_____ LETTERS TO THE EDITOR

Liquid-Phase Oxidation of Pentamethyldisilane with Oxygen

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Tris(trimethylsilyl)silane reacts with oxygen to form bis(trimethylsiloxy)(trimethylsilyl)silane (Me₃SiO)₂Si(H)SiMe₃ as a major reaction product [1]. Oxidation of pentamethyldisilane can be used as a model reaction for studying oxidative conversions of silane polymers [2]. However, this reaction has not yet been studied.

Using IR spectroscopy, gas chromatography, and mass spectrometry we found that the major oxidation

products of pentamethyldisilane at 25–65°C are pentamethyldisiloxanol (I), pentamethyldisilanol (II), and pentamethyldisiloxane (III). The IR spectra of oxidized pentamethyldisilane samples contained absorption bands at 1060 and 3200–3600 cm⁻¹, characteristic of Si–O and O–H bonds, respectively. The silylhydroperoxide Me₃SiSi(OOH)Me₂ was not found among the reaction products. The formation of the major reaction products can be represented by the following scheme.

$$\begin{split} & \underbrace{\mathsf{Me_{3}SiSi(H)Me_{2}}\overset{O_{2}}{\longrightarrow} \mathsf{Me_{3}SiSi'Me_{2}}\overset{O_{2}}{\longrightarrow} \mathsf{Me_{3}SiSi(OO')Me_{2}} \overset{\mathsf{Me_{3}SiSi(OO')Me_{2}}}{\longrightarrow} \mathsf{Me_{3}SiSi(OO')Me_{2}}\overset{\mathsf{pentamethyldisilane}}{\longrightarrow} \mathsf{Me_{3}SiSi(OOH)Me_{2}}, \\ & \underbrace{\mathsf{Me_{3}SiSi(OO')Me_{2}}\overset{\mathsf{pentamethyldisilane}}{\longrightarrow} \mathsf{Me_{3}SiSi(OOH)Me_{2}}\overset{\mathsf{pentamethyldisilane}}{\longrightarrow} \mathsf{Me_{3}SiSi(OOH)Me_{2}}, \\ & \mathbf{II} \\ & \\ & \mathbf{Me_{3}SiSi(O')Me_{2}}\overset{\mathsf{pentamethyldisilane}}{\longrightarrow} \mathsf{Me_{3}SiOSi(H)Me_{2}}. \\ & \mathbf{III} \\ \end{split}$$

Pentamethyldisilane was prepared from chloropentamethyldisilane [3]. Pentamethyldisilanol (II) and pentamethyldisiloxanol (I) were synthesized starting from chloropentamethyldisilane and 3-acetoxy-1,1,1, 3,3-pentamethyldisiloxane, respectively [4, 5]. Pentamethyldisiloxane (III) is a commercial product (ABCR).

The oxidation of pentamethyldisilane with oxygen was performed in a temperature-controlled glass reactor with a magnetic stirrer. The temperature of the reaction mixture was maintained constant to within ± 1 °C. Oxygen was fed from a rubber balloon at 1 atm.

Thin-layer chromatography was performed on Silicagel-60 F254 plates (Merck). The IR spectra were obtained on a Nicolet-205 FT-IR spectrophotometer in a NaCl cell (0.5 mm) with a standard resolution of 2 cm⁻¹ in the range 400–4000 cm⁻¹. Gas chromatography-mass spectrometry was performed on an HP-5890 gas chromatograph with an HP-5972 mass-selective detector, column HP-5, temperature program

70-280°C (10 deg/min).

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