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Communications

Autoxidation of Tris(trimethylsilyl)silane

C. Chatgilialoglu,*[,1] A. Guarini,[2] A. Guerrini,[1] and G. Seconi[1]

I.Co.C.E.A., Consiglio Nazionale delle Ricerche, 40064 Ozzano Emilia, Italy, and Istituto Guido Donegani, Via Fauser 4, 28100 Novara, Italy

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Summary: Tris(trimethylsilyl)silane reacts spontaneously at ambient temperature with molecular oxygen to form $(Me_3SiO)_2Si(H)SiMe_3$ in high yield. The reaction proceeds via a free-radical chain mechanism and probably involves three consecutive unimolecular processes which are unknown in the literature.

The reactions of silanes with molecular oxygen, under free radical conditions, have been studied in some detail.[3] These oxidation processes, which proceed via chain mechanisms, gave silanols as the major products, and no species corresponding to a hydroperoxide or peroxide was isolated, in contrast with the oxidation of carbon analogues. Possible reaction schemes for such behavior have been proposed in the literature.[4] However, electron spin resonance studies indicate that alkyl- and aryl-substituted silylperoxyl radicals behave like alkyl peroxyl at low temperatures (below 233 K) and exist in equilibrium with a tetroxide.[5] The latter studies also indicate that the two oxygen nuclei in silylperoxyl radicals are magnetically non equivalent and that these radicals have more π spin density on the terminal oxygen than alkylperoxyl radicals.

Recently, we have shown that tris(trimethylsilyl)silane, TTMSS, functions as a free-radical reducing agent and is an attractive alternative to tributyltin hydride for the majority of its uses.[6] In this paper we report our preliminary work on the autoxidation[7] of tris(trimethylsilyl)silane.

During our initial work on TTMSS[8] as a radical-based reducing agent we noticed that this silane reacts spontaneously and slowly at ambient temperature with air to form a major product together with other minor ones. Isolation of the major product by preparative GC (purity >95% by analytical GC) followed by spectroscopic investigation based on NMR, IR, and mass spectrometry led to the following equation:[9]

$$(Me_3Si)_3SiH + O_2 \rightarrow (Me_3SiO)_2Si(H)SiMe_3 \qquad (1)$$

Several experimental procedures were employed to study the reaction of molecular oxygen with TTMSS, for example, exposure to air or O_2 bubbled into the pure material or its solutions. The percentages of conversion and yield depend upon the experimental conditions. For example, after 1 h of air bubbled into 1 mL of pure silane, GC analysis showed that the consumption of TTMSS reached about 50%, whereas the yield of $(Me_3SiO)_2Si(H)SiMe_3$ was almost quantitative. The fact that the reaction is retarded by common inhibitors, e.g., 2,6-*tert*-butyl-4-methylphenol, suggests a free-radical chain reaction. Tetrakis(trimethylsilyl)silane[8] cannot be oxidized under the same conditions. This also suggests that reaction 1 occurs by

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[1] Consiglio Nazionale delle Ricerche.

[2] Istituto Guido Donegani.

[3] For a recent review, see: Dohmaru, T. In *Chemical Kinetics of Small Organic Radicals. Vol. III: Reactions of Special Radicals*; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, 1988; pp 165–195.

[4] For example, see: Curtice, J.; Gilman, H.; Hammond, G. S. *J. Am. Chem. Soc.* **1957**, *79*, 4754.

[5] Howard, J. A.; Tait, J. C.; Tong, S. B. *Can. J. Chem.* **1979**, *57*, 2761. Bennett, J. E.; Howard, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 8244.

[6] Chatgilialoglu, C. *Acc. Chem. Res.*, in press.

[7] The term autoxidation actually applies to any slow oxidation with atmospheric oxygen. For example, see: March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985.

[8] $(Me_3Si)_3SiH$, $(Me_3Si)_3SiD$, and $(Me_3Si)_4Si$ were prepared following literature procedure: Buerger, H.; Kilian, W. *J. Organomet. Chem.* **1969**, *18*, 299. $(Me_3Si)_3SiH$ and $(Me_3Si)_4Si$ are also commercially available (Fluka or Aldrich).

[9] **Bis(trimethylsiloxy)methylsilane**: NMR spectroscopy was carried out on a Varian XL 300 spectrometer at 300, 75.429, and 59.591 MHz for ^1H, ^{13}C, and ^{29}Si, respectively. For all nuclei the chemical shifts (in ppm) are given with respect to TMS as internal standard: ^1H NMR (C_6D_6) δ 5.46 (1 H), 0.18 (18 H), 0.15 (9 H); ^{13}C NMR ($CDCl_3$) δ 1.68 [$OSi(CH_3)_3$], −3.06 [$SiSi(CH_3)_3$]; ^{29}Si NMR ($CDCl_3$) δ 25.44 (1Si), 23.68 (1Si), 21.58 (2Si); MS *m/z* 280 (M^+), 279 ($M^+ - 1$), 265 ($M^+ - 15$), 207 ($M^+ - 73$), 191 ($M^+ - 89$); IR ν_{Si-H} 2095 cm^{-1}. Anal. Calcd for $C_9H_{28}O_2Si_4$ (280.66): C, 38.52; H, 10.06; Found: C, 38.66; H, 10.12.

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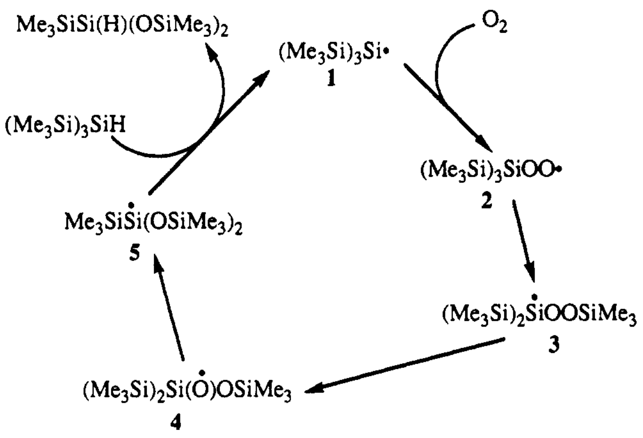
Scheme I. Intramolecular Mechanism



a free-radical mechanism rather than by direct insertion of any oxygen molecule to the Si–Si bond followed by a molecular rearrangement. When the SiH function in TTMSS is replaced by SiD,[8] $(Me_3SiO)_2Si(D)SiMe_3$ is formed exclusively.

The mechanisms that we conceive for reaction 1, following the fundamental concepts of free-radical chemistry, are two and are called *intermolecular* and *intramolecular*, respectively. By intermolecular mechanism we intend that the two oxygen atoms in the final product arise from two different oxygen molecules whereas in the intramolecular mechanism the two oxygen atoms arise from the same oxygen molecule.

Oxygen-labeling experiments were carried out to distinguish between intramolecular and intermolecular mechanisms. The tris(trimethylsilyl)silane was treated with a mixture of $^{16}O_2$ and $^{18}O_2$ (ca. 60/40 ratio).[10] The crude products were analyzed by mass spectrometry to determine the isotopic distribution. From the EI mass spectrum recorded by GC/MS analysis of the reaction mixture,[11] the relative amounts of the coeluting isotopomers $(Me_3Si^{16}O)_2Si(H)SiMe_3$, $(Me_3Si^{16}O)(Me_3Si^{18}O)Si(H)SiMe_3$, and $(Me_3Si^{18}O)_2Si(H)SiMe_3$ could be determined by measuring the relative abundance of the corresponding $[M - 15]^+$ (and $[M - 17]^+$) ions. A completely intramolecular mechanism would result in the same label distribution in the products as in the reactants whereas an intermolecular mechanism would lead to a statistical distribution of the labels in the products. The mass spectrometric results are reported in the following equation:

$$(Me_3Si)_3SiH + (\text{ca. } 60\%\ ^{16}O{-}^{16}O/40\%\ ^{18}O{-}^{18}O) \longrightarrow (Me_3Si^{16}O)_2Si(H)SiMe_3 + (Me_3Si^{18}O)_2Si(H)SiMe_3 \quad (2)$$

$$64:36$$

Therefore, an intramolecular free-radical chain process is responsible for such behavior.

The reaction sequence shown in Scheme I would agree with the above experimental data. That is, silyl radical 1 adds to molecular oxygen to form the peroxyl 2 which may rearrange to 3 by means of an unusual 1,3-shift of the Me_3Si group which then undergoes a homolytic internal substitution to form the silyloxyl radical 4. The latter could rearrange to 5 by a 1,2-shift of the Me_3Si group.[12,13] Hydrogen abstraction from the silane by radical 5 gives the desired product and the $(Me_3Si)_3Si^\bullet$ radical, thus completing the cycle of this chain reaction.[14] To our knowledge the unimolecular steps 2 → 3 (1,3-shift), 3 → 4 (S_Hi), and 4 → 5 (1,2-shift) in Scheme I are unknown reactions.[15] We believe that the strength of the silicon–oxygen bond is a potent driving force in these novel rearrangements. Further work on the mechanism of reaction 1 as well as on the autoxidation of other silanes is in progress.[17]

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Registry No. TTMSS, 1873-77-4; $(Me_3SiO)_2Si(H)SiMe_3$, 139347-50-5.

Supplementary Material Available: Spectra and details of the mass spectroscopic studies (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) The molar ratio of the $^{16}O_2/^{18}O_2$ gas mixture was determined from the intensities of $^{16}O_2^{\bullet+}$ and $^{18}O_2^{\bullet+}$ molecular ion peaks, recorded by electron impact ionization of the gas mixture.

(11) GC/MS was performed by using a Varian 3600 GC linked to a Finnigan MAT 8400 double-focusing instrument. The mass spectrometer was operated in EI ionization (70 eV) and at resolution of 1000, while the magnet was scanned from m/z 33 to 500 in 0.8 s.

(12) For 1,2-migration of the trimethylsilyl group in free radicals, see: Harris, J. M.; MacInnes, I.; Walton, J. C.; Maillard, B. *J. Organomet. Chem.* **1991**, *403*, C25 and references cited therein.

(13) A similar 1,2-migration of the Me_3Si group from Si to O has recently been observed: Ballestri, M.; Chatgilialoglu, C.; Lucarini, M.; Pedulli, G. F. *J. Org. Chem.* **1992**, *57*, 948.

(14) The initiation step remains in doubt.

(15) The reactions 2 → 3 (1,3-shift) and 4 → 5 (1,2-shift) in Scheme I are predicted to be exoergonic by at least 40 kcal mol^{-1}, on the basis of the known values of the bond dissociation energies[16] for $Me_3Si{-}SiMe_3$, 84.5 kcal mol^{-1}, and for $Me_3Si{-}OH$, 128 kcal mol^{-1}.

(16) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; pp 371–391.

(17) The oxygen-induced production of radicals from $(Me_3Si)_3SiH$ could be used to initiate some important reactions, such as the reduction of organic halides: Chatgilialoglu, C. Unpublished results.

Stereoselective Synthesis of (*E*)- and (*Z*)-1-Azabicyclo[3.1.0]hex-2-ylidene Dehydroamino Acid Derivatives

Robert W. Armstrong,* John E. Tellew, and Edmund J. Moran

Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90024

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Summary: Bromination of dehydroamino acid derivatives with NBS or Br_2/2,6-lutidine yields (*E*)- or (*Z*)-β-bromodehydroamino acid derivatives selectively. Subsequent intramolecular Michael addition–elimination of an aziridine proceeds with complete retention of olefin geometry to provide the 1-azabicyclo[3.1.0]hex-2-ylidene ring system

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