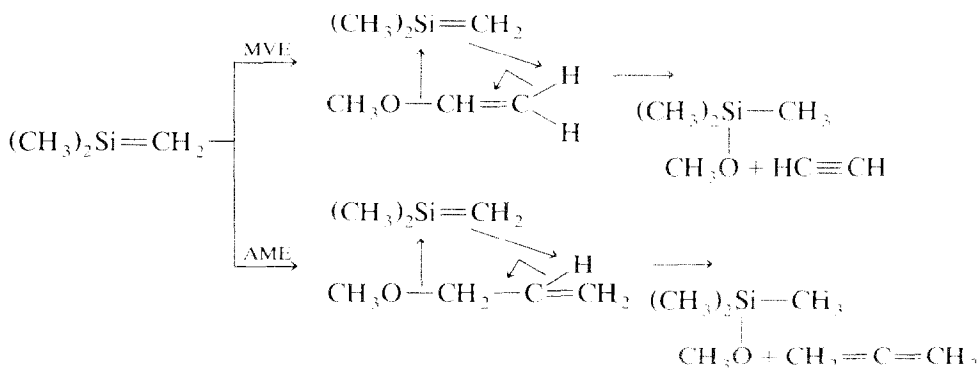
Formation of ethoxytrimethylsilane can be attributed to reaction of trimethylsilanol with ethene. Ethene is produced by decomposition of DMSCB, and trimethylsilanol could be formed only by reaction of dimethylsilane with traces of water [1]. This view is in accord with the results of the irradiation of mixtures  $Me_3SiOH$  (1.3 kPa)— $SF_6$  (1.3–4.0 kPa)— $C_2H_4$  (1.3–6.7 kPa) which show formation of ethoxytrimethylsilane and hexamethyldisiloxane (Fig. 2).

This previously unreported gas-phase addition of silanol to alkene under homogeneous conditions probably proceeds via a four-centered transition state (Scheme 2). The reaction is of interest in that no catalyst is needed, as it is for well-known electrophilic or nucleophilic additions of alcohols to olefins.

Methoxytrimethylsilane was observed only after the irradiation of mixtures of DMSCB— $SF_6$ —MVE and DMSCB— $SF_6$ —AME. It is tempting to assume that this



Scheme 2



Scheme 3

compound arises by reaction of both methyl ethers with dimethylsilene, as depicted in Scheme 3.

The mechanism of this type of reaction could involve nucleophilic attack by oxygen of silicon and abstraction of hydrogen from  $sp^2$ -hybridized carbon in a sterically-feasible 6-membered cyclic transition state. Its occurrence would be supported by observation of the presence of ethyne and propadiene among the reaction products. Ethyne was observed in most LP runs, but propadiene was not, presumably because of its high reactivity in polymerization reactions. The appearance of  $[(\text{CH}_3)_2\text{SiO}]_n$  where  $n = 3, 4$  and of  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{OCH}_3$  upon irradiation of DMSCB-SF<sub>6</sub>-MVE (or AME) confirms the transient formation of  $(\text{CH}_3)_2\text{Si}=\text{O}$  and its cyclodimerization and its insertion into  $(\text{CH}_3)_3\text{SiOCH}_3$  (eq. 2). In addition to these products, formation of  $(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{OCH}_3$  might also have been expected, since DMS is known [32,33] to add regiospecifically to the silicon-oxygen bond of  $(\text{CH}_3)_3\text{SiOCH}_3$ . The absence of this compound indicates that reactions of DMS with RCHO (R = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>; products of MVE and AME decomposition) to yield  $(\text{CH}_3)_2\text{Si}=\text{O}$  and some more complex processes giving  $[(\text{CH}_3)_2\text{Si}]_2\text{O}$  are preferred.

Polymerization reactions taking place in the system appear to involve mainly dimethylsilanone. Neither direct trapping of DMS by cyclic siloxanes [1,2] nor reactions of DMS with monomers leading to polymers can be excluded. Solid or viscous involatile materials were observed from all monomers, but their yields were highest with MA and MMA. Infrared spectra of all the deposits on NaCl windows of the reactor show absorption bands at 800–850  $\text{cm}^{-1}$  ( $\nu(\text{Si}-\text{C})$  and  $\rho(\text{CH}_3)$ ), 950, 1030–1130 ( $\nu(\text{SiOSi})$ ,  $\nu(\text{SiOC})$ , or  $\nu(\text{SiCH}_2\text{Si})$ ), 1280–1285 ( $\delta_s(\text{CH}_3\text{Si})$ ),  $\sim 1400$  ( $\delta_{as}(\text{CH}_3\text{Si})$ ) and 2950–3000  $\text{cm}^{-1}$  ( $\nu(\text{CH})$ ) and indicate polysiloxane structures. With MA, MMA and VA, the polymeric deposits also show absorptions at  $\sim 1750$   $\text{cm}^{-1}$  arising from the  $\nu(\text{C}=\text{O})$  vibration.

The formation of polymeric and that of volatile products apparently compete, and their relative importance varies from monomer to monomer. Figure 1 (a and b) reveals the preponderance of the cyclodimer when DMSCB is in excess, and also shows that there is a very low concentration of gaseous organosilicon products when MA predominates in the initial DMSCB-SF<sub>6</sub>-MA mixture. The ratio of consumed DMSCB to MA approaches 1 when MA content of the initial mixture is increased (Fig. 3). These facts are consistent with the view that DMS and MA



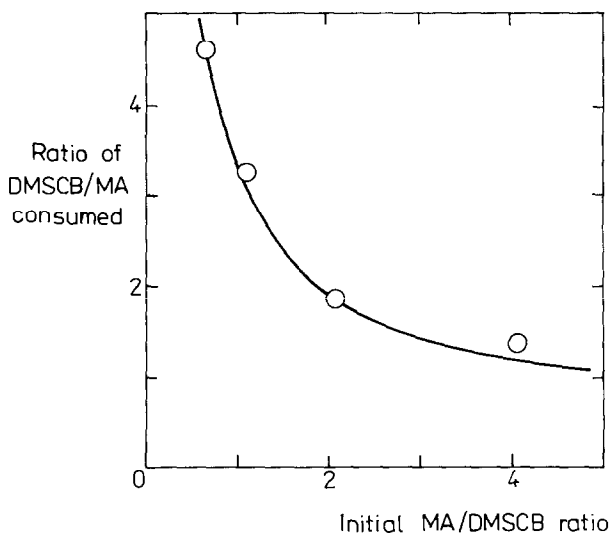


Fig. 3. Plot of the ratio of DMSCB/MA consumed against the initial MA/DMSCB ratio in DMSCB (1.3–4 kPa)—SF<sub>6</sub> (1.3 kPa)—MA (1.3–6.7 kPa) mixtures at DMSCB depletion 70–80%.

react with each other in a copolymerization reaction. The IR spectrum of the deposit (Fig. 4) shows an absorption at 1760 cm<sup>-1</sup> ( $\nu(\text{C}=\text{O})$ ), keeping in line with the assumption that this copolymerization involves 1,2-addition (eq. 3):

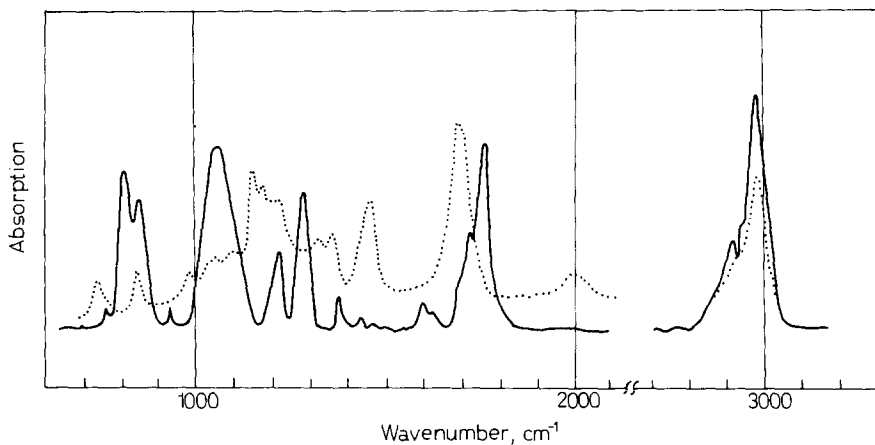
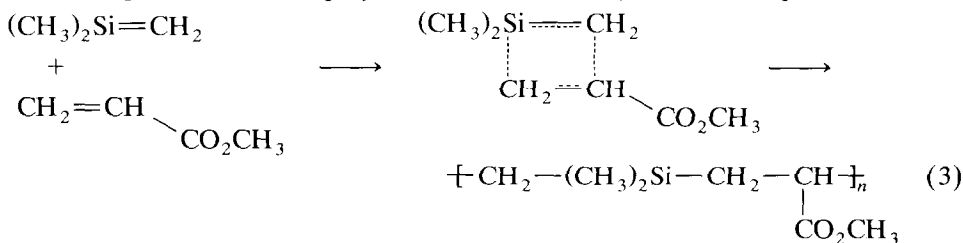


Fig. 4. Infrared spectrum of the deposit formed from DMSCB-SF<sub>6</sub>-MA mixture (solid curve) and poly(methylacrylate) (dotted curve, Ref. 34).

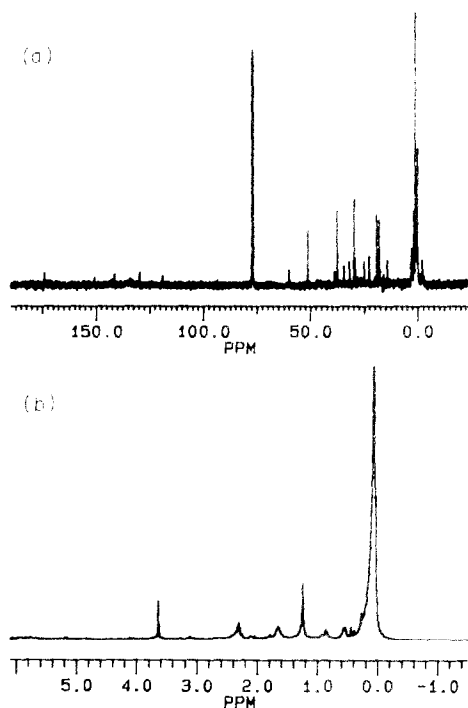


Fig. 5.  $^{13}\text{C}$  (a) and  $^1\text{H}$  (b) NMR spectrum of the deposit obtained upon irradiation of DMSCB- $\text{SF}_6$ -MA mixture.

A strong and broad band at  $1080\text{ cm}^{-1}$  can be attributed to  $\nu(\text{SiOC})$  and/or  $\nu(\text{SiOSi})$  vibrations, and implies that the 1,2-addition is not the only polymerization process. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the isolated polymer (see Fig. 5) show that the most important proton resonances are those arising from  $\text{COOCH}_3$  ( $\delta = 3.63$ ) and  $\text{Si-CH}_3/\text{Si-CH}_2$  groups ( $\delta = 0.02\text{--}0.29$ ). In case of a pure polymer of the type  $\text{[-CH}_2\text{-(CH}_3\text{)}_2\text{Si-CH}_2\text{CH(COOCH}_3\text{)]}_n$ , the intensity ratio for these signals should be 3/10, but it is clear from the spectrum that the intensity of the  $\text{Si-CH}_3/\text{Si-CH}_2$  signals is much greater. Signals between  $\delta\ 0.5\text{--}2.4$  correspond to various  $\text{CH}_2$  and  $\text{CH}$  groups. In the  $^{13}\text{C}$  NMR spectrum, the signals of  $\text{COOCH}_3$  groups ( $\delta = 174.0$  and  $51.3$ ) are typical of a methoxycarbonyl group in polyacrylates [35]. Several types of  $\text{Si-CH}_3/\text{Si-CH}_2$  signals can be seen in Fig. 5a.  $^{13}\text{C}$  chemical shifts close to 0 (Ref. 36). Weak signals from 118.7 to 150.6 ppm are consistent with carbons in unsaturated systems but not those of the starting methyl acrylate. In agreement with these findings, NMR measurements reveal that 1,2-addition is not the only polymerization pathway.

The deposits are soluble in organic solvents, and analysis by gel-permeation chromatography reveals a broad molecular weight distribution (Fig. 6). Scanning electron microscopy reveals that they have a smooth surface, with only a small number of separate solid particles, after the irradiation of DMSCB- $\text{SF}_6$ -MA. The processes occurring upon the irradiation of DMSCB- $\text{SF}_6$ -monomer mixtures are consistent with polymer structures composed of various units as  $(\text{CH}_3)_2\text{SiO}$ ,  $(\text{CH}_3)_2\text{SiCH}_2$  and  $(\text{CH}_3)_2\text{SiCH}_2\text{-C(O-)}$ . The appearance of separate polymer

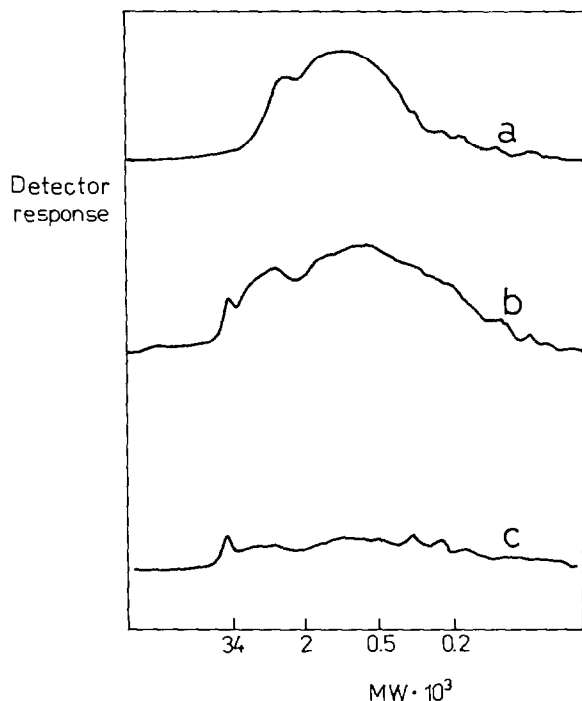


Fig. 6. Elution profile in gel permeation chromatography of polymeric deposits obtained upon irradiation of DMSCB-SF<sub>6</sub>-monomer. a-c are related to MA, VA and AME, respectively.

particles suggests that polymerization occurs in the gas phase, and ceases after deposition on reactor surface. The very minor proportion of these particles and the predominance of a continuous smooth pattern of the deposited material seems to indicate [37] that the deposited material tends to undergo further polymerization.

Although laser photopolymerization in the liquid phase in the presence of the radiation-absorbing photoinitiators [38] is a well-known phenomenon, polymerization of common monomers by CO<sub>2</sub> laser irradiation cannot be induced [39] in the gas phase owing to the high ceiling temperature and thermodynamically-precluded chain growth. The results reported above show that laser heating of some monomers with DMSCB can be used as an efficient way for bringing about gas-phase deposition of organosilicon polymers, arising from a variety of chemical reactions of DMS with these monomers and with the products of their thermal decomposition.

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