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Contribution from the Department of Chemistry,
The University of Oklahoma, Norman, Oklahoma 73019

# High-Pressure Reactions of Small Covalent Molecules. 9. Reaction of Methylsilanes with Covalent Oxides[1]

ARNULF P. HAGEN* and DON J. JONES

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The siloxane linkage forms when silicon compounds having an alkyl group are combined with covalent oxides at increased pressure. Tetramethylsilane forms hexamethyldisiloxane when combined with $CO_2$ (200 °C), $H_2O$ (250 °C), and $N_2O$ (360 °C) at 4000 atm. Methylfluorosilanes of the type $(CH_3)_xSiF_y$ ($x + y = 4$) also react with nitrous oxide with the reactivity declining in the order $(CH_3)_2SiF_2 > (CH_3)_3SiF > (CH_3)_4Si \gg CH_3SiF_3$. When dimethyldifluorosilane is combined with nitrous oxide at 3800 atm (230 °C), a 90% yield of the previously unreported substance $(CH_3SiF_2)_2O$ is obtained.

The silicon–carbon linkage in alkylsilanes is considered to be nonreactive at conditions which do not lead to thermal decomposition. The cleavage of this linkage followed by the subsequent formation of a silicon–oxygen bond is thermodynamically permitted at 25 °C (1 atm); however, the rate of reaction is exceedingly slow when nitrous oxide, carbon dioxide, or water provides the oxygen at moderate temperatures and at normal pressures. The cleavage reaction does not take place at moderate temperatures when the pressure is increased to at least 500 atm with the best yields occurring at pressures in excess of 1500 atm. This reaction also provides a general synthetic route for the formation of a silicon–oxygen linkage without the use of a hydrolysis reaction of a difficultly prepared precursor.

## Results and Discussion

**Reactions of Tetramethylsilane.** The experimental results for the reaction of tetramethylsilane with carbon dioxide, nitrous oxide, and water are summarized in Table I. The reaction in each case leads to the formation of hexamethyldisiloxane and appropriate other materials representative of the oxygen source

$$CO_2 + 4(CH_3)_4Si \rightarrow 2[(CH_3)_3Si]_2O + C + 2C_2H_6 \tag{1}$$

$$N_2O + 2(CH_3)_4Si \rightarrow [(CH_3)_3Si]_2O + N_2 + C_2H_6 \tag{2}$$

$$H_2O + 2(CH_3)_4Si \rightarrow [(CH_3)_3Si]_2O + 2CH_4 \tag{3}$$

The reaction with carbon dioxide below 400 °C takes place exactly as given by eq 1 with a 83% conversion at 200 °C (4000 atm). When the temperature is above 400 °C, nonvolatile siloxanes and methane are also obtained.

The reaction with $N_2O$ does not take place below 360 °C (2000 atm). The reaction does not form any other products, and a 63% conversion is obtained at 3700 atm. However, when the temperature is increased to 400 °C, a greater variety of products is obtained which includes $CH_4$, $C_2H_6$, $CO_2$, and nonvolatile siloxanes.

The reaction with water continues beyond the first cleavage. At 325 °C (1000 atm), reaction 3 takes place with a 48% conversion, but when the pressure reaches 2000 atm, the hexamethyldisiloxane undergoes further reaction to form a mixture of nonvolatile silicone oils. At 400 °C (4000 atm) 95% of the tetramethylsilane reacts forming a complex mixture of volatile and nonvolatile siloxanes.

Table I. Tetramethylsilane Reactions[a]

| Pressure, atm | Temp, °C | Conversion, % | Pressure, atm | Temp, °C | Conversion, % |
|---|---|---|---|---|---|
| | | Carbon Dioxide | | | |
| 4000 | 200 | 83 | 4000 | 150 | 0 |
| 3000 | 250 | 62 | 3000 | 200 | 0 |
| 1900 | 290 | 48 | 1700 | 250 | 0 |
| 1000 | 290 | 11 | 1000 | 250 | 0 |
| | | | 500 | 300 | 0 |
| | | Water | | | |
| 4000 | 250 | 55 | 4000 | 200 | 0 |
| 3000 | 300 | 52 | 3000 | 270 | 0 |
| 2000 | 300 | 52 | 2300 | 270 | 0 |
| 1000 | 325 | 48 | 1500 | 270 | 0 |
| 500 | 300 | 10 | 400 | 300 | 0 |
| | | | 200 | 400 | 0 |
| | | Nitrous Oxide | | | |
| 4000 | 360 | 55 | 4000 | 260 | 0 |
| 2900 | 360 | 55 | 2900 | 280 | 0 |
| 2500 | 400 | 52 | 2000 | 280 | 0 |
| 900 | 400 | 21 | 900 | 320 | 0 |
| | | | 300 | 400 | 0 |

[a] Conversion based on recovered methylfluorosilane. All reactions were for 18 h.

It is reasonable to propose that, of the reactions described in this report, some take place via the same general mechanism since the reaction conditions and products are similar. The initial reaction is postulated as the formation of a silyl radical, viz.

$$(CH_3)_4Si \rightarrow CH_3\cdot + (CH_3)_3Si\cdot$$

which then attacks the oxygen source. This hypothesis is supported by the isolation of simple substances which are reasonable reaction products of the methyl radicals. When elemental sulfur is added to the reaction tube containing one of the oxygen sources and tetramethylsilane, a mixture of sulfides is obtained and no hexamethyldisiloxane is isolated.

This is reasonable since sulfur readily forms free radicals which react with the methyl free radicals. The free-radical route for this reaction is also specifically supported by the reaction of $N_2O$ since it has been shown to readily form nitrogen below 400 °C when in the presence of a free-radical source[2] in an oxygen abstraction reaction

$$R\cdot + N_2O \rightarrow RO\cdot + N_2$$

Since no dimethyl ether was isolated in this study, it would be reasonable to postulate the $(CH_3)_3Si\cdot$ radical reacts with $N_2O$ faster than the methyl radical, or at least the combination reaction

$$2CH_3\cdot \rightarrow C_2H_6$$

takes place faster than the oxygen abstraction reaction. Also, the expected reaction of the methyl free radical to form products based on the abstraction of a hydrogen to form methane was not observed.

$$H_3C\cdot + (CH_3)_3SiF \rightarrow CH_4 + \cdot CH_2(CH_3)_2SiF$$

The use of pressure to activate a reaction with nitrous oxide is important since previous studies have shown $NO_2$ to react with Si–H, Si–C, and Si–Si linkages[3-5] but no reaction with the silicon–carbon linkage has been reported with thermally activated $N_2O$.[3] Also, no evidence exists for the thermal decomposition of tetramethylsilane taking place inside the gold ampules used in these experiments at conditions up to 500 °C (4000 atm); of course this may simply indicate an equilibrium which favors tetramethylsilane.

The effect of pressure is clearly shown to be important for the reactions. Since the reactions occur in sealed tubes, the major effect may be to increase the concentration of the reactants. The greatest change in concentration will take place in the first 500–1000 atm, since at pressures greater than 1000 atm the density of the fluid is near that of common organic liquids and the compressibility would be expected to be similar. This effect is important and most likely is the major role of pressure in these reactions if the rate-determining step is the formation of free radicals from the silane, since the volume of activation would be positive for the homolytic cleavage of the silicon–carbon linkage.

If the rate-determining step for the reactions described in this paper is second order, then the observed rate increase can also be explained in terms of an increase in the rate constant since the volume of activation would be negative. This would be reasonable if an interaction between the initially generated free radical with the oxygen source is the rate-determining step.

**Reactions of Methylfluorosilanes.** The reaction with $N_2O$ is also important since it offers a route to siloxanes which does not involve a hydrolysis step or form reactive intermediate products. Indeed, when fluorosilanes are combined with $N_2O$, the methyl–silicon linkage is selectively cleaved to form a siloxane

$$N_2O + 2(CH_3)_3SiF \rightarrow [(CH_3)_2SiF]_2O + N_2 + C_2H_6 \qquad (4)$$

$$N_2O + 2(CH_3)_2SiF_2 \rightarrow (CH_3SiF_2)_2O + N_2 + C_2H_6 \qquad (5)$$

$$N_2O + 2(CH_3)SiF_3 \rightarrow (SiF_3)_2O + N_2 + C_2H_6 \qquad (6)$$

As expected from thermodynamic calculations, no reaction takes place with $SiF_4$, and there is no indication of any products forming in the above reactions which result from the cleavage of the Si–F linkage.

The siloxanes from reactions 4 and 6 have been isolated in other reactions; however, this is the first report of $(CH_3SiF_2)_2O$ even though it has been sought by other research groups. For example, it would be expected to form from the mild fluorination of $(CH_3SiCl_2)_2O$ with ammonium fluoride, but none is isolated in this reaction, with 90% of the silicon being recovered as $CH_3SiF_3$.[6] When Tables I and II are compared, the thermal reactivity order is shown to be $Me_2SiF_2 > Me_3SiF > Me_4Si \gg MeSiF_3$.

Table II. Methylfluorosilane Reactions with Nitrous Oxide[a]

| Pressure, atm | Temp, °C | Conversion, % | Pressure, atm | Temp, °C | Conversion, % |
|---|---|---|---|---|---|
| | | Trimethylfluorosilane | | | |
| 3800 | 230 | 90 | 3800 | 200 | 0 |
| 3000 | 300 | 65 | 2500 | 230 | 0 |
| 1800 | 320 | 28 | 1700 | 290 | 0 |
| 700 | 390 | 10 | 600 | 390 | 0 |
| | | Dimethyldifluorosilane | | | |
| 4000 | 190 | 81 | 4000 | 120 | 0 |
| 3000 | 200 | 52 | 3000 | 140 | 0 |
| 1800 | 210 | 38 | 1800 | 180 | 0 |
| 700 | 280 | 15 | 700 | 200 | 0 |
| | | | 500 | 280 | 0 |
| | | | 300 | 380 | 0 |
| | | Methyltrifluorosilane | | | |
| 4000 | 500 | 80 | 3800 | 450 | 0 |
| 2300 | 500 | 80 | 2300 | 450 | 0 |
| 700 | 500 | 70 | 700 | 450 | 0 |

[a] Conversion based on recovered tetramethylsilane. All reactions were for 18 h.

## Experimental Section

A borosilicate glass vacuum system with Teflon stopcocks (Fischer & Porter Co., Warmininster, Pa.) was employed to purify and analyze volatile materials. High pressures were generated using a nitrogen gas pressure booster (High Pressure Equipment Co., Erie, Pa.) attached to a high pressure–high temperature hydrothermal research unit (Model HR-1B-4, Tem-Pres Research, State College, Pa.). Ampules made from 3-mm diameter thin-walled gold metal tubing contained the samples which were placed in a high-pressure reactor. At the end of a reaction period the reactor was cooled to −196 °C before releasing the pressure. The ampule was then placed into an opening device attached to the vacuum line and after warming of the ampule to room temperature, all condensable materials on the surface of the gold tubing were pumped away. The volatile substances were transferred directly into a vacuum line. Solid material was recovered in a glovebag under an $N_2$ or Ar atmosphere. All products were identified and confirmed by two or more techniques including infrared spectroscopy, mass spectroscopy, vapor pressure measurements, melting point determinations, or elemental analysis. Authentic samples of volatile molecular materials were used for identification of reaction products.

**Instrumentation.** Infrared absorption spectra were obtained in the 4000–300 $cm^{-1}$ region using a Beckman Model IR-10 double-beam, grating spectrophotometer. Volatile materials were confined in a 100-mm gas cell fitted with KBr windows sealed with rubber O-rings at reduced pressure. The instrument was calibrated using polystyrene. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-7E mass spectrometer. Tetramethylsilane was used as an internal standard for the fluorine spectra.

**Reagents.** The methylfluorosilanes were synthesized from the corresponding methylchlorosilane and antimony trifluoride.[7] Commercial $N_2O$ (Matheson), $CO_2$ (Matheson), and tetramethylsilane (Marshallton Research Laboratories, Inc.) were used. The water was triply distilled, deionized conductivity grade and was volatilized into the reaction vessel.

## Representative Reactions

Additional experiments are summarized in Tables I and II. In all cases a total of approximately 2 mmol of reactants was used. Some silane was recovered even when a deficit was used.

**Reaction of Tetramethylsilane with $N_2O$.** Commercial $N_2O$ (53.2 mg, 1.21 mmol) and tetramethylsilane (78.3 mg, 0.880 mmol) were condensed into a gold metal tube. The tube was sealed and held at 360 °C (4000 atm) for 18 h. A noncondensable gas was observed at −196 °C on opening. The condensable material was passed through traps cooled to −78 °C (solid $CO_2$/acetone mixture) and −126 °C (methylcyclohexane slush) into a −196 °C trap. The first trap contained hexamethyldisiloxane (40.1 mg, 0.248 mmol; identified by infrared spectrum[8] and confirmed by mass spectrum) and the second contained tetramethylsilane (29.0 mg, 0.329 mmol; identified by infrared spectrum).[9] The −196 °C trap contained $N_2O$ and ethane (identified by infrared spectrum).[10]

**Reaction of Tetramethylsilane with $CO_2$.** The same procedure was used for the carbon dioxide reactions.

**Reaction of Tetramethylsilane with Water.** Deionized distilled water (15.5 mg, 0.861 mmol) and tetramethylsilane (99.4 mg, 1.13 mmol) were condensed into a gold metal tube which was sealed and held at 250 °C (4000 atm) for 18 h. The tube was opened and methane was recovered as a noncondensable gas at −196 °C (identified by infrared spectrum). The material which condensed at −196 °C was passed through a trap cooled to −78 °C (solid $CO_2$/acetone mixture) into a −196 °C trap. The former trap contained a mixture of hexamethyldisiloxane, (identified by infrared spectrum and confirmed by mass spectrum) and water (identified by infrared spectrum). The mixture was then condensed into a tube containing a small amount of anhydrous magnesium sulfate to remove the water from the hexamethyldisiloxane (44.7 mg, 0.276 mmol). The −196 °C trap contained tetramethylsilane (42.0 mg, 0.487 mmol, identified by infrared spectrum).

**Reaction of Dimethyldifluorosilane with $N_2O$.** Commercial $N_2O$ (85.3 mg, 1.94 mmol) and $Me_2SiF_2$ (103 mg, 1.08 mmol) were condensed into a gold metal tube at −196 °C which was sealed and then held at 360 °C (4000 atm) for 18 h. The tube was opened and a noncondensable gas was observed at −196 °C. The condensable material was passed through traps cooled to −196 °C. The condensable material was passed through traps cooled to −117 °C (ethanol slush) and −130 °C (*n*-pentane slush) into a trap cooled to −196 °C. The −196 °C trap contained a mixture of ethane and nitrous oxide (identified by infrared spectrum)[10] and the −130 °C trap contained $Me_2SiF_2$. The −117 °C trap contained $(MeSiF_2)_2O$ (85.4 mg, 0.480 mmol; 90% conversion based on $Me_2SiF_2$ employed; bp −38 to −40 °C). Ir: 2995 (w), 1278 (s), 1150 (vs), 980 (vs), 940 (vs), 820 (s) $cm^{-1}$. Gas-phase mol wt: calcd, 178.2; found, 177.1. Mass spectrum (*m*/*e*): 163 (11), 161 (6), 160 (13), 159 (100), 131 (12), 129 (16), 81 (23), 77 (17), 51 (4), 49 (12), 47 (30), 43 (6).

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**Registry No.** $(CH_3)_4Si$, 75-76-3; $(CH_3)SiF_3$, 373-74-0; $(CH_3)_2SiF_2$, 353-66-2; $(CH_3)_3SiF$, 420-56-4; $[(CH_3)_3Si]_2O$, 107-46-0; $(MeSiF_2)_2O$, 63089-45-2; $N_2O$, 10024-97-2; $CO_2$, 124-38-9; $H_2O$, 7732-18-5.

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Contribution from Chemistry Division, Argonne National Laboratory,
Argonne, Illinois 60439

# Kinetic Study of the Reduction of Neptunium(VII) and Americium(VI) by Bromide Ion in Aqueous Perchlorate Media[1]

J. N. COOPER, M. WOODS, R. SJOBLOM, and J. C. SULLIVAN*

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The oxidation of $Br^-$ to bromine by the actinides, Am(VI) and Np(VII), has been found to proceed by the rate laws $-1/2(d \ln [Am(VI)]/dt) = k_1[Br^-] + k_2[Br^-]^2$ and $-d \ln [Np(VII)]/dt = [Br^-](k_1[H^+] + k_2[H^+]^2)$. The apparent activation parameters are $\Delta H_1^{\ddagger} = 15.7 \pm 0.1$ kcal/mol, $\Delta H_2^{\ddagger} = 12.5 \pm 0.1$ kcal/mol, $\Delta S_1^{\ddagger} = 2.5 \pm 2.7$ eu, and $\Delta S_2^{\ddagger} = -1.5 \pm 1.6$ eu for Am(VI) and $\Delta H_1^{\ddagger} = 9.4 \pm 0.3$ kcal/mol, $\Delta H_2^{\ddagger} = 3.9 \pm 0.5$ kcal/mol, $\Delta S_1^{\ddagger} = -8.8 \pm 1.1$ eu, and $\Delta S_2^{\ddagger} = -26.3 \pm 1.8$ eu for Np(VII). The rate laws are accounted for by mechanisms consistent with other oxidations of $Br^-$ and are compared with similar rate laws observed for the dioxo cation, $VO_2^+$.

## Introduction

The previous kinetic studies of the reactions between Np(VII) and a variety of reagents have led to an apparent correlation between the order with respect to $[H^+]$ in the rate law and the p$K_a$'s of the reductants.[2] The present investigation was undertaken, in part, to explore the consequences in the $[H^+]$ dependency when a nonacidic species is the reductant. Additional considerations that prompted this study were to determine the role of hydrogen ion in the oxidation of $Br^-$ by $AmO_2^{2+}$ (a metal ion that undergoes a 1-equiv reduction to the isostructural $AmO_2^+$), and add to the phenomenological description of the dynamics for the production of $Br_2$ using 1-equiv oxidants.[3]

## Experimental Section

**Reagents and Analysis.** The preparation and standardization of Np(VII), $LiClO_4$, and $HClO_4$ have been described previously.[4] Stock solutions of Am(III) were prepared as described previously[5] and for each kinetic run Am(VI), free of Am(V) and Am(III), was prepared by ozonizing a dispersion of Am(III) hydroxide in 0.1 M $NaHCO_3$, followed by acidification with $HClO_4$. Extinction coefficients for Am(VI) and Am(V) in 1.0 M $HClO_4$ were established by a photometric titration of Am(VI) with Np(V) according to the reaction

$$Am(VI) + Np(V) = Am(V) + Np(VI) \tag{1}$$

following both the decrease in absorbance at 996 nm due to loss of Am(VI) and the increase in absorbance at 980.5 nm after the endpoint due to unreacted Np(V). The resulting extinction coefficients at the principal maxima are listed in Table I.

**Table I.** Extinction Coefficients of Am(III), Am(V), and Am(VI) at Principal Maxima[a]

| | λ, nm | ε, $M^{-1}$ $cm^{-1}$ |
|---|---|---|
| Am(III) | 503.5 | 450 ± 4 |
| Am(V) | 514 | 50 ± 1 |
| | 718 | 66 ± 1 |
| Am(VI) | 667 | 30 ± 1 |
| | 996 | 107 ± 2 |

[a] At 1.00 M $HClO_4$, *T* = 25 °C.

Reagent LiBr was triply recrystallized from triply distilled water and standardized with silver nitrate using an eosin indicator. Bromine production was estimated with the strong absorption at 267 nm due to $Br_3^-$ formation in large excess $Br^-$ ($\epsilon \sim 3.8 \times 10^4$ $M^{-1}$ $cm^{-1}$). In all cases, the effective extinction coefficient of $Br_3^-$ was determined independently at the same $[Br^-]$ using the $BrO_3^-$–$Br^-$ reaction and a standard $BrO_3^-$ solution.

**Equipment and Procedures.** The computer-interfaced, stopped-flow instrumentation, as well as the basic procedures used in this work, have been detailed previously.[6] The reduction of Np(VII) was followed at 440 nm where the molar extinction coefficient of Np(VII) (ca. 410