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Decomposition of Di-*tert*-butyl Peroxide in Siloxane: An Approach of the Free Radical Cross-Linking of Silicones

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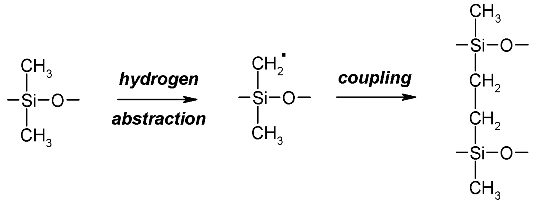
ABSTRACT: The decomposition of di-*tert*-butyl peroxide (TBP) in hexamethyldisiloxane (SiH), in the presence and the absence of pentamethylvinyldisiloxane (Vi), was studied with different relative ratios of reactants. The identification of the numerous products generated during these decompositions was performed, allowing to suggest free radical and carbene reactions to account for their formation. The mechanisms advanced in the literature, to explain the cross-linking of silicones, were compared to the ones proposed for the formation of the products of the above reactions in order to confirm or to exclude the involvement of such chemical reactions in the cross-linking. This allowed the selection of the mechanism proposed by Dunham et al. and the rejection of the one of Bork and Roush. From these analyses, an explanation of the classification of this peroxide in the family of "vinyl specific peroxides" can be given.

Introduction

Silicone rubbers are very important materials because of their unique properties[1] such as thermal stability, electric insulation capacity, hydrophobic nature, etc. They are generally produced from linear macromolecules which are cross-linked to get elastomeric materials. In 1948, Wright and Oliver[2] discovered the possibility of such a transformation by the decomposition of peroxides. For this purpose, the main peroxides used are classified in two families:[3−5] (i) "vinyl groups specific peroxides" mainly constituted of dialkyl peroxides which are unable to cross-link poly(dimethylsiloxane)s (PDMS) but poly(methylvinylsiloxane)s (PMVS) because they contain vinyl groups on the chain;[6] (ii) "vinyl groups nonspecific peroxides" corresponding to the family of diaroyl peroxides because they can be used to cross-link PDMS whether they contain vinyl groups or not.[3,7]

This "peroxidic" cross-linking of the PDMS was explained by some propositions of mechanisms reported in the numerous literature surveys on this topic.[3,7−9] Loan[10] asserted that a creation of such a link between two chains resulted from the coupling of radicals generated by abstraction of hydrogen atoms from two methyl groups bearing to different chains (Scheme 1). He attributed the ineffectiveness of dialkyl peroxides to their inability to produce radicals attacking such hydrogen atoms sufficiently rapidly. This was confirmed by Dluzneski,[5] who reached the same conclusion comparing the energies of generated and broken bonds. Considering the high efficiency of alkoxy radicals to abstract a hydrogen atom,[11,12] it was difficult for us to accept this conclusion. The lack of knowledge on the free radical reactions occurring during the decomposition of peroxides in siloxanes prompted us to start such a study.

Scheme 1. Mechanism of Cross-Linking of PDMS



This work began with a differential scanning calorimetry (DSC) analysis of the decomposition of several peroxides in PDMS and siloxanes to define the best model of PDMS for the study of the free radical reactions on these compounds.[13] Octamethylcyclotetrasiloxane (D_4) was thus selected, and the analysis of the reaction products, generated by the TBP decomposition in it, was performed. Besides the reaction products arising from the peroxide (*tert*-butyl alcohol, acetone, and 2,2-dimethyloxirane), the dehydrodimer of D_4 was identified with a modest yield relative to peroxide (7%). However, the main compounds produced in the reaction were present in the residue of distillation which was very difficult to analyze. By reproducing the reaction in the presence of 2,2,5,5-tetramethylpiperidinyloxyl (TEMPO), it was proved that these high boiling products were originated from the free radicals generated by hydrogen abstraction from D_4. Taking into account the difficulty to identify these high molecular compounds, we decided to replace D_4 by hexamethyldisiloxane (SiH). Because of the presence of a single type of methyl and its low boiling point, SiH was chosen as a model of PDMS, even if it does not contain the repetitive unit ($-SiMe_2O-$). The classification of TBP in the family of "vinyl specific peroxides" prompted us to extend the study of the decomposition of this peroxide in SiH in the presence of pentamethylvinyldisiloxane (Vi) to analyze the difference of behavior regarding the radicals arising from the siloxane.

Experimental Part

Instead of naming the numerous compounds obtained in the various reactions by a number, we decided, to have in mind their formula more easily, to consider their constitution and their origin based on the starting molecules (SiH and Vi), e.g., Si_2 for the dehydrodimer of SiH, SiViMe and SiViH for the products resulting from the addition of a pentamethyldisiloxanylmethyl radical ($Si^\bullet$) to the vinylsiloxane (Vi) followed respectively by the coupling with a methyl radical ($Me^\bullet$) or by a hydrogen transfer (H). This was completed by the adjunction of subscripts L for linear, U for unsaturated, c for cyclic, b for branched (Si or C to indicate where was the branching), and

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UC for unsaturated resulting from a rearrangement of a cyclopropane. PMS represents the pentamethyldisiloxanyl substituent.

Materials. TBP, 1,2-bis(chlorodimethylsilyl)ethane, chlorotrimethylsilane, Vi, and TEMPO were purchased from Aldrich, SiH was from Avocado, and (dichloromethyl)dimethylchlorosilane was from Lancaster. 2,2,6,6-Tetramethylpiperidinyloxymethane (Me-TEMPO) was synthesized as previously described.[13]

Analytical Techniques. *Gas Chromatography (GC).* GC analyses were performed on a Varian 3400 with a FID detector (detector temperature 250 °C and injector temperature 220 °C) fitted with a computer running Star Chromatography software. The apparatus was equipped with a CP-SIL 5CB column (30 m length, 0.25 mm inside diameter, 0.25 μm internal phase thickness, pressure 10 psi, nitrogen gas carrier). It was used to identify (by comparison with standards) and to determine the amounts of products arising from the thermal decomposition of the peroxy derivatives in SiH. The titrations of "dimer", "trimers", and "tetramers" of SiH were performed using calibration graphs reported in the Supporting Information. The titrations of the various products generated in the reactions performed in the presence of Vi were based on approximations of the response coefficients (similar values for: MeViH and Vi; SiViH, SiViMe, MeViSi, MeVi$_2$H and Si$_2$; SiViSi, Si$_2$ViH, SiVi$_{UC}$, SiVi$_{2U}$, SiVi$_2$H, SiVi$_2$Me, and trimers; SiVi$_{2UC}$, SiVi$_2$Si, and tetramers).

Mass Spectrometry (GC/MS). GC/MS studies were performed on a Thermoquest Trace GC apparatus, running a Excalibur software, and equipped with a DB5 column (5% Ph, 30 m length, 0.25 mm inside diameter, 0.25 μm internal phase thickness, pressure 10 psi nitrogen gas carrier).

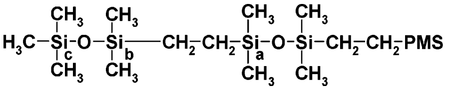
Size Exclusion Chromatography (SEC). Molecular weight and molecular weight distribution of polymers were measured by SEC at 35 °C on a system equipped with a guard column and two 10 μm mixed B columns (Polymer Laboratories) with toluene as eluent at 1 mL min^{-1}. A triple SEC detector (model TDA 302, Viscotek) with RALLS, differential refractometer, and viscosimeter in series was used to analyze samples. The data obtained were treated with OmniSEC software (Viscotek).

Nuclear Magnetic Resonance (NMR). NMR spectra (^{1}H, ^{13}C, and DEPT) were recorded with Bruker AC 250 (250 MHz for ^{1}H and 62.9 MHz for ^{13}C) and DPX 300 (300 MHz for ^{1}H, 75.4 MHz for ^{13}C, and 59.6 MHz for ^{29}Si INEPT). The solvent was CDCl$_3$, and chemical shifts are reported relative to tetramethylsilane.

Reference Product Syntheses. H[CH$_2$–SiMe$_2$–O–SiMe$_2$–CH$_2$]$_n$H with $n = 2-4$.[14] A solution of 1,2-bis(chlorodimethylsilyl)ethane (0.06 mol, 12.9 g) in anhydrous ether (50 mL) and chlorotrimethylsilane (0.36 mol, 39.5 g) were simultaneously added to 150 mL of distilled water in a 250 mL tricol. After stirring for 3 h, the two phases were separated. The aqueous layer was extracted three times with 40 mL of ether. The organic phases were then washed with a saturated solution of K$_2$CO$_3$ (2 × 20 mL) and brine. After drying over anhydrous magnesium sulfate, the solvent and SiH were evaporated under reduced pressure, and the products were distilled giving three fractions: (i) F1: Eb$_{10Hgmm}$ = 95–100 °C, m = 6.6 g, Si$_2$; (ii) F2: Eb$_{0.5Hgmm}$ = 140 °C, m = 6 g, mixture of Si$_{3L}$ and Si$_{3c}$; (iii) F3: Eb$_{0.01Hgmm}$ = 160 °C, m = 2.5 g, Si$_{4L}$ and Si$_{4c}$.

$PMS-CH_2-CH_2-PMS$, **Si$_2$**, *322 g/mol*

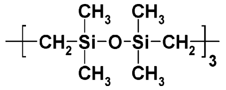
^{1}H NMR (300 MHz, CDCl$_3$, δ ppm): 0.4 (s, 4H, CH$_2$); 0.06 (s, 18H, Si(CH$_3$)$_3$); 0.03 (s, 12H, Si(CH$_3$)$_2$). ^{13}C NMR (75.4 MHz, CDCl$_3$, δ ppm): 9.5 (CH$_2$); 1.9 (Si(CH$_3$)$_3$); −0.5 (Si(CH$_3$)$_2$). ^{29}Si NMR (59.6 MHz, CDCl$_3$, δ ppm): 8.4 (Si–(CH$_3$)$_2$); 7 (Si–(CH$_3$)$_3$). GC/MS (m/z, intensity): 322 (1); 307 (9); 219 (13); 160 (19); 148 (26); 147 (100); 145 (35); 131 (7); 117 (7); 73 (34).



$H_3C-\underset{c}{Si}(CH_3)_2-O-\underset{b}{Si}(CH_3)_2-CH_2-CH_2-\underset{a}{Si}(CH_3)_2-O-Si(CH_3)_2-CH_2-CH_2-PMS$

, **Si$_{3L}$**, *482 g/mol*

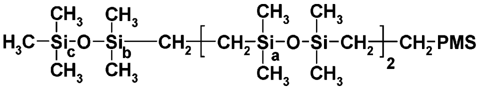
^{1}H NMR (300 MHz, CDCl$_3$, δ ppm): 0.43 (s, 8H, CH$_2$); 0.08 (s, 18H, Si(CH$_3$)$_3$); 0.06 (s, 24H, Si(CH$_3$)$_2$). ^{13}C NMR (75.4 MHz, CDCl$_3$, δ ppm): 10 (CH$_2$); 2.3 (Si(CH$_3$)$_3$); −0.1 (Si(CH$_3$)$_2$). ^{29}Si NMR (59.6 MHz, CDCl$_3$, δ ppm): 8.5 (Si$_b$–(CH$_3$)$_2$); 8.1 (Si$_a$–(CH$_3$)$_2$); 6.9 (Si$_c$–(CH$_3$)$_3$). GC/MS (m/z, intensity): 482 (1); 467 (1); 309 (12); 308 (23); 307 (71); 305 (7); 233 (23); 221 (8); 220 (11); 219 (50); 191 (7); 160 (6); 149 (13); 148 (27); 147 (100); 145 (44); 133 (6); 117 (12); 73 (67).



$\left[-CH_2-Si(CH_3)_2-O-Si(CH_3)_2-CH_2-\right]_3$

, **Si$_{3c}$**, *480 g/mol*

GC/MS (m/z, intensity): 480 (8); 465 (9); 307 (19); 306 (32); 305 (100); 291 (12); 277 (10); 247 (11); 233 (31); 231 (14); 220 (10); 219 (43); 218 (16); 217 (25); 203 (10); 191 (16); 159 (9); 147 (43); 145 (67); 133 (16); 131 (11); 119 (16); 117 (31); 85 (15); 73 (96); 59 (14); 44 (31); 40 (10).

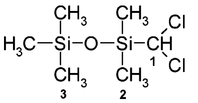


$H_3C-\underset{c}{Si}(CH_3)_2-O-\underset{b}{Si}(CH_3)_2-CH_2-\left[CH_2-\underset{a}{Si}(CH_3)_2-O-Si(CH_3)_2-CH_2\right]_2-CH_2-PMS$

, **Si$_{4L}$**, *642 g/mol*

^{1}H NMR (300 MHz, CDCl$_3$, δ ppm): 0.44 (s, 12H, CH$_2$); 0.09 (s, 18H, Si(CH$_3$)$_3$); 0.07 (s, 36H, Si(CH$_3$)$_2$). ^{13}C NMR (75.4 MHz, CDCl$_3$, δ ppm): 10 (CH$_2$); 2.3 (Si(CH$_3$)$_3$); −0.05 (Si(CH$_3$)$_2$). ^{29}Si NMR (59.6 MHz, CDCl$_3$, δ ppm): 8.3 (Si$_b$–(CH$_3$)$_2$); 8.12 (Si$_a$–(CH$_3$)$_2$); 6.9 (Si$_c$–(CH$_3$)$_3$). GC/MS (m/z, intensity): 627 (1); 467 (6); 307 (44); 291 (3); 233 (62); 191 (5); 147 (100); 145 (42); 131 (5); 117 (8); 73 (51).

Synthesis of 1,1-Dichloromethyl-1,1,3,3,3-pentamethyldisiloxane (PMS–CHCl$_2$). A solution of chlorotrimethylsilane (0.3 mol, 32.5 g) and of (dichloromethyl)dimethylchlorosilane (0.1 mol, 17.8 g) in anhydrous ether (50 mL) was slowly added to 50 mL of distilled water in a 250 mL tricol. After stirring for 4 h at room temperature, the two phases were separated. The aqueous layer was extracted three times with 15 mL of ether. The organic phases were then washed with a saturated solution of K$_2$CO$_3$ (2 × 20 mL) and brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated under reduced pressure. A distillation step allowed us to recover the desired product PMSCHCl$_2$ (Eb$_{20Hgmm}$ = 65 °C), with a yield of 60%.

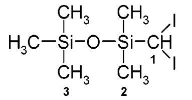


$H_3C-Si(\underset{3}{CH_3})_2-O-Si(\underset{2}{CH_3})_2-\underset{1}{CH}Cl_2$

, *230 g/mol*

^{1}H NMR (250 MHz, CDCl$_3$, δ ppm): 5.2 (s, 1H, CH); 0.29 (s, 6H, Si(CH$_3$)$_2$); 0.13 (s, 9H, Si(CH$_3$)$_3$). ^{13}C NMR (62.9 MHz, CDCl$_3$, δ ppm): 62.6 (C$_1$); 1.97 (C$_3$); −2.69 (C$_2$). ^{29}Si NMR (59.6 MHz, CDCl$_3$, δ ppm): 10.88 (Si–(CH$_3$)$_2$); −0.78 (Si–(CH$_3$)$_3$).

Synthesis of 1,1-Diiodomethyl-1,1,3,3,3-pentamethyldisiloxane (PMS–CHI$_2$). A solution of PMS–CHCl$_2$ (0.02 mol, 4.6 g) and sodium iodide (0.12 mol, 18 g) in acetone (50 mL) was prepared and poured into a 300 mL PARR 4766 stainless steel autoclave, equipped with an ACIM 300 oven with a temperature control. This was then heated at 100 °C for 48 h. After the reaction, 30 mL of diethyl ether was added. The solution was then filtered to eliminate the sodium chloride formed and washed with a solution of sodium thiosulfate in order to remove the iodine produced. The aqueous phase was extracted three times with 15 mL of ether. The combined organic phases were dried over anhydrous magnesium sulfate. Solvents (acetone and ether) were evaporated under reduced pressure. The crude product was distilled with a B-580 Bucchi tubular oven. The desired product, PMSCHI$_2$ (Eb$_{20Hgmm}$ = 95°C) was recovered (m = 5 g), with a yield of 60%.



$H_3C-Si(\underset{3}{CH_3})_2-O-Si(\underset{2}{CH_3})_2-\underset{1}{CH}I_2$

, *414 g/mol*

^{1}H NMR (250 MHz, CDCl$_3$, δ ppm): 4.3 (s, 1H, CH); 0.3 (s, 6H, Si(CH$_3$)$_2$); 0.1 (s, 9H, Si(CH$_3$)$_3$). ^{13}C NMR (62.9 MHz,

$CDCl_3$, δ ppm): 2.29 (C3); −2.11 (C2); −35 (C1). ^{29}Si NMR (59.6 MHz, $CDCl_3$, δ ppm): 10.1 (Si−$(CH_3)_2$); 1.39 (Si−$(CH_3)_3$). GC/MS (*m/z*, intensity): 414 (1); 399 (13); 371 (24); 259 (5); 243 (3); 229 (5); 185 (9); 147 (100); 133 (10); 122 (18); 117 (6); 73 (20); 59 (9); 44 (28).

Decomposition of TBP in SiH. The decomposition of TBP (*x* mmol) in SiH (*y* mmol) was performed at 165 °C (heated for 8 h) in a 300 mL PARR 4766 stainless steel autoclave equipped with an ACIM 300 oven with a temperature control. After the reaction, the SiH was eliminated under reduced pressure, and the remaining products were separated by distillation with a B-580 Bucchi tubular oven; a residue and the three fractions were obtained: (i) F1: Eb$_{4Hgmm}$ = 100−120 °C, mixture of Si$_2$, Si$_{2U}$, and Si$_2$Me. (ii) F2: Eb$_{0.5Hgmm}$ = 140 °C, mixture of Si$_{3bC}$, Si$_{3L}$, Si$_{3bSi}$, and Si$_{3UC}$. (iii) F3: Eb$_{0.01Hgmm}$ = 160 °C, mixture of Si$_{3bC}$ and isomers of Si$_{4L}$.

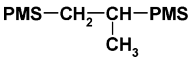
Reaction with a ratio TBP/SiH = 1/6.7: TBP (*x* = 20 mmol) and SiH (*y* = 133 mmol); F1 + F2 + F3 = 1.95 g, residue R1 = 0.98 g.

Reaction with a ratio TBP/SiH = 1/220: Distillation of the mixture obtained by the combination of four batches performed with the following amounts of TBP (*x* = 5 mmol) and SiH (*y* = 1100 mmol); F1 + F2 + F3 = 0.8 g, no residue.

The identifications of the various reaction products were generally based on analyses (NMR, GC/MS) of the various distillation fractions. The GC titrations of the various compounds in the reaction mixture for the reaction with a ratio 1/6.7 were performed from samples obtained by the decomposition in an ampulla of a solution of TBP (1 mmol) in SiH (6.7 mmol). In the case of the more dilute solution, the titration was directly performed on the reaction mixture from the autoclave. In each case, a known amount of nonane was directly added as standard to a known quantity of sample.

PMS−CH=CH−PMS , **Si$_{2U}$**, *320 g/mol*

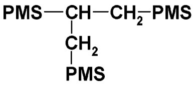
^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 5.8 (s, 2H, CH); 0.06−0 (m, $SiCH_3$). ^{13}C NMR (62.9 MHz, $CDCl_3$, δ ppm): 138 (CH); 1.9 ($Si(CH_3)_3$); −0.5 ($Si(CH_3)_2$). GC/MS (*m/z*, intensity): 320 (1); 305 (18); 217 (26); 148 (15); 147 (100); 143 (7); 133 (5); 131 (5); 73 (39); 44 (27); 40 (43).



$\text{PMS}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{PMS}$

, **Si$_2$Me**, *336 g/mol*

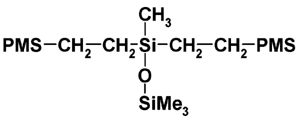
GC/MS (*m/z*, intensity): 321 (3); 233 (2); 205 (3); 174 (11); 148 (15); 147 (100); 133 (29); 131 (5); 73 (21); 44 (6); 40 (9).



$\text{PMS}-\underset{\underset{\text{PMS}}{\text{CH}_2}}{\text{CH}}-\text{CH}_2-\text{PMS}$

, **Si$_{3bC}$**, *482 g/mol*

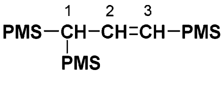
^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 0.9 (m, 1H, CH); 0.8−0.5 (m, 4H, CH_2); 0.06−0 (m, Si−CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$, δ ppm): 21 (CH_2); 15 (CH); 1.9 ($Si(CH_3)_3$); −0.5 ($Si(CH_3)_2$). ^{29}Si NMR (59.6 MHz, $CDCl_3$, δ ppm): 8.4 (Si−$(CH_3)_2$); 7 (Si−$(CH_3)_3$). GC/MS (*m/z*, intensity): 482 (1); 467 (2); 335 (4); 305 (3); 221 (8); 205 (5); 173 (32); 172 (10); 157 (7); 149 (7); 148 (15); 147 (100); 133 (5); 131 (6); 73 (25).



$\text{PMS}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{\underset{\text{SiMe}_3}{\text{O}}}{\text{Si}}}-\text{CH}_2-\text{CH}_2-\text{PMS}$

, **Si$_{3bSi}$**, *482 g/mol*

GC/MS (*m/z*, intensity): 482 (1); 467 (23); 305 (14); 277 (15); 231 (8); 221 (13); 217 (7); 207 (6); 205 (6); 157 (11); 149 (7); 148 (15); 147 (100); 133 (9); 117 (3); 73 (45); 44 (52); 40 (75).



$\text{PMS}-\overset{1}{\underset{\text{PMS}}{\text{CH}}}-\overset{2}{\text{CH}}=\overset{3}{\text{CH}}-\text{PMS}$

, **Si$_{3UC}$**, *480 g/mol*

^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 6 (m, 1H, =CH−C); 5.3 (d, 1H, =CH−Si); 1.3 (d, 1H, −CH); 0.06−0 (m, Si−CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$, δ ppm): 145 (C_2); 128 (C_3); 36 (C_1); 0−2 (Si−CH_3). GC/MS (*m/z*, intensity): 480 (1); 465 (8); 319 (8); 318 (25); 303 (24); 289 (17); 232 (10); 231 (21); 230 (69); 229 (24); 223 (9); 222 (16); 221 (67); 217 (13); 216 (21); 215 (72); 207 (10); 205 (11); 189 (24); 158 (21); 157 (46); 156 (87); 149 (57); 148 (64); 147(100); 133 (26); 131 (49); 117 (19); 75 (20); 74 (34); 73 (86); 59 (19); 45 (18).

Decomposition of TBP in SiH in the Presence of Vi. The decomposition of TBP (*x* mmol) in a mixture of Vi (*z* mmol) and of SiH (*y* mmol) was performed at 165 °C (8 h of heating) in a 300 mL PARR 4766 stainless steel autoclave equipped with an oven ACIM 300 with a temperature control. After the reaction, the SiH was eliminated under reduced pressure, and the remaining products were separated by distillation with a B-580 Bucchi tubular oven, giving a residue and the following fractions: (i) F1: Eb$_{4Hgmm}$ = 110−130 °C, mixture of Si$_2$, SiViH, SiViMe, MeSiVi, and MeVi$_2$H; (ii) F2: Eb$_{0.5Hgmm}$ = 140 °C, mixture of SiVi$_{UC}$, SiVi$_{2U}$, SiVi$_2$H, Si$_2$ViH, and/or SiViSi; (iii) F3: Eb$_{0.01Hgmm}$ = 160 °C, mixture of SiVi$_{2UC}$ and SiVi$_2$Si.

Reaction with TBP/SiH/Vi: 1/6.7/0.67 mmol. From 20 mmol of TBP: F1 + F2 + F3 = 2.51 g, residue R3 = 2.74 g.

Reaction with TBP/SiH/Vi: 0.67/6.7/0.67 mmol. From 20 mmol of TBP: F1 + F2 + F3 = 1.65 g; residue R5 = 2.98 g.

Reaction with TBP/SiH/Vi: 0.067/6.7/0.67 mmol. From 20 mmol of TBP: F1 + F2 + F3 = 9.1 g; residue R6 = 2.94 g.

Reaction with TBP/SiH/Vi: 1/220/0.67 mmol. From 20 mmol of TBP: F1 + F2 + F3 = 2.38 g; residue R7 = 1.06 g.

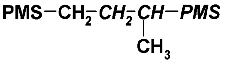
The identification of the different reaction products was generally realized from analyses (NMR, GC/MS) of the distillation fractions. The GC titrations of the various compounds present in the different reaction mixtures were carried out as in the experiments involving only TBP and SiH.

H_3C−*CH_2−CH_2−PMS* , **MeViH**, *190 g/mol*

GC/MS (*m/z*, intensity): 190 (0.7); 175 (7); 147 (100); 133 (58); 131 (5); 117 (4); 73 (15); 66 (13); 59 (9); 45 (4).

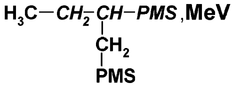
PMS−CH_2−CH_2−CH_2−PMS , **SiViH**, *336 g/mol*

^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 1.39 (m, 2H, CH_2); 0.7−0.6 (m, 4H, CH_2); 0.07 (s, 18H, $Si(CH_3)_3$); 0.05 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR (62.9 MHz, $CDCl_3$, δ ppm): 23 (C_1, C_3); 17 (C_2); 2.2 ($Si(CH_3)_3$); 0.7 ($Si(CH_3)_2$). GC/MS (*m/z*, intensity): 336 (0.4); 321 (3); 233 (9); 221 (2); 205 (4); 174 (4); 159 (27); 147 (100); 133 (6); 131 (7); 117(3); 73 (19); 59 (3).



$\text{PMS}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{PMS}$

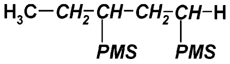
SiViMe, or



$\text{H}_3\text{C}-\text{CH}_2-\underset{\underset{\text{PMS}}{\text{CH}_2}}{\text{CH}}-\text{PMS}$

,**MeViSi**, *350 g/mol*

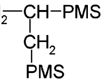
GC/MS (*m/z*, intensity): 350 (0.4); 335(2); 207 (2); 205 (3); 202 (4); 188 (5); 173 (4); 147 (100); 133 (33); 131 (5); 117 (4); 73 (20); 59 (3); 45 (2). GC/MS (*m/z*, intensity): 350 (0.4); 335 (5); 247 (8); 221 (3); 205 (12); 189 (5); 173 (26); 147 (100); 146 (9); 133 (10); 131 (12); 117 (3); 73 (20); 59 (3); 45 (2).



$\text{H}_3\text{C}-\text{CH}_2-\underset{\text{PMS}}{\text{CH}}-\text{CH}_2-\underset{\text{PMS}}{\text{CH}}-\text{H}$

, **MeVi$_2$H**, *364 g/mol*

GC/MS (*m/z*, intensity): 349 (0.5); 261 (2); 221 (2); 216 (5); 205 (2); 202 (5); 187 (5); 174 (5); 159 (2); 147 (100); 133 (31); 131 (8); 117 (3); 73 (15).



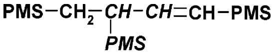
$\text{PMS}-\text{CH}_2-\text{CH}_2-\underset{\underset{\text{PMS}}{\text{CH}_2}}{\text{CH}}-\text{PMS}$

, **Si$_2$ViH or SiViSi**, *496 g/mol*

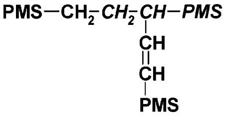
$Si_6C_{19}H_{52}$

^{1}H NMR (250 MHz, $CDCl_3$, δ ppm): 1.48 (m, 2H, CH_2); 0.8 (m, H, CH); 0.6−0.4 (m, 4H, CH_2); 0.06−0 (m, Si−CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$, δ ppm): 27 (C_2); 26 (C_3); 18−19 (C_1,C_4); 2.2 ($Si(CH_3)_3$); 0.7 ($Si(CH_3)_2$). GC/MS (*m/z*, intensity):

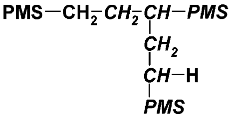
496 (0.4); 481 (2); 348 (5); 334 (1); 319 (3); 306 (1); 291 (1); 277 (1); 245 (1); 231 (3); 221 (7); 207 (2); 189 (1); 186 (20); 171 (5); 147 (100); 133 (8); 131 (7); 117 (3); 73 (15).


$\mathrm{PMS{-}CH_2{-}\underset{\substack{|\\ PMS}}{CH}{-}CH{=}CH{-}PMS}$, $\mathbf{SiVi_{UC}}$, *494 g/mol*

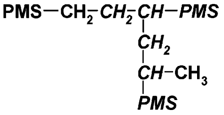
GC/MS (*m/z*, intensity): 494 (0.3); 479 (0,4); 317 (2); 258 (4); 243 (1); 229 (4); 221 (32); 205 (1); 189 (0.5); 170 (17); 147 (100); 131 (5); 117 (2); 105 (0.3); 103 (0.6); 73 (20); 59 (1); 45 (1).


$\mathrm{PMS{-}CH_2{-}CH_2{-}\underset{\substack{|\\ CH\\ \|\\ CH\\ |\\ PMS}}{CH}{-}PMS}$, $\mathbf{SiVi_{2U}}$, *508 g/mol*

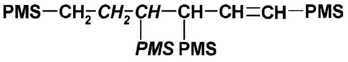
GC/MS (*m/z*, intensity): 508 (0.2); 493 (0.6); 418 (0.4); 346 (0.7); 331 (3); 272 (2); 257 (1); 243 (1); 221 (17); 215 (1); 207 (3); 198 (3); 184 (10); 156 (16); 147 (100); 133 (6); 131 (5); 117 (2); 110 (3); 73 (16).


$\mathrm{PMS{-}CH_2{-}CH_2{-}\underset{\substack{|\\ CH_2\\ |\\ CH{-}H\\ |\\ PMS}}{CH}{-}PMS}$, $\mathbf{SiVi_2H}$, *510 g/mol*

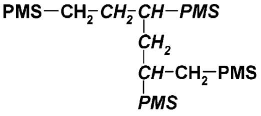
GC/MS (*m/z*, intensity): 495 (0.4); 362 (2); 333 (2); 319 (1); 277 (1); 245 (3); 221 (3); 207 (2); 200 (23); 185 (5); 173 (1); 157 (2); 147 (100); 133 (17); 131 (6); 117 (2); 73 (14).


$\mathrm{PMS{-}CH_2{-}CH_2{-}\underset{\substack{|\\ CH_2\\ |\\ CH{-}CH_3\\ |\\ PMS}}{CH}{-}PMS}$, $\mathbf{SiVi_2Me}$, *524 g/mol*

GC/MS (*m/z*, intensity): 509 (1); 376 (1); 347 (1); 228 (3); 221 (6); 215 (21); 207 (3); 198 (2); 191 (1); 187 (4); 173 (1); 147 (100); 133 (19); 131 (6); 124 (2); 117 (3); 73 (15).


$\mathrm{PMS{-}CH_2{-}CH_2{-}\underset{\substack{|\\ PMS}}{CH}{-}\underset{\substack{|\\ PMS}}{CH}{-}CH{=}CH{-}PMS}$, $\mathbf{SiVi_{2UC}}$, *668 g/mol*

GC/MS (*m/z*, intensity): 653 (0.4); 520 (1); 432 (2); 358 (1); 346 (1); 345 (2); 344 (5); 329 (1); 316 (2); 270 (6); 256 (2); 242 (2); 228 (4); 221 (14); 207 (15); 205 (2); 196 (7); 191 (0.7); 182 (2); 147 (100); 145 (0,5); 143 (0.4); 133 (5); 131 (4); 117 (2); 73 (17); 59 (1); 45 (0.7).

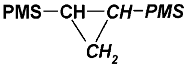

$\mathrm{PMS{-}CH_2{-}CH_2{-}\underset{\substack{|\\ CH_2\\ |\\ CH{-}CH_2{-}PMS\\ |\\ PMS}}{CH}{-}PMS}$, $\mathbf{SiVi_2Si}$, *670 g/mol*

GC/MS (*m/z*, intensity): 655 (0.3); 493 (0.3); 405 (0.5); 335 (11); 305 (0.8); 277 (2); 257 (0.8); 247 (0.8); 242 (0.7); 228 (1); 221 (9); 205 (3); 196 (0.7); 185 (1); 173 (40); 157 (2); 147 (100); 133 (4); 131 (5); 117 (1); 73 (15). GC/MS (*m/z*, intensity): 655 (0.5); 523 (4); 361 (1); 331 (0.5); 293 (1); 221 (4); 219 (2); 212 (1); 205 (3); 199 (10); 171 (12); 147 (100); 133 (4); 131 (4); 117 (1); 73 (10).

Simmons−Smith Reaction in SiH. The first step was the preparation of the "ZnCu" couple. In a beaker, 10 g of zinc powder was washed four times with a solution of chlorhydric acid (3%, 15 mL). The "Zn,HCl" mixture was then stirred with a porcelain spatula and let a few minutes to decant. The remaining solution was carefully removed in order to avoid contact between the treated zinc and the air. A series of washings were performed with distilled water (4 times, 20 mL) and a solution of copper sulfate (2%, 2 times, 25 mL). As soon as the solution of $CuSO_4$ was added to the "zinc", the mixture lost its color, indicating the formation of the "ZnCu" couple. To remove the excess of $CuSO_4$, the couple "ZnCu" was washed again with distilled water (4 times, 15 mL), absolute ethanol (4 times, 15 mL), and then anhydrous ether (4 times, 15 mL). Thus, a gray solid was obtained and dried under vacuum.

The second step was the reaction with the $PMSCHI_2$ previously prepared. In a 25 mL flask fitted with a condenser, a mixture of SiH (92 mmol, 15 g), the "ZnCu" couple (13.2 mmol, 1.7 g), and $PMSCHI_2$ (12 mmol, 4.97 g) was heated under reflux of SiH (101 °C) for 5 days. After the reaction, the hydrolysis was carried out with a saturated solution of NH_4Cl. The solid formed was eliminated by filtration. After extraction of the aqueous phase with ether (3 times, 10 mL), the combined organic phases were washed with a saturated solution of K_2CO_2 and brine and dried over anhydrous $MgSO_4$. A mixture of three compounds was obtained and analyzed by NMR and GC/MS. The first one was iodomethyl-1,1,3,3,3-pentamethyldisiloxane ($PMS{-}CH_2I$). ^1H NMR (250 MHz, $CDCl_3$, δ ppm): 2 (s, 2H, CH_2); 0.15−0.09 (m,15H, $SiCH_3$). ^{13}C NMR (62,9 MHz, $CDCl_3$, δ ppm): 0 (CH_3); −1.74 (CH_3); −14.5 (CH_2). GC/MS (*m/z*, intensity): 288 (1); 273 (72); 245 (93); 147 (100); 131 (12); 115 (14); 73 (23). The other compounds corresponded to the cis and trans isomers of Si_{2U} (its characterization was previously described).

Simmons−Smith Reaction in Ether and in the Presence of PMS−Vi. A mixture of the "ZnCu" couple (13.2 mmol, 1.7 g), $PMSCHI_2$ (12 mmol, 4.97 g), and Vi (12 mmol, 2.09 g) was poured into a flask containing 15 mL of anhydrous ether. After heating at the ether reflux for 5 days, analyses of the crude product allowed to identify the presence of $PMSCH_2I$, the isomers (cis and trans) of Si_{2U}, and the following cyclopropane:


334 g/mol

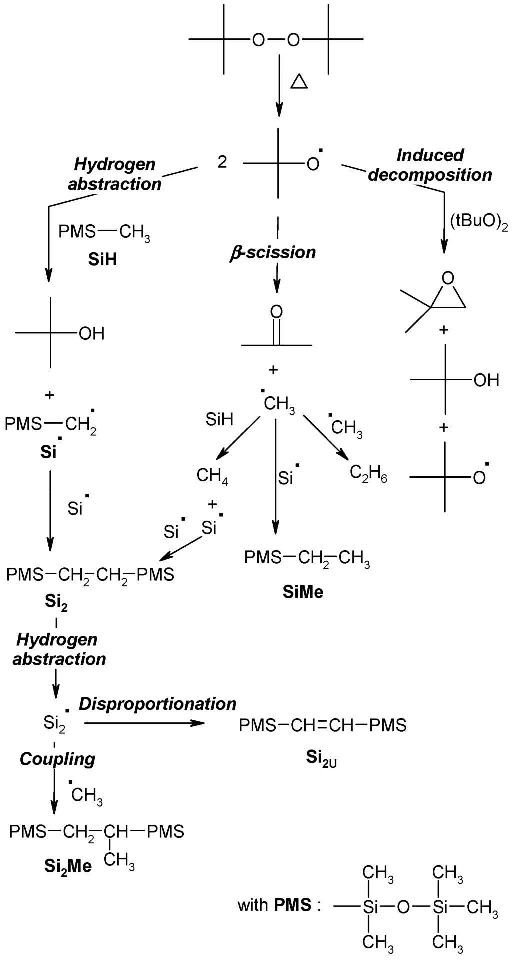
^1H NMR (250 MHz, $CDCl_3$, δ ppm): 0.5 (m, 1H, CH); 0.14 (s, 12H, $Si(CH_3)_2$); 0.12 (m, 2H, CH_2); 0.09 (s, 18H, $Si(CH_3)_3$); −0.43 (m, 1H, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$, δ ppm): 3.2 (CH_2); 0 ($SiCH_3$); −1.74 ($SiCH_3$); −3.1 (CH). GC/MS (*m/z*, intensity): 334 (0.4); 319 (3); 231 (9); 221 (4); 172 (12); 147 (100); 131 (5); 73 (52).

"Preparation" of $PMSCH_2{-}O{-}NEt_2$. In a 100 mL flask, sodium ethanolate (EtONa, 0.03 mol, 2.1 g) was added to a solution of absolute ethanol (3 mL) and anhydrous tetrahydrofuran (THF, 30 mL). After the dissolution of EtONa in the solvent, the mixture cleared. *N*,*N*-Diethylhydroxylamine (Et_2NOH, 0.03 mol, 2.7 g) was then slowly added, at room temperature under nitrogen. The mixture was heated at reflux of THF for 1 h. After cooling the mixture content, chloromethyl-1,1,3,3,3-pentamethyldisiloxane ($PMS{-}CH_2Cl$, 0.03 mol, 5.9 g) was added. The conversion of the reaction was followed by GC chromatography. It was necessary to heat the mixture for 15 h at reflux of THF to observe the formation of a sodium chloride precipitate and the disappearance of $PMSCH_2Cl$. Part of the THF was then evaporated under reduced pressure. The remaining product was mixed with ether (10 mL) and washed with a minimum quantity of water enabling to dissolve the sodium chloride. After separation from the aqueous phase, the organic phase was dried over anhydrous magnesium sulfate. After evaporating the ether, a crude product was obtained (2 g) and analyzed. The synthesis did not conduct to the expected product $PMSCH_2{-}O{-}NEt_2$, but to a mixture of siloxanic products with the following structure: $Me_3Si(OSiMe_2)_nCH_3$ with $n = 2-5$, determined by GC/MS. GC/MS (*m/z*, intensity): $n = 2$: 236 (1); 221 (100); 205 (10); 189 (5); 133 (12); 103 (10); 73 (65). $n = 3$: 310 (1); 295 (15); 207 (100); 191 (10); 73 (80). $n = 4$: 384 (1); 369 (20); 281 (100); 265 (10); 249 (8); 207 (10); 147 (100); 73 (90). $n = 5$: 458 (0.4); 443 (1); 355 (10); 281 (30); 267 (20); 221 (80); 147 (65); 73 (100).

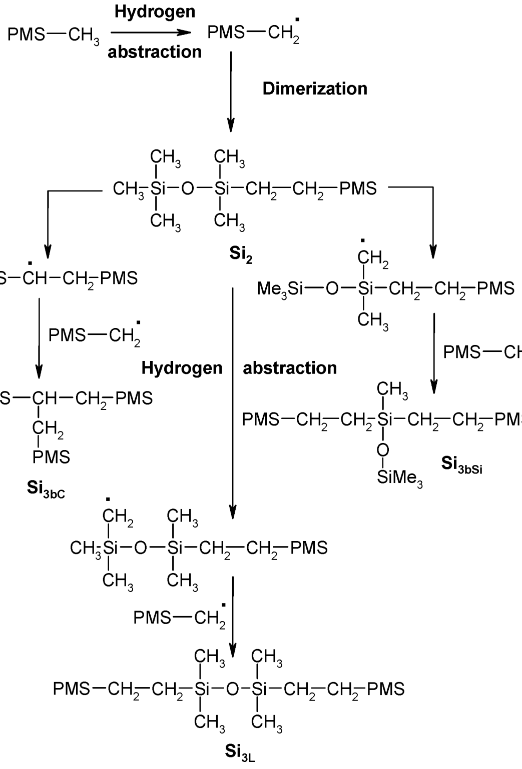
Results and Discussion

Decomposition of TBP in SiH. After the thermolysis of TBP in SiH at 165 °C for 8 h (ratios **TBP/SiH** of 1/6.7 and 1/220) methane and ethane were identified in the gas phase. The distillation of the liquid phase

Scheme 2. Mechanism of Formation of the Various Products Arising from the TBP Decomposition in SiH



Scheme 3. "Trimers" Formations



enabled to separate several fractions and a residue: (i) excess of SiH and low boiling products arising from the decomposition of TBP; (ii) products distilling under the pump vacuum; (iii) residue of distillation.

Besides the SiH used in excess, *tert*-butyl alcohol, acetone, and 2,2-dimethyloxirane, arising from the decomposition of the peroxide (Scheme 2), were identified in the low boiling fraction, but residual TBP was not. A quantitative analysis of the two former compounds was not successful because of the reproducibility of the measurements despite the precautions taken. Nevertheless, the identification of a very low amount of oxirane for each measurement (yield <2% relative to TBP) proved that TBP was essentially disappearing by spontaneous decomposition and not by the induced one, which generates this heterocycle.

The structure of the main reaction products contained in the different fractions was determined by NMR and GC/MS.

The first fraction was essentially constituted by the Si_2 dehydrodimer of the siloxane, the Si_{2U} "unsaturated dehydrodimer", and a Si_2Me compound. Si_2 dehydrodimer was produced by the dimerization of the silylalkyl radicals $Si^•$ generated by hydrogen abstraction from SiH (Scheme 2). Si_{2U} and Si_2Me might result from the radical arising from a hydrogen abstraction from a methylene of the dimer, terminating respectively by disproportionation to give Si_{2U} and by coupling with a methyl radical to form Si_2Me (Scheme 2).

The second distillation fraction (F2) contained three compounds with a molar mass of 482 g/mol, corresponding to the association of three entities arising from SiH, and one with a molar mass of 480 g/mol. Starting from the Si_2 dehydrodimer, it was possible to design only the three structures (Si_{3bC}, Si_{3L}, Si_{3bSi}), reported in Scheme 3, by substitution of one of the hydrogens present in Si_2 by a Si group to produce compounds with a 482 g/mol molar mass. The identification of the major isomer, Si_{3bC}, was carried out from the NMR and GC/MS analyses of the second fraction (see Supporting Information). To attribute the structure of both the other isomers, we decided to synthesize Si_{3L} according to a general synthesis[14] of $H[CH_2{-}SiMe_2{-}O{-}SiMe_2{-}CH_2]_nH$ with $n = 2-4$, from trimethylchlorosilane and 1,2-bis(chlorodimethylsilyl)ethane. This reaction led to a mixture of compounds separated by distillation and identified by GC/MS and NMR as Si_2, "trimers" (Si_{3L} and Si_{3c}), and "tetramers" (Si_{4L} and Si_{4c}). The comparison of the reference Si_{3L} mass spectra and the one of the second fraction F2 allowed an unambiguous identification of Si_{3L} in the reaction mixture and by difference the third one, Si_{3bSi}. Such "trimers" might be formed by the coupling of a $Si^•$ radical with the different radicals obtained by hydrogen abstraction from the Si_2 (Scheme 3). The relative ratios of these three compounds in the experiment TBP/SiH = 1/6.7 were $Si_{3bC}/Si_{3L}/Si_{3bSi} = 69/17/14$. These are in agreement with a higher free radical reactivity of the hydrogen borne by a CH_2 than a CH_3 and the relative ratios of these entities in the dimer. The formation mechanism of these compounds was proved by their increasing amounts when Si_2 was added to the reactants prior to the decomposition of TBP (Table 1).

The increase of Si_{4L} as well as of other Si_4 "tetramers" (molar masses of 642 g/mol in GC/MS) resulting from the addition of Si_2 to the medium confirms their presence as well as their origin.

The F2 fraction contained also a compound of 480 g/mol molar mass which could only be attributed to a

Table 1. Decomposition of TBP (1 mmol) in SiH in the Presence and Absence of Si_2

TBP/SiH/Si_2 (eq)	$Si_{2\,added}$ (μmol)	Si_2 (μmol)	Si_{2U} (μmol)	Si_2Me (μmol)	Si_{3bC} (μmol)	Si_{3L} (μmol)	Si_{3bSi} (μmol)	Si_4 (μmol)
1/6.7/–		63	30	28	39	9	8	21
1/6.7/1	1000	524	64	93	174	133	119	115

Table 2. Decomposition of TBP (1 mmol) in SiH with Different Reactants Ratios

TBP/SiH (eq)	Si_2 (μmol)	Si_{2U} (μmol)	Si_2Me (μmol)	Si_{3bC} (μmol)	Si_{3L} (μmol)	Si_{3bSi} (μmol)	Si_{3UC} (μmol)	Si_4 (μmol)	residue (mg)
1/6.7	63	30	28	39	9	8	32	21	49
1/220	135	94	93	101	traces		100		

"trimer" having either an unsaturation or a cycle. The ^1H NMR spectrum of F2 showed signals at 5.3 and 6 ppm. This agrees with the presence of ethylenic protons which was confirmed by ^{13}C NMR and DEPT 135 analyses (see Supporting Information). COSY 45 $^1H-^1H$ correlation proved the existence of the following sequence: $-Si-CH-CH{=}CH-Si-$ leading to the proposition of the Si_{3UC} structure for the fourth compound present in the F2 fraction. None of the free radical intermediate involved in the mechanism mentioned in Scheme 3 can explain the formation of such a Si_{3UC} compound.

Titrations of the various compounds separated by distillation from the residue are given Table 2 for the reactions performed with 1 mmol of TBP for the following relative ratios of the reactants: TBP/SiH = 1/6.7 and 1/220.

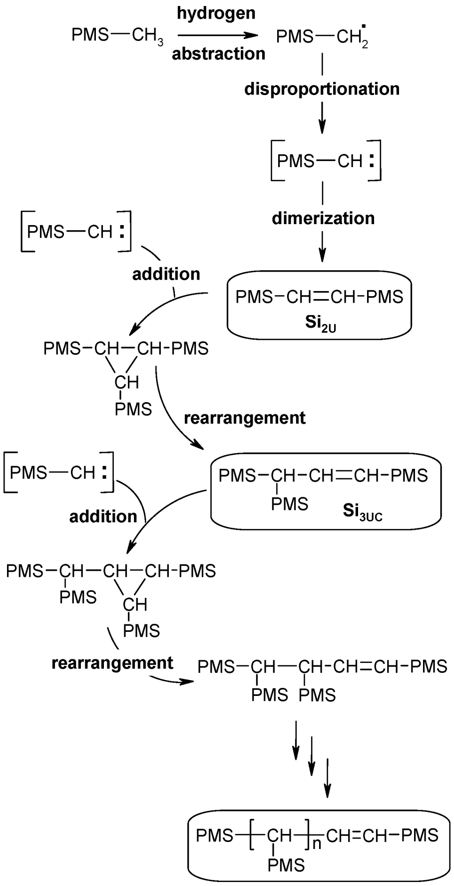
A distillation residue (R1) was only obtained when TBP was decomposed in SiH with a ratio of TBP/SiH of 1/6.7. The ^1H NMR analysis of this residue R1 showed the presence of two large signals at 0.03 and 2.06 ppm (see Supporting Information), corresponding respectively to the protons of $Si-CH_3$ and of methine linked to two carbon atoms in a $-C-CH-C-$ sequence.^{13}C NMR and DEPT analyses confirmed the presence of numerous $-CH$ carbons at 30 ppm; this broad signal was correlated to the protons present at 2.06 ppm (see Supporting Information). Ethylenic methines were also present in R1 (NMR spectra: ^1H 5.3−6 ppm and ^{13}C 128 and 145 ppm). DOSY 2D (see Supporting Information) of this residue showed that all the signals of the protons are borne to macromolecules, having similar diffusion coefficients and then certainly very similar molecular masses. The SEC analysis of this residue confirmed this result since a single peak with a narrow molecular weight distribution (Ip = 1.1) was observed. Taking into account all these elements, we may assume that R1 was mainly constituted of repetitive units $[-CH(-PMS)-]$ with end groups as $-CH_2-PMS$ or $-CH{=}CH-PMS$. To consolidate this attribution, MALDI−TOF analyses were performed but were not successful because of the difficulty in ionizing this residue.

To confirm the free radical origin of the residue pointed out in the decomposition of TBP in D_4,[13] the reaction was rerun in SiH in the presence of 2 mol equiv of TEMPO. If Me-TEMPO (yield = 42% relative to TBP) was identified in the reaction products, the expected 2,2,6,6-tetramethylpiperidinyloxymethylpentamethyldisiloxane (Si-TEMPO) could not be identified; meanwhile, a R2 residue containing different types of silicon atoms ($-Si(alkyle)_2O-$, $-Si(alkyle)O_2$, and $-SiO_3$) was obtained. To take these results into account, we have to consider the formation of $Si-O$ bond instead of a $Si-C$ one via a sigmatropic rearrangement with the migration of the oxygen from the carbon to the silicon in the alkoxyamine produced by the coupling of the TEMPO with $Si^\bullet$. This hypothesis was confirmed through the formation of high molecular weight compounds containing silicon atoms linked to two oxygen atoms in the reaction of the diethylhydroxylamine sodium salt with chloromethypentamethyldisiloxane. The formation of MeTEMPO with a yield of 42% indicated that about 60% of the *tert*-butoxy radicals were able to abstract hydrogen from a methyl linked to a silicon, confirming the results obtained in the case of D_4.[13] A higher production of MeTEMPO in the case of this model showed a reactivity of *tert*-butoxy radical toward a hydrogen of a methyl borne by a silicon atom linked with two oxygens (D_4) about 3 times higher than the one of a silicon linked with only one oxygen (SiH). On the other hand, the comparison of ^1H NMR spectra of R1 and R2 (see Supporting Information) confirmed the difference of the type of molecule constituting them. It is in particular important to underline the disappearance of the methine protons ($-CH(PMS)-$) at 2.1 ppm when the reaction was performed in the presence of TEMPO.

The identification of a $-CH(PMS)-$ repetitive unit, the possible end groups of the macromolecule, and the absence of free radical mechanism capable to explain the formation of Si_{3UC} prompted us to imagine the structure represented in Scheme 4 for the oligomers contained in the R1 residue, the first one of the series being Si_{3UC} and its precursor Si_{2U}. To try to explain the formation of these compounds, we considered the formation of the silylcarbene "PMSCH": by disproportionation of a radical $Si^\bullet$. Such a reaction is unusual since we found only one article written by Feldhues and Schäfer[15] describing a similar type of reaction. As will be shown below, the formation of Si_{2U} might be considered as an argument in favor of such a mechanism since this compound could be produced by the dimerization of the silylcarbene.

To trap the suspected silylcarbene, the decomposition of TBP in SiH was carried out in the presence of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), known as a carbene trap.[16] This trial failed due to the instability of PTAD in the reaction conditions. Thus, various attempts to produce this silylcarbene were made. The synthesis of the pentamethyldisiloxanyldiazomethane, based on the one of trimethylsilyldiazomethane,[17,18] failed. A Simmons−Smith reaction performed, in refluxing SiH, from $PMS-CHI_2$ produced a mixture of $PMS-CH_2I$ and both Si_{2U} isomers. The formation of Si_{2U} might be considered in favor of the generation of a carbene in the TBP reaction in SiH, despite of, here, the absence of formation of Si_{3UC} and/or oligomers of $-CH(PMS)-$ repetitive units. However, it is important to underline that the conditions of reaction were very different: temperature (101 °C instead of 165 °C) but also the place of production of the carbene. Indeed, in the Simmons−Smith reaction, it was produced at the surface of the zinc instead of in solution for the free radical

Scheme 4. Proposed Mechanism for the Formation of High Molecular Weight Products Based on the Carbene Generation



reaction. Thus, it was not possible to confirm unambiguously the existence of such a mechanism from carbenes (Scheme 4) to produce Si_{3UC} and residue.

On the basis of the proposed mechanisms, it appeared interesting to discuss the results obtained for the decomposition of TBP with the lower TBP/SiH ratio (1/220). If, in this reaction, no residue was isolated, the compound Si_{3UC} was formed. Thus, we estimated the balance of the radicals involved in the formation of all the reaction products according to the written mechanisms (Table 3). The agreement between the number of radicals produced and consumed in the formation of the various products can be considered as a confirmation of the existence of the competitive free radical and carbene mechanisms.

The balance was similarly established for the reaction performed with TBP/SiH = 1/6.7 (Table 3). To estimate the number of radicals consumed to generate the residue, we assumed that it was uniquely constituted of −CH−PMS repetitive units, neglecting the chain ends. For the production of such an entity, two radicals were necessary. The balance of the consumed radicals compared with the number of produced ones showed a discrepancy which did not confirm the existence of both competitive mechanisms but did not exclude them. Indeed, this difference might be attributed to the absence of consideration of the products resulting from the coupling of methyl radicals (essentially ethane and SiMe), produced here in much higher concentration (high concentration of TBP) than in the previous reaction. Such a hypothesis is reasonable if we consider the identification of Si_2Me generated by coupling of a methyl radical and a dimer one ($Si_2^•$), although present in much lower amount than $Si^•$. However, unfortunately, it was not possible to detect and titrate SiMe which has a retention time close to SiH and is present in much lower quantity.

Decomposition of TBP in SiH in the Presence of Vi. The reaction mixtures obtained after the decomposition of TBP in SiH in the presence of Vi were distilled to separate several fractions from a residue, as for the reactions performed above. In the low boiling products, besides SiH, *tert*-butyl alcohol, acetone, and 2,2-dimethyloxirane (all arising from TBP by the mechanisms previously described) were identified. Another compound, MeViH, was also detected by GC/MS (190 g/mol molar mass). In the second distillation fraction, dehydrodimer Si_2 and compounds SiViH (336 g/mol molar mass), two isomers SiViMe and MeViSi (350 g/mol molar mass), and $MeVi_2H$ (364 g/mol molar mass) were detected by GC/MS. A third fraction contained a compound of molar mass 496 g/mol, clearly identified by NMR, which can be either SiViSi or Si_2ViH, since they have the same formula ($Si_6C_{19}H_{52}$), and others $SiVi_{UC}$, $SiVi_{2U}$, and $SiVi_2H$, having respectively molar masses of 494, 508, and 510 g/mol. The distillation enabled the separation from the residue of a fourth fraction, constituted of two compounds of molar masses of 668 and 670 g/mol, which might be $SiVi_{2UC}$ and $SiVi_2Si$.

To identify the compounds produced by reaction of the radicals, arising only from TBP on Vi, we performed a similar decomposition of TBP in a benzene solution of Vi (TBP/benzene/Vi: 0.1/10/1). The distillation fraction was mainly constituted by MeViH and $MeVi_2H$. The ^1H and ^{13}C NMR analyses of the R4 residue (Supporting Information) showed the presence of $-CH_2-CH(PMS)-$ repetitive units [−CH (broad signals, $\delta_{1H} = 1.4$ ppm and $\delta_{13C} = 33$ ppm); $-CH_2$ (broad signals, $\delta_{1H} = 0.6$ ppm and $\delta_{13C} = 25$ ppm); "−SiMe" (broad signals, $\delta_{1H} = 0$ ppm and $\delta_{13C} = 0.8$ and 1.5 ppm)] which was confirmed by the identification of a 174 g/mol repetitive unit observed in the MALDI−TOF spectrum (Supporting Information).

The identification of these various products in the different distillation fractions indicated the formation of several radicals: $Si^•$, $Me^•$, $SiVi^•$, $SiVi_2^•$. They were consumed by the reactions indicated in Scheme 5: (i) hydrogen transfer to give adducts (MeViH, SiViH, $MeVi_2H$, and $SiVi_2H$)); (ii) combinations (Si_2, SiViMe, MeViSi, SiViSi, and $SiVi_2Si$); (iii) disproportionation to produce unsaturated compounds ($SiVi_U$ and $SiVi_{2U}$).

As pointed out above, disproportionation of *tert*-butoxy radicals and $Si^•$ might generate carbenes, which are able to react on the unsaturation present in the medium to lead to cyclopropanes rearranging to unsaturated compounds ($SiVi_{UC}$ and $SiVi_{2UC}$) (Scheme 5).

Since the relative ratios of the various compounds may differ with the relative amounts of the reactants, we decided to perform several reactions to identify the influence of these parameters.

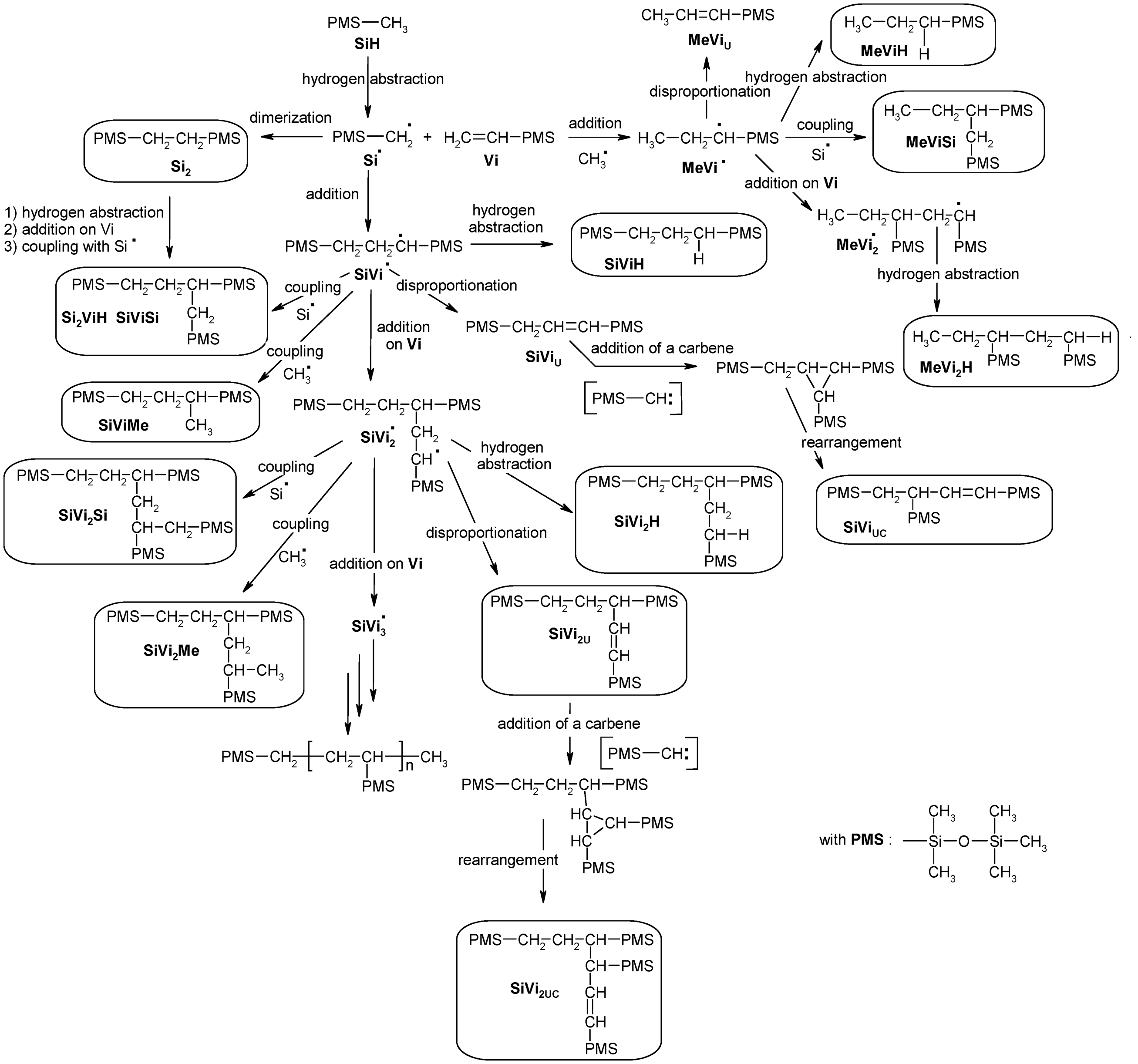
Influence of the Concentration of Vinyl Groups. As indicated in Table 4, similar yields of Si_2 were obtained in the presence and absence of the vinylsiloxane. Conversely, the absence of the trimer Si_{3bC} has to be pointed out for the reaction in the presence of vinylsiloxane. Taking into account the mechanism of its formation (coupling of a radical arising from the Si_2 dehydrodimer and a $Si^•$ radical, Scheme 3), this can be

Table 3. Yields of Radicals Involved in the Generation of the Various Products According to the Proposed Mechanisms (Relative to the Radicals Generated from the Peroxide)

		Si_2	Si_{2U}	Si_2Me	Si_{3bC}	Si_{3L}	Si_{3bSi}	Si_{3UC}	Si_4	residue	yield[l] of radicals
TBP/SiH (eq)	no. of radicals necessary for the products formation	2	4	4	4	4	4	6	6	2*n*	
1/6.7	no. of μmol	63	30	28	39	9	8	32	21	612	
	radicals yield[l] (%)	6[a]	6[b]	6[c]	8[d]	2[e]	2[f]	10[g]	6[h]	31[i]	77[j]
1/220	no. of μmol	135	94	93	101	traces	traces	100			
	radicals yield[l] (%)	14[a]	19[b]	19[c]	20[d]			30[g]			102[k]

[a] Yield = $2n_{Si_2}/2n_{TBP} \times 100$. [b] Yield = $4n_{Si_{2U}}/2n_{TBP} \times 100$. [c] Yield = $4n_{Si_2Me}/2n_{TBP} \times 100$. [d] Yield = $4n_{Si_{3bC}}/2n_{TBP} \times 100$. [e] Yield = $4n_{Si_{3L}}/2n_{TBP} \times 100$. [f] Yield = $4n_{Si_{3bSi}}/2n_{TBP} \times 100$. [g] Yield = $6n_{Si_{3UC}}/2n_{TBP} \times 100$. [h] Yield = $6n_{Si_4}/2n_{TBP} \times 100$. [i] Yield = no. of moles in the residue/$2n_{TBP} \times 100$. [j] Balance = $a + b + c + d + e + f + g + h + i$. [k] Balance = $a + b + c + d + g$. [l] Relative to TBP.

Scheme 5. Proposed Mechanism for the Formation of the Various Products in the Decomposition of TBP in a Solution of Vi in SiH



explained by a decrease of the coupling reactions given by the Si• radical. This is not surprising if we compare the concentrations of the radicals and of Vi. Nevertheless, the hydrogen abstraction from Si_2 occurred since the identification of Si_2ViH may be attributed to the addition of such a Si_2• radical to Vi followed by an hydrogen transfer (Scheme 5).

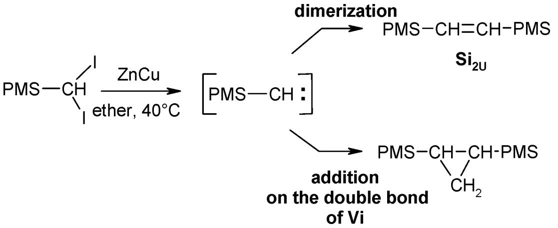
The comparison of the amounts of XViH and XViX (X = Me or Si) showed that there was a very important competition for the XVi• radical adduct (MeVi• and SiVi•) between the hydrogen transfer from a molecule of siloxane and the coupling reactions with methyl and silylalkyl radicals for the SiVi• radicals.

Table 4. Decomposition of TBP in SiH in the Presence and Absence of Vi[a]

trial	C_{Vi} (μmol)	Si_2 (μmol)	Si_{3bC} (μmol)	Si_{2U} (μmol)	XViH (μmol)	XViX (μmol)	XVi_2H (μmol)	$SiVi_{2U}$ (μmol)	residue (name; mg)
1		63	39	30					R1; 49
2	670	59		traces	139	91	79	25	R3; 137

[a] With X = Me and/or Si.

Scheme 6. Reaction of Silylalkylcarbene on Vi



The identification of only traces of Si_{2U} would indicate the absence of formation of carbene in the presence of Vi and/or of disproportionation of $Si_2^{\bullet}$ radicals or their trapping by Vi. The identification of Si_2ViH confirmed the existence of such a reaction for the radical. The high reactivity of carbenes on double bond might be responsible for the absence of formation of this unsaturated dimer. To verify this, we generated the carbene by the reaction of the PMS−CHI_2 with zinc in refluxing ether and Vi. After the reaction, the major part of Vi was recovered unchanged; meanwhile, the expected cyclopropane (Scheme 6) was identified as well as both isomers of Si_{2U}. Despite the absence of such a cyclopropane and of Si_{2U} in the products formed during the TBP decomposition in the mixture of siloxanes, we cannot exclude the formation of carbenes in the medium according to the presence of the methines at about 2.1 ppm in the R3 residue (see Supporting Information). This hypothesis will be confirmed in the study on the influence of the peroxide concentration.

The comparison of the ^1H of the R1, R3, and R4 residues (see Supporting Information) showed that R3 is certainly constituted of a mixture of polymers arising from the telomerization of the vinylsiloxane and the reactions of the carbene. However, it is difficult to tell whether the macromolecules contained in the residue are homo- or copolymers.

Influence of the Concentration of Peroxide. Table 5 summarizes the results of the reactions performed for various concentrations of TBP (molar ratios: TBP/SiH/Vi = C_{TBP}/6.7/0.67). The observation of the recovery of 25% of unchanged Vi after reaction in the essay 4 indicated that the free radical reactions involved in the disappearance of this unsaturated compound were not long chain reactions. This is certainly the main reason for the use of a relatively high ratio of peroxide relative to the vinyl groups in the cross-linking of the silicones.

If we consider the relative amounts of XViH and XVi_2H (X = Me or Si), one can notice the higher consumption of Vi by silylalkyl radicals than by methyl with the decrease of the peroxide concentration, which agrees with a lower production of $Me^{\bullet}$ at lower concentration of peroxide, than the $Si^{\bullet}$ production.

The analysis of the competition for $Si^{\bullet}$ radicals between the addition to the double bond and the dimerization, based on the balance of SiViH and $SiVi_2H$ on one hand and Si_2 on the other hand, indicated a favored addition, regardless of the peroxide concentration.

It appeared interesting to establish the balance of the consumed Vi in the low molecular weight compounds (Table 6), since it is difficult to do it for the residues, according to the following equation: $n_{\mathrm{Vi\ consumed}} = n_{\mathrm{XViH}} + n_{\mathrm{XViX}} + 2n_{\mathrm{XVi_2H}} + 2n_{\mathrm{XVi_{2U}}}$. The analysis of the results of these calculations (Table 6) shows that the increase of C_{TBP} afforded a higher consumption of Vi to generate low molecular weight products due to a higher level of radical combinations at the expense of the telomerization. If there was a decrease in the weight of the residue going from R3 to R5 and R6, their ^1H NMR analyses (see Supporting Information) showed a simultaneous decrease of the amount of "carbenic polymer" (see signal at 2.1 ppm) with the decrease of C_{TBP}. These two results indicate the consumption of adduct radicals by two different ways, disproportionation and coupling, during the time of the reaction but do not show if there is a competition of these two processes along the reaction or if they are successive phenomena. Indeed, taking into account that $Si^{\bullet}$ radicals react by disproportionation with *tert*-butoxy in the absence of Vi, it appeared important to determine the relative disappearance of TBP and Vi with time. Such a study was performed in the conditions of essay 3 (TBP/SiH/Vi: 0.67/6.7/0.67). The results summarized Table 7 show that, if the competition exists in the first part of the reaction, the Vi consumption is faster than the peroxide one and then that the carbenic polymer might be generated mainly at the end of the heating. On the other hand, the carbene generated reacts on unsaturated compounds as $SiVi_U$ and $SiVi_{2U}$ since $SiVi_{UC}$ and $SiVi_{2UC}$ are identified in the reaction products. The absence of $SiVi_U$ in the reaction products, and the formation of $SiVi_{2U}$, would then be explained by a higher reactivity of carbenes with the former than the latter due to a lower bulk of the double bond.

Influence of the "Dilution" of the Reaction Mixture. The influence of the "dilution" of the medium in the course of the reactions, occurring during the decomposition of TBP in the presence of Vi in SiH, was approached by the comparison of both essays reported in Table 8.

On one hand, the analysis of the formation of Si_2 in both conditions agreed with the results previously reported for the reactions performed in absence of vinylic compound: an increase of its formation yield relative to peroxide with the increase of the "dilution", due to the decrease of the disproportionation reaction between $Si^{\bullet}$ and $tBuO^{\bullet}$ radicals.

On the other hand, the increase of the amount of SiViH with the dilution proved that hydrogen transfer to the $SiVi^{\bullet}$ radical was favored compared to the other competitive processes of disappearance of this radical: coupling or disproportionation with other radicals and addition to an other molecule of vinylsiloxane. This analysis was confirmed by the decrease of SiViSi (coupling), $SiVi_{2U}$ (disproportionation), and $SiVi_2H$ (addition).

The decrease of the amount of residue with the dilution and the analysis of ^1H NMR spectra of R3 and R7 (see Supporting Information) confirmed the absence of carbene formation at low peroxide concentration.

Table 5. Decomposition of TBP, in Variable Concentrations, in SiH in the Presence of Vi (0.67 mmol; Molar Ratios TBP/SiH/Vi: C_{TBP}/6.7/0.67)

trial	C_{TBP} (μmol)	Si_2 (μmol)	X	XViH (μmol)	SiViMe and MeViSi (μmol)	Si_2ViH and SiViSi (μmol)	XVi_2H (μmol)	XVi_{2U} (μmol)	residue (name; mg)
2	1000	59	Me	72	48		38		R3; 137
			Si	67		43	41	25	
3	670	20	Me	20	19		18		R5; 100
			Si	30		20	20	12	
4	68	7	Me	9	9		9		R6; 10
			Si	19		7	14	8	

Table 6. Consumption of Vi in the Distillation Products[a]

trial	C_{TBP} (μmol)	Vi reacted (μmol)	Vi consumed in distillated products (μmol)	Vi consumed in distillated products (%)
2	1000	670	438	65
3	670	670	189	28
4	68	503	106	21

[a] Vi consumed in distillated products = $n_{\text{Vi consumed}}/n_{\text{Vi reacted}}$.

Table 7. Disappearance of TBP and Vi during Their Heating in SiH

reaction time (min)	Vi consumed (%)	TBP left (%)
15	76	36
30	98	23

Analysis of the Reaction of Cross-Linking of Silicones by TBP on the Basis of the Model Studies. First, it is important to recall that in the literature cross-linking of PDMS was attributed to a coupling of silylalkyl radicals resulting from the abstraction of a hydrogen from a methyl by radicals generated in the decomposition of peroxide.[10] The absence of cross-linking of these macromolecules by TBP was attributed by Dunham, Bailey, and Mixer[6] to the "inactivity" of *tert*-butoxy radicals. Dluzneski[5] confirmed the inefficiency of such a hydrogen abstraction through bond energies comparison.On the other hand, PDMS containing some vinyl groups could be cross-linked by TBP. To account for this, two mechanisms were respectively proposed one by Dunham, Bailey, and Mixer[6] and the other by Bork and Roush[9] (Schemes 7 and 8). These mechanisms were mentioned by researchers,[3,7,8] but none of them were proved. In this paper, we are going to successively consider the existence of the various mechanisms on the basis of the identified products in the model study performed with ratios of PTB/SiH = 1/220 and PTB/SiH/Vi = 1/220/0.67, which are close to the industrial conditions to cross-link silicones.[19]

The first remark is related to the affirmation of Dluzneski[5] and Dunham[6] regarding the inefficiency of *tert*-butoxy radicals to abstract a hydrogen from a methyl of PDMS. Indeed, the study of the TBP decomposition in SiH confirmed that it is not the case, as shown previously by radical trapping with D_4.[13] On the other hand, if we consider the mechanism given by these authors to explain the efficient cross-linking of silicones bearing vinyl groups by such a peroxide, the addition of a silylalkyl radical to the double bond of a vinyl group is the key step. However, to get such a reaction, it is necessary, first of all, to generate these radicals, and thus according to the affirmation of these authors, it is very difficult to understand why *tert*-butoxy and/or methyl radicals would abstract hydrogen to methyl borne by a silicon atom only in the presence of a vinyl group.

In the study of PMVS cross-linking by TBP, Dunham, Bailey, and Mixer[6] excluded first the existence of a possible symmetrical coupling of silylalkyl radicals ($Si-CH_2^•$) (Scheme 1), based on the absence of cross-linking of PDMS by this peroxide alone. Regardless of the reactions conditions in the model study, the dehydrodimer of SiH, Si_2, was identified in significant amounts, indicating that this coupling appears "chemically possible". Second, these authors rejected the possible telomerization of the vinylic double bond (Scheme 9), based on the low concentration of the unsaturation. In the model study, oligomers of Vi were identified, even at low concentration of this compound, which would contradict the hypothesis of Dunham et al.[6] However, it is important to consider that, in the silicone, many unsaturations are present in the same macromolecule and then linked, which "restricts" their diffusion freedom, as it was the case for the independent low molecular reactants. On the other hand, it is important to consider the viscosity of the medium, which is lower in the case of the small siloxanes and also not affected by the creation of linkages between these molecules through the free radical reactions occurring, unlike in the case of the macromolecules.

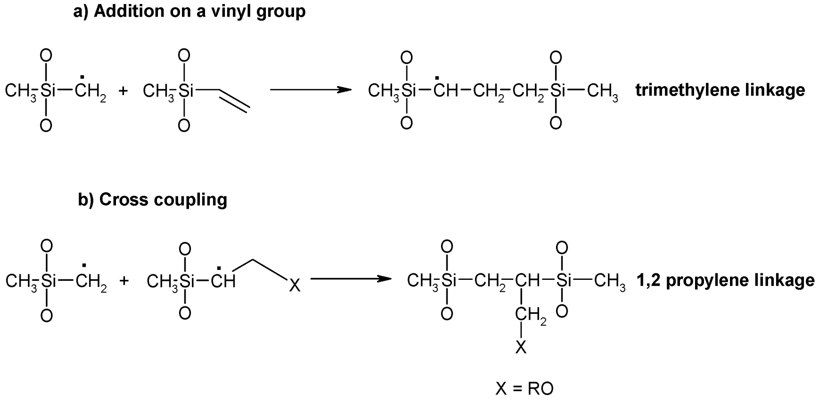
In the proposal of Dunham et al.,[6] cross-linking was explained by two mechanisms involving a silylalkyl radical and a vinylic unsaturation. The first one is due to the addition of the radical to the double bond. The identification of SiViH and SiViSi, in the model reaction, can be considered as an argument for such a reaction, indicating also that the adduct radical may terminate by hydrogen transfer or coupling with a radical present in the medium. The second mechanism involves a reaction of coupling of the radical, obtained in addition of *tert*-butoxy radical to the unsaturation with a silylalkyl radical (Scheme 7). In the model reaction, no compound resulting from the addition of *tert*-butoxy radical to Vi could be found. This is not surprising if we consider the inefficiency of the addition of *tert*-butoxy radical to terminal alkenes,[20] preferring to react by hydrogen abstraction or fragmentation. However, the reaction involving a methyl radical, which would lead to the same type of cross-linking, appears to be possible, since addition of a methyl radical to Vi occurred, as shown by the formation of MeViH and $MeVi_U$ in the model reaction. The possible presence of MeViSi (a compound of 350 g/mol molar mass was identified in the medium, but two formulas, MeViSi and SiViMe, could be attributed to it) would assert the involvement of such a mechanism in the cross-linking (Scheme 5).

Now, if we consider the mechanism proposed by Bork and Roush[9] (Scheme 8), the first step appears to be confirmed as discussed above if X corresponds to a methyl and not a *tert*-butoxy. The trouble comes from the second one. Indeed, the written reaction cannot correspond to an elementary reaction. Indeed, it cannot be reasonable to imagine to create in one step C−C and C−H bonds and breaking C−X and C−H ones. Taking into account the starting reactants, on the basis of the known types of free radical reactions, one could imagine to have the following combination of (i) a hydrogen

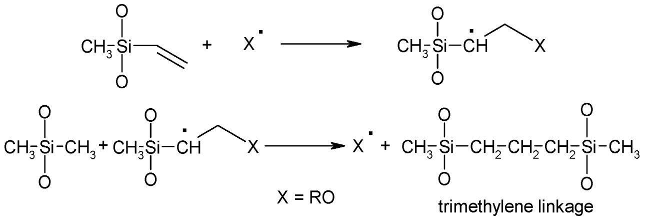
Table 8. Decomposition of TBP, in Variable Proportions of SiH in the Presence of Vi (0.67 mmol; Molar Ratios: TBP/SiH/Vi: 1/C_{SiH}/0.67)

trial	C_{SiH} (eq)	Si_2 (μmol)	X	XViH (μmol)	SiViMe and MeViSi (μmol)	Si_2ViH and SiViSi (μmol)	XVi_2H (μmol)	XVi_{2U} (μmol)	residue (name; mg)	Vi consumed in distillated products (%)
2	6.7	59	Me	72	48		38		R3; 137	65
			Si	67		43	41	25		
5	220	166	Me	12	30		28		R7; 53	56
			Si	126		53	30	18		

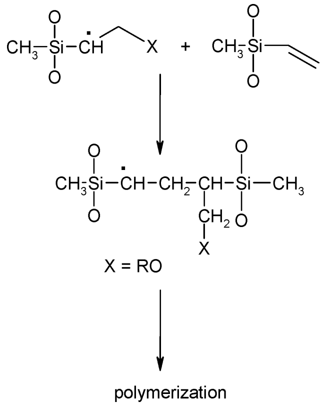
Scheme 7. Mechanism Proposed by Dunham, Bailey, and Mixer



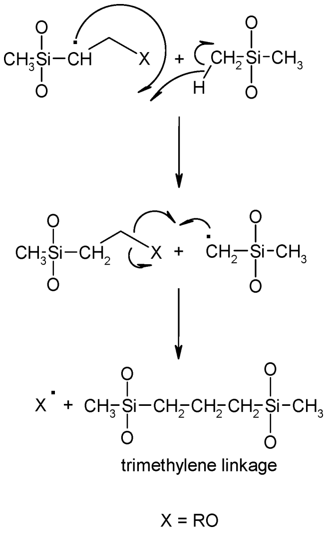
Scheme 8. Mechanism Proposed by Bork and Roush



Scheme 9. Oligomerization of Vinylsiloxanes



Scheme 10. Proposal for the "Second Step" of the Mechanism Suggested by Bork and Roush



transfer and (ii) a S_H2 reaction on a carbon with the simultaneous creation of the C−C bond and the breaking of C−X bond (Scheme 10). If the hydrogen transfer can be confirmed by the identification of MeViH in the model reaction, no S_H2 corresponding to the attack of a primary alkyl radical on a carbon with elimination of a methyl radical is known. Moreover, it is rather difficult to consider this, in particular, for thermodynamic reasons.

Thus, to explain the cross-linking of the silicone-containing vinyl groups by TBP, our model study led us to select the proposal of Dunham et al.[6] and reject the one of Bork and Roush.[9]

Another interesting point to discuss, on the basis of the model study, is the classification of TBP as "vinyl specific peroxide". Assuming that cross-linking occurs by coupling of silylalkyl radicals, in the absence of vinyl group, and by the mechanism of Dunham et al.,[6] for reactions occurring in the presence of vinyl groups, it was possible to estimate the number of links created by the decomposition of 1 mmol of TBP in the model reactions. On the basis of the rejection of telomerization of vinyl group in the cross-linking of PMVS, we had to consider the identified low telomers in the model study only as the creation of one link between two siloxane units (one Vi and one Si). We did not take into account the ones contained in the residue, due to the difficulty to estimate the mole numbers. The first point to underline is the high number of linkages created (Tables 9 and 10), which is in total opposition with the well-known inefficiency of TBP for PDMS cross-linking.[5,6] Thus, if the model study showed the free radical reactions which may occur by decomposition of this peroxide in a medium containing SiMe groups, its direct transposition to the decomposition of TBP in PDMS is not realistic, due certainly to a different orientation in the competitive reactions given by the free radicals

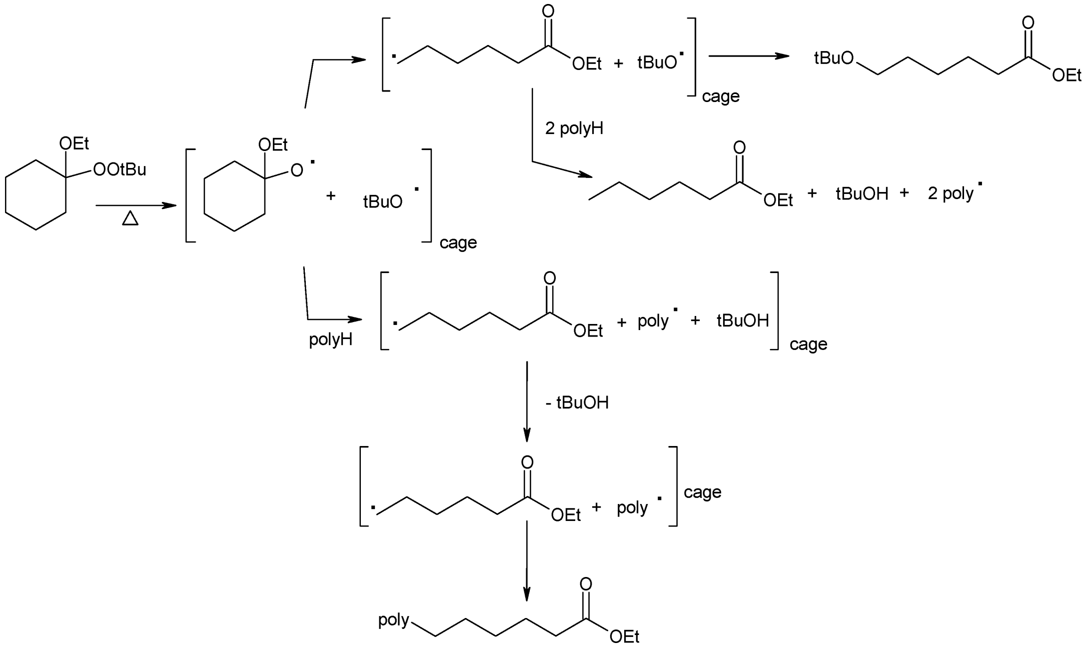
Table 9. Estimation of the Number of Links Formed during the TBP Decomposition in SiH

		Si_2	Si_{2U}	Si_2Me	Si_{3bC}	Si_{3L}	Si_{3bSi}	Si_{3UC}	Si_4	
TBP/SiH/Vi (eq)	no. of μmol	135	94	93	101	traces	traces	100		
1/220/–	no. of links	1	1	1	2			2		
	total	135	94	93	202			200		724

Table 10. Estimation of the Number of Links Formed during the TBP Decomposition in SiH and in the Presence of Vi

		Si_2	SiViH	SiViMe and MeViSi	Si_2ViH and SiViSi	XVi_2H	XVi_{2U}	
TBP/SiH/Vi (eq)	no. of μmol	166	126	30	53	58	18	
1/220/0.67	no. of links	1	1	1	2	1	1	
	total	166	126	30	106	58	18	504

Scheme 11. Mechanism of a Peroxyketal Decomposition in a Polymer as PE and PP



produced in the medium, silylalkyl, methyl, and *tert*-butoxyl radicals. Since there was no remaining peroxide at the end of the heating, we cannot imagine the absence of homolysis of the O–O bond. So, we have to consider either an inefficiency of the production of silylalkyl radicals by mechanisms consuming the radicals afforded in the homolysis of O–O bond before they abstracted hydrogen to PDMS or consumption of silylalkyl radicals before their "symmetric" coupling to create links between the different macromolecules. It is important to point out the main differences existing between the model and the macromolecule which would influence the radical reactions. As mentioned above, in the discussion about the telomerization of the vinylic groups, the viscosity of the medium is very different between the small molecules and the macromolecules. Such a parameter drastically affects the diffusion of the radicals and their reactions.

We have been previously concerned with such phenomena of diffusion in the peroxyderivatives decomposition in molten polymers.[21–23] During the functionalization of polyolefins by cyclic peroxyketal decompositions, differences appeared between polyethylene (PE) and polypropylene (PP), functionalization being efficient in PE and not in PP. The fragmentation of alkoxyalkoxy radical generated instantaneously, in both cases, an alkyl radical close to its counter *tert*-butoxy radical (Scheme 11). In the case of PE, hydrogen abstraction to a methylene by a *tert*-butoxy radical was fast enough to allow the production of a macroradical, able to couple with the counter alkyl radical; meanwhile, with PP the main identified reaction of this pair of radicals was their combination to make a *tert*-butyl ether (Scheme 11). Despite the presence of very reactive tertiary hydrogen in PP, the lack of their abstraction was explained by the steric effect of the adjacent methyl prohibiting their approach by *tert*-butoxy radicals. If abstraction of hydrogen occurred on methyl, it was not fast enough to compete efficiently with the combination of both radicals. On this basis, reactivity of hydrogen present in PDMS toward *tert*-butoxy radicals would be closer to PP ones than to PE ones. Thus, even if the fragmentation of the *tert*-butoxy radical is much slower than the one of the alkoxyalkoxy radical, we may consider it. The methyl radical so generated may combine in the cage with the counter *tert*-butoxy radical or a methyl radical produced from it, then prohibiting the formation of silylalkyl radicals which would have to dimerize in order to enable the cross-linking of PDMS. Another possibility would be the "cage" coupling between a silylalkyl radical (obtained by hydrogen abstraction to a methyl group by one of the *tert*-butoxy radical) and a methyl radical arising from the other *tert*-butoxy radical. Such a hypothesis must be considered precautionously since, on the basis of the existence of cross-linking of PDMS containing some vinyl groups, we must admit that silylalkyl radicals were produced by the decomposition of TBP in PDMS. Indeed, this identified cross-linking involves the addition of a silylalkyl radical borne by a macromolecule to the vinyl of another one. A proposed termination of such an adduct radical by coupling with an other silylalkyl radical was then considered although the steric effect arising from the presence of three chains in the same neighborhood is not favorable for such a termination. However, even if this is accepted, one can see that whatever the mechanism considered (direct coupling or coupling after addition to the unsaturation) two radicals are necessary to create one or two links between macromolecules. The presence of a vinyl group would not favor so efficiently the cross-linking. Now, if we consider that the adduct radical reacts by hydrogen abstraction to a methyl of any chain, the radical acts only as "catalyst" to create a link between two macromolecules, since a new silylalkyl radical would be generated. Thus, the number of links generated would only depend on the number of unsaturations present in the medium, as it was observed by Falender.[24] So, one would easily understand the high change that was observed for the cross-linking of PDMS in the presence and absence of vinyl groups on the chain, if a partial unproductive consumption of PTB occurs.

A second hypothesis related to the increase of viscosity, going from siloxane to PDMS, is a a faster reaction of one *tert*-butoxy radical of the initial pair with the surrounding than the other one to generate a silylalkyl radical. This would produce in a close space a pair of a silylalkyl radical and a *tert*-butoxy one. They may either combine to provoke the grafting of a *tert*-butoxy or generate a carbene by disproportionation, as observed in the TBP decomposition in SiH at high level of peroxide. However, if such a reaction occurs, this transient would have to react, but certainly not to produce a link between two macromolecular chains, since it would enable cross-linking of PDMS. The main reaction given by these carbenes in the model study were dimerization and addition on a double bond to lead to oligomers. The assumption of the absence of free radical telomerization of vinylic entities present on polysiloxane chains, admitted above, ruled out, for the same reasons, the formation of oligomers by the carbenic way, conversely to the siloxane case. Complementary studies will be necessary to check these hypotheses. In particular, NMR studies (similar to the ones performed in this work) of the materials obtained after TBP decomposition in PDMS—since they do have a very low level of cross-linking (or none)—would allow to obtain interesting information on the production of unsaturations or new C−C sequences.

Conclusion

The TBP decomposition in SiH leads to the formation of silylalkyl radicals which reacts essentially by symmetric coupling to generate the dehydrodimer of the siloxane or by disproportionation with *tert*-butoxy radicals to create a carbene. This one dimerize and reacts with unsaturated compounds to give high molecular compounds. The competition between these two processes depend on the relative amount of TBP used. When the decomposition is carried out in the presence of Vi, the silylalkyl radicals produced add to the unsaturation of the vinylsiloxane to give radical adducts reacting by coupling with one of the radicals present in the medium, by disproportionation with *tert*-butoxy radicals, by hydrogen abstraction to SiH, or by addition to another molecule vinylsiloxane.

The comparison of these mechanisms with the ones proposed in the literature led us to select the proposition of Dunham et al.[6] and to reject the one of Bork and Roush[9] to explain the cross-linking efficiency for PDMS and PMVS.

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Supporting Information Available: NMR spectra of different compounds cited in the paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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