The Hydroxyl Radical Reaction Rate Constants and Atmospheric Reaction Products of Three Siloxanes

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Received 7 August 1996; accepted 7 November 1996

ABSTRACT: The relative rate technique has been used to measure the hydroxyl radical (OH) reaction rate constant of hexamethyldisiloxane (MM, $(CH_3)_3Si{-}O{-}Si(CH_3)_3$), octamethyltrisiloxane (MDM, $(CH_3)_3Si{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_3$), and decamethyltetrasiloxane (MD_2M, $(CH_3)_3Si{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_3$). Hexamethyldisiloxane, octamethyltrisiloxane, and decamethyltetrasiloxane react with OH with bimolecular rate constants of $1.32 \pm 0.05 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}, $1.83 \pm 0.09 \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}, and $2.66 \pm 0.13 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}, respectively. Investigation of the OH + siloxane reaction products yielded trimethylsilanol, pentamethyldisiloxanol, heptamethyltetrasiloxanol, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and other compounds. Several of these products have not been reported before because these siloxanes and the proposed reaction mechanisms yielding these products are complicated. Some unusual cyclic siloxane products were observed and their formation pathways are discussed in light of current understanding of siloxane atmospheric chemistry. © 1997 John Wiley & Sons, Inc. Int J Chem Kinet **29:** 445–451, 1997.

INTRODUCTION

Volatile methyl siloxanes promise to be a more environmentally acceptable alternative to the volatile organic compounds used in solvents, penetrating oils, and lubricants [1]. The Air Force is investigating the possibilities of using these volatile methylsiloxanes for degreasing and wipe solvents to clean instruments and parts vital to Air Force missions. Siloxanes are very good cleaners which rapidly evaporate leaving no residue. These organosilicon solvents are not predicted to be stratospheric ozone depleters [2] or to be seriously toxic. Due to the characteristics previously mentioned, a potential increase in the use of these organosilicon compounds could occur, and this has stimulated recent activity investigating the environmental chemistry of several volatile organosilicon compounds [2–6]. The tropospheric OH radical is the primary oxidizing species for organosilicons in

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Contract grant Sponsor: Air Force
Contract grant number: Air Force contract F-08635-93-C-0020

the atmosphere [2–4]. The detailed atmospheric chemistry of these volatile compounds has not been fully investigated, resulting in knowledge gaps in the atmospheric assessment of these chemicals. The atmospheric impact of these new chemicals must be assessed before full-scale implementation occurs. Therefore, the rate constants and reaction products were determined for the gas-phase reactions of hydroxyl radical (OH) with hexamethyldisiloxane (MM, $(CH_3)_3Si{-}O{-}Si(CH_3)_3$), octamethyltrisiloxane (MDM, $(CH_3)_3Si{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_3$), and decamethyltetrasiloxane (MD_2M, $(CH_3)_3Si{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_3$).

During the course of this investigation, organosiloxanols and cyclic organosiloxane products were observed and the mechanisms leading to their formation are proposed.

EXPERIMENTAL METHODS

Apparatus and Materials

Experiments to measure the gas-phase rate constant of the OH + siloxane reaction were conducted with a previously described apparatus [7,8]. A brief description is provided here for convenience. Reactants were introduced and samples were withdrawn through a 6.4-mm Swagelok fitting attached to ca. 100 L Teflon® film chamber. Dry compressed air was added as a diluent to the reaction chambers and measured with a 0–100 $L\text{-}min^{-1}$ mass flow controller. The filler system was equipped with a syringe injection port facilitating the injection of both liquid and gaseous reactants into the chambers in a flowing airstream. All reactant mixtures and calibration standards were generated by this system. Irradiations were carried out in a light tight chamber using 2-mil FEP Teflon® film bags (ca. 100 liters), which were surrounded by the following mix of lamps: 6-Philips TL40W/03; 1-GE F40BL; 2-QPANEL UV351; and 7-QPANEL UV340.

All samples were quantitatively monitored using an Hewlett-Packard (HP) gas chromatograph (GC) 5890 with a flame ionization detector (FID) and an HP series 3396 integrator. Gas samples for GC analysis were cryogenically collected on a Hastelloy C sample loop (ca. 1.3 mL) and injected onto the GC column (J&W Scientific DB-5 column (0.25 mm i.d., 30 m, 1.0 μm film thickness)) with a heated rotary valve [9]. The GC temperature program used was as follows: 40°C for 6 min and 15°C/min to 110°C for 16 min. The GC column pressure program utilized was: 15 psi for 6 min and 0.10 psi/min to 19.6 psi for 19.14 min. Helium, UHP grade from Air Products, Inc., was used as the carrier gas.

OH, the primary oxidizing radical in the atmosphere, was generated from the photolysis of methyl nitrite (CH_3ONO) in the presence of nitric oxide (NO) in air [10].

$$CH_3ONO + h\nu \longrightarrow CH_3O + NO \tag{1}$$

$$CH_3O + O_2 \longrightarrow CH_2O + HO_2 \tag{2}$$

$$HO_2 + NO \longrightarrow \mathbf{OH} + NO_2 \tag{3}$$

CH_3ONO was prepared in gram quantities using the method of Taylor et al. [11] and stored in a lecture bottle at room temperature. The CH_3ONO purity was verified by GC/MS/FTIR.

Hexamethyldisiloxane (MM), octamethyltrisiloxane (MDM), and decamethyltetrasiloxane (MD_2M), (99%, 98%, and 95% purity, respectively) were obtained from Dow Corning and used as received. The reference compounds, cyclohexane, hexane, *n*-nonane (all 99%+), hexamethylcyclotrisiloxane (D_3, 98%), and ocatamethylcyclotetrasiloxane (D_4, 98%) were used as received from Aldrich Chemical. The nitric oxide (99%+ pure) was obtained from Matheson Gases and used as received. Experiments were carried out at 297 ± 3 K at about 1 atmosphere.

Experimental Procedures

The experimental procedures for determining the OH + siloxane reaction kinetics were similar to those described previously [7,8].

$$\text{Siloxane} + OH \xrightarrow{k_S} \text{Products} \tag{4}$$

$$\text{Reference} + OH \xrightarrow{k_R} \text{Products} \tag{5}$$

The rate equations for reactions 4 and 5 are combined and integrated resulting in the following equation:

$$\ln\left(\frac{[\text{Siloxane}]_0}{[\text{Siloxane}]_t}\right) = \frac{k_S}{k_R}\ln\left(\frac{[R]_0}{[R]_t}\right) \tag{6}$$

If reaction with OH is the only removal mechanism for siloxane and reference, a plot of $\ln([\text{Siloxane}]_0/[\text{Siloxane}]_t)$ vs. $\ln([R]_0/[R]_t)$ yields a straight line with an intercept of zero. Multiplying the slope of this linear plot by k_R yields k_s. The OH rate constant experiments employed the use of two reference compounds for each siloxane. The use of two different reference compounds with different OH rate constants more rigorously tested the accuracy of the siloxane/OH rate constant. Cyclohexane (reference for MM and MD_2M), hexane (reference for MM, MDM, and MD_2M), and *n*-nonane (reference for MDM) were the reference compounds (R) employed.

The typical concentrations of the pertinent species in the 100 liter Teflon® chamber were 0.5–1.0 ppm siloxane, 1.5–2.0 ppm reference, 9.0 ppm CH_3ONO, and 2.3 ppm NO in air. These mixtures were allowed to stand for 30–60 min before background chamber samples were collected. The samples were collected on a cryogenic (−110°C) sample loop for 4 min at 7.5 ml min^{-1} and then flash injected (260°C) onto the GC column. The flame ionization detector (FID) signal was used to determine siloxane, reference, and product concentrations. Pure samples of the reaction products that were commercially available were obtained to check for matching retention time and instrument calibration.

Siloxane/OH reaction product experimental methods were identical to those for reaction rate experiments except the reference compound was excluded from the reaction mixture. The the formation of products was plotted against loss of the parent siloxane generating a straight line with a slope equal to the product yield. Product identification was performed using the same GC, elution parameters, and column mentioned above with the column effluent analyzed by a Hewlett Packard 5972 mass selective detector (MS). The resulting mass spectra were compared against a Wiley 138 mass spectral library.

Typically, 15–30 s irradiation intervals were used on the reaction mixture for a combined total photolysis time of approximately 90 s. All measurements were at least duplicated. A relative standard deviation of approximately 2.5% was achieved with the described sampling method. All compounds were tested for interferences as follows: methyl nitrite and NO injected into the bag to determine elution times; methyl nitrite, NO and reference injected into bag, initial measurement taken to locate the reference, photolyzed for 3 min and further measurements taken to determine elution time of products, this procedure repeated for the siloxane; the reference and siloxane injected into the bag, measured and photolyzed for 6 min to determine stability; methyl nitrite, NO, reference and the siloxane injected into the bag, initial measurements taken and left overnight with further measurements to determine stability. None of these preliminary experiments yielded chromatographic peak overlaps nor observable reactions occurring without photoinitiation. At the end of each run, the Teflon® bag was cleaned by flushing the bag 10 times with zero-air. Measurements of an air filled bag showed no cross contamination between runs.

RESULTS

Hydroxyl Radical/Siloxane Reaction Rates

The OH rate constants for hexamethyldisiloxane, $(CH_3)_3Si{-}O{-}Si(CH_3)_3$, octamethyltrisiloxane, $(CH_3)_3Si{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_3$, decamethyltetrasiloxane, $(CH_3)_3Si{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_3$, were obtained using the relative rate method described above. Typically five experimental runs were conducted on each siloxane/reference pair. The plot of eq. (6) with hexane as the reference for all three siloxanes is shown in Figure 1. The MD_2M data set has been offset by 0.05 units on the y axis for clarity. The data points at the origin are experimental points because preirradiation $t = 0$, data showed no detectable loss of siloxane or reference. The slopes of these linear plots in Figure 1 are multiplied by the OH rate constant for hexane (5.61×10^{-12} $cm^3 molecule^{-1} s^{-1}$ [12]) yielding the rate constant for the respective siloxane. Similar rate constant plots were constructed for cyclohexane ((reference for MM and MD_2M) 7.49×10^{-12} $cm^3 molecule^{-1} s^{-1}$[12]) and *n*-nonane ((reference for MDM) 10.2×10^{-12} $cm^3 molecule^{-1} s^{-1}$[12]) as reference compounds. The silox-

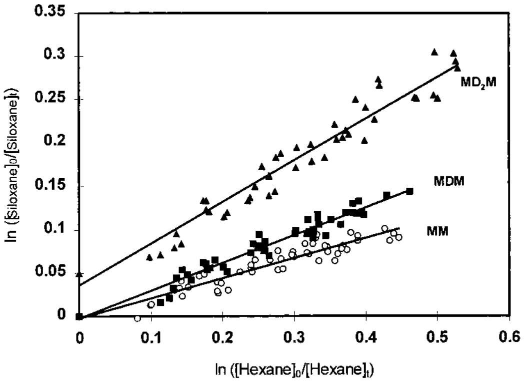

Figure 1 Plot of the relative rate of siloxane/OH reaction for hexamethyldisiloxane (MM,O, $(CH_3)_3Si{-}O{-}Si(CH_3)_3$), octamethyltrisiloxane (MDM, ■, $(CH_3)_3Si{-}(CH_3)_3Si{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_3$), decamethyltetrasiloxane (MD_2M, ▲, $(CH_3)_3Si{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_3$) against the reference compound, *n*-hexane. MD_2M data is shifted up on the y axis by 0.05 units to avoid confusion with MM and MDM. The slopes of the linear least-squares analysis with 95% confidence intervals are 0.231 ± 0.008, 0.320 ± 0.016, 0.4807 ± 0.023 for MM, MDM, and MD_2M, respectively.

ane/reference plots resulted in MM + OH, MDM + OH, and MD_2M + OH having bimolecular rate constants of $1.32 \pm 0.05 \times 10^{-12}$ $cm^3molecule^{-1}s^{-1}$, $1.83 \pm 0.09 \times 10^{-12}$ $cm^3molecule^{-1}s^{-1}$, $2.66 \pm 0.13 \times 10^{-12}$ $cm^3molecule^{-1}s^{-1}$, respectively. The errors in the rate constants are the 95% confidence level from the random uncertainty in the slope. This error does not include uncertainties associated with the reference rate constant that was used to derive the siloxane/OH rate constant. The MM/OH rate constant has been measured previously by Atkinson et al. ($1.38 \pm 0.36 \times 10^{-12}$ $cm^3molecule^{-1}s^{-1}$ [3]) and Sommerlade et al. ($1.19 \pm 0.30 \times 10^{-12}$ $cm^3molecule^{-1}s^{-1}$ [4]), and our MM/OH measurement is in agreement with the literature. To the best of our knowledge, the OH rate constants for MDM and MD_2M have not been previously reported. Assuming an $[OH] = 1 \times 10^6$ molecules cm^{-3}, the atmospheric (1/e) lifetimes calculated for MM, MDM, and MD_2M are 8.8, 6.3, and 4.3 days, respectively.

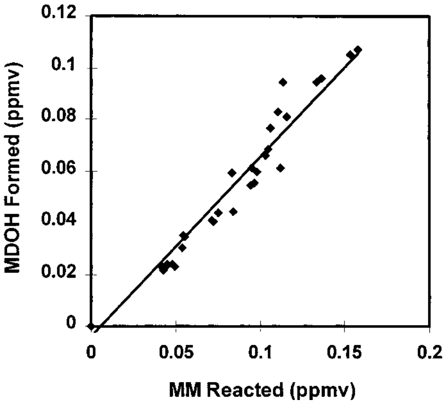

Figure 2 Plot of pentamethyldisiloxanol (MDOH, $HO(CH_3)_2Si{-}O{-}Si(CH_3)_3$) formed vs. hexamethyldisiloxane (MM, $(CH_3)_3Si{-}O{-}Si(CH_3)_3$) reacted. The slope of the linear least-squares analysis with a 95% confidence interval is 0.692 ± 0.021.

Hydroxyl Radical/Siloxane Reaction Products

OH/siloxane reaction products were observed in experiments performed in a similar manner to the reaction rate experiments except the reference compound was excluded from the reaction mixture. For clarification the observed products will be grouped by parent siloxane.

Hexamethyldisiloxane (MM)

The two main products observed in the OH/MM reaction were trimethylsilanol ($(CH_3)_3Si{-}OH$) and pentamethyldisiloxanol (MDOH, $(CH_3)_3Si{-}O{-}Si(CH_3)_2OH$). MDOH has been observed as an MM/OH reaction product by Carter et al. [2]. Atkinson et al. [6] have recently reported that MDOH is most likely a "secondary" product with the primary ester ($(CH_3)_3Si{-}O{-}(CH_3)_2Si{-}OCHO$) reacting with water to form MDOH. Because of the humidity of the air surrounding our experimental chambers, this could explain the observation of the silanol formation.

The yield data for pentamethyldisiloxanol (MDOH) is shown in Figure 2. The calibration factor used to determine the concentration of MDOH was the average of the calibration factors for MM, MDM, and MD_2M. The calibration factors for the three siloxanes were almost identical leading to the reasonable assumption that the addition of an OH group onto the siloxane backbone would have a negligible effect on the calibration factor. A method was employed to evaluate the effect of secondary reaction on the observed yield of MDOH. This method uses a two step mechanism, the formation of product (MDOH) due to reaction of OH + MM followed by OH + MDOH. This approach, which has been previously described in detail [13,14], yields an expression of the following form:

$$F = \frac{(k_R - k_P)}{k_R} \times \frac{1 - \dfrac{[\text{Siloxane}]_t}{[\text{Siloxane}]_0}}{\left(\dfrac{[\text{Siloxane}]_t}{[\text{Siloxane}]_0}\right)^{k_P/k_R} - \dfrac{[\text{Siloxane}]_t}{[\text{Siloxane}]_0}}$$

F represents the correction, k_R is the rate constant of OH + siloxane reaction, and k_P is the rate constant for the reaction of OH with MDOH. This expression was applied to the MDOH data. Work by Atkinson provided the OH rate constant for MDOH ($k_P = 1.89 \pm 0.36 \times 10^{-12}$ $cm^3molecule^{-1}s^{-1}$) [12]. The average MDOH concentration correction was on the order of 6%. From the plot shown in Figure 2 a MDOH yield of ca. 70% can be determined.

The same calibration assumptions made for MDOH cannot be made for $(CH_3)_3SiOH$, because the—OH group may have an effect on the calibration factor vs. $(CH_3)_4Si$. In any event, the $(CH_3)_3SiOH$ yield data were not linear and therefore not conclusive.

Octamethyltrisiloxane (MDM)

The MDM/OH reaction products observed included 1,1,3,3,5,5,5-heptamethyl-1-trisiloxanol (MD_2OH, $(CH_3)_2Si(OH)-O-(CH_3)_2Si-O-Si(CH_3)_3$), 1,1,1,3,5,5,5-heptamethyl-3-trisiloxanol (M_2TOH, $(CH_3)_3Si-O-(CH_3)Si(OH)-O-Si(CH_3)_3$), $(CH_3)_3SiOH$, MDOH, hexamethylcyclotrisiloxane (D_3, $((CH_3)_2Si-O-)_3$), and octamethylcyclotetrasiloxane, (D_4, $((CH_3)_2Si-O-)_4$). The major products observed were MD_2OH and M_2TOH. The rationale for the calibrations of these compounds is the same as above for MDOH. The MD_2OH and M_2TOH yield data is shown in Figures 3(a)(MD_2OH) and 3(b)(M_2TOH). The plots in Figure 3 show a distinct gap in the rise of the siloxanol relative to MDM loss. This gap may be an indication that these siloxanols are indeed secondary products resulting from the ester, $OCHO-Si-R_1R_2$ [6], reacting with water. No siloxane ester was observed using the experimental system described. The gap in the plot could be because (a) the k_{H2O} rate constant is slow, (b) a low concentration of $OCHO-Si-R_1R_2$ or (c) a combination of both. The lines drawn in Figures 3(a) and 3(b) are visual guides. The formation of the observed siloxanols might indeed be a complicated process.

Both $((CH_3)_2Si-O)_3$ and $((CH_3)_2Si-O)_4$ were verified on the GC/FID system by comparing the retention times of the pure cyclic siloxanes vs. the observed experimental product retention times. $((CH_3)_2Si-O)_3$ was also verified by comparing the mass spectrum of the product vs. the mass spectrum of the pure compound. The $((CH_3)_2Si-O)_4$ product has one more dimethylsilicone moiety than the parent compound. This is unusual and suggests that potential heterogeneous wall reactions may be occurring. Both of the cyclic siloxane products observed were commercially available so that calibration factors could be determined and the observed yield for each cyclic compound was on the order of 4%.

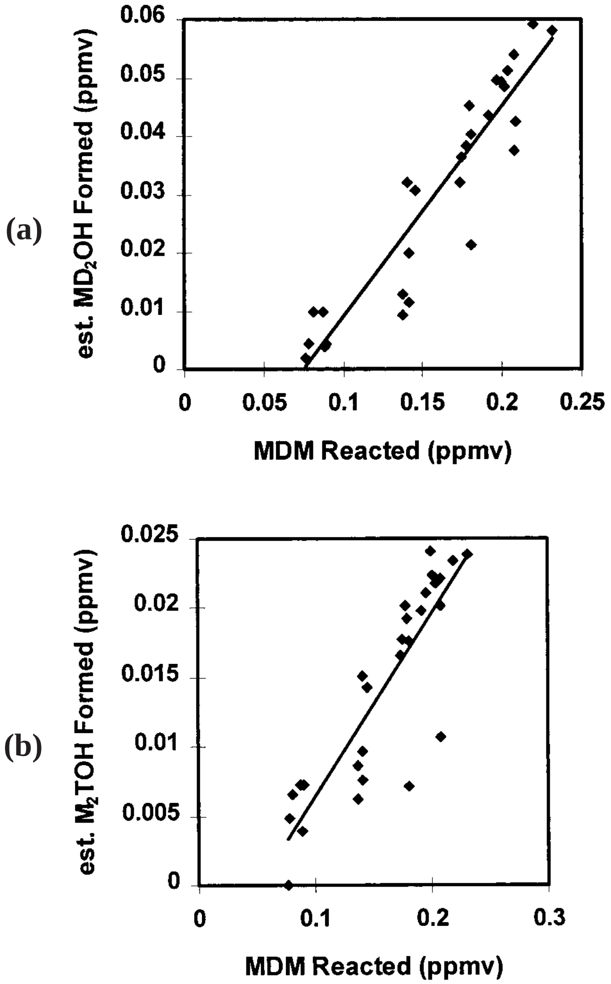

Figure 3 (a) Plot of 1,1,3,3,5,5,5 heptamethyl-1-trisiloxanol (MD_2OH, $(CH_3)_2Si(OH)-O-Si\ (CH_3)_2-O-Si(CH_3)_3$) formed vs. octamethyltrisiloxane (MDM, $(CH_3)_3Si-O-Si(CH_3)_2-O-Si(CH_3)_3$) reacted. The line is drawn as a visual guide. (b) Plot of 1,1,1,3,5,5,5 heptamethyl-3-trisiloxanol (MT_2OH, $(CH_3)_3Si-O-(OH)Si\ (CH_3)-O-Si(CH_3)_3$) formed vs. octamethyltrisiloxane (MDM, $(CH_3)_3Si-O-Si(CH_3)_2-O-Si(CH_3)_3$) reacted. The line is drawn as a visual guide.

Decamethyltetrasiloxane (MD_2M)

All of the observed products for MD_2M/OH were in low and inconsistent concentrations resulting in nonlinear [product] vs. [MD_2M] yield plots, suggesting a significant product loss mechanism. Sticking to the chamber walls could be the main reason for the nonlinear yield data and lack of a major product(s). However, some products were observed: MD_2OH, M_2TOH, $(CH_3)_3SiOH$, MDOH, $((CH_3)_2Si-O)_4$, and other unidentified products. As the reaction products get bigger, there could be a sticking process that would prevent the compounds from being observed.

Some unusual OH + siloxane reaction products were observed and verified. The cyclic siloxane products formed were unusual and unexpected.

DISCUSSION

OH reacts with MM, MDM, and MD_2M by H-atom abstraction from a methyl group attached to the silicon [2–4]. The reaction mechanisms, based upon the observed products are proposed in reactions (7) through (20). The formation of cyclic siloxane compounds from MDM and MD_2M present interesting mechanistic pathways where the RO_2 siloxane folds back on itself, loses a methyl group and adds an oxygen-silicon bond.

The experimental parameters were set to minimize other side reactions and highlight the first OH hydrogen abstraction step. Nitric oxide (NO) was added to facilitate the generation of OH and to quench ozone (O_3) formation and thus prevent unnecessary side reactions. However, siloxane/O_3 reaction rates have been shown to be negligible [3]. The OH generation was controlled by minimizing the total photolysis time so that only 20–30% of the siloxane was removed by reaction with the hydroxyl radical. The following mechanisms are proposed for the formation of OH + siloxane reaction products:

Mechanism for MM

$$\mathrm{OH} + (\mathrm{CH_3})_3\mathrm{Si{-}O{-}Si(CH_3)_3} \longrightarrow \mathrm{CH_2(CH_3)_2Si{-}O{-}Si(CH_3)_3} + \mathrm{H_2O} \quad (7)$$

$$\mathrm{CH_2(CH_3)_2Si{-}O{-}Si(CH_3)_3} + \mathrm{O_2} \longrightarrow \mathrm{OOCH_2(CH_3)_2Si{-}O{-}Si(CH_3)_3} \quad (8)$$

$$\mathrm{OOCH_2(CH_3)_2Si{-}O{-}Si(CH_3)_3} + \mathrm{NO} \longrightarrow \mathrm{OCH_2(CH_3)_2Si{-}O{-}Si(CH_3)_3} + \mathrm{NO_2} \quad (9)$$

$$\mathrm{OCH_2(CH_3)_2Si{-}O{-}Si(CH_3)_3} + \mathrm{O_2} \longrightarrow \mathrm{OCHO(CH_3)_2Si{-}O{-}Si(CH_3)_3} + \,? \quad (10)$$

$$\mathrm{OCHO(CH_3)_2Si{-}O{-}Si(CH_3)_3} + \mathrm{H_2O} \longrightarrow \mathrm{HO(CH_3)_2Si{-}O{-}Si(CH_3)_3}\ \mathbf{(MDOH)} + \mathrm{HC(O)OH} \quad (11)$$

Reaction (11) has been proposed by Atkinson et al. [3]. The ester ($OCHO(CH_3)_2Si{-}O{-}Si(CH_3)_3$) was proposed as the product responsible for the data observed in their atmospheric pressure ionization mass spectral (API MS/MS) and long path FTIR experiments. However, water in the atmosphere would drive reaction (11) so that while MDOH is a “second generation” product, it is likely to be the important product from the atmospheric transformation of MM. The data presented here supports this fact as the observed product MDOH is in ca. 70% yield.

Mechanism for MDM

The first step of this mechanism, the removal of a hydrogen from a methyl group by OH, is left out for brevity. The $\underline{\check{\mathbf{S}}}$ is defined as the rest of the siloxane molecule.

Formation of both MD_2OH and M_2TOH most likely have very similar mechanisms:

$$\mathrm{CH_2}\underline{\check{\mathbf{S}}} + \mathrm{O_2} \longrightarrow \mathrm{OOCH_2}{-}\underline{\check{\mathbf{S}}} \quad (12)$$

$$\mathrm{OOCH_2}{-}\underline{\check{\mathbf{S}}} + \mathrm{NO} \longrightarrow \mathrm{OCH_2}{-}\underline{\check{\mathbf{S}}} + \mathrm{NO_2} \quad (13)$$

$$\mathrm{OCH_2}{-}\underline{\check{\mathbf{S}}} + \mathrm{O_2} \longrightarrow \mathrm{OCHO}{-}\underline{\check{\mathbf{S}}} \quad (14)$$

$$\mathrm{OCHO}{-}\underline{\check{\mathbf{S}}} + \mathrm{HO_2} \longrightarrow \mathrm{HO}{-}\underline{\check{\mathbf{S}}}\ \mathbf{(MD_2OH\ and\ M_2TOH)} \quad (15)$$

Formation of the cyclic compound requires the addition of an oxygen molecule to an open site on the silicon and the loss of a methyl group as the ring closes. In the gas phase: ($\underline{\mathrm{Si}} = (\mathrm{CH_3})_2\mathrm{Si}$)

$$\mathrm{CH_2}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}(\mathrm{CH_3}) + \mathrm{O_2} \longrightarrow \mathrm{OOCH_2}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}(\mathrm{CH_3}) \quad (16)$$

$$\mathrm{OOCH_2}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}(\mathrm{CH_3}) + \mathrm{NO} \longrightarrow \mathrm{OCH_2}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}(\mathrm{CH_3}) + \mathrm{NO_2} \quad (17)$$

$$\mathrm{OCH_2}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}(\mathrm{CH_3}) \longrightarrow \underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}(\mathrm{CH_3}) + \mathrm{CH_2O} \quad (18)$$

$$\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}(\mathrm{CH_3}) + \mathrm{O_2} \longrightarrow \mathrm{OO}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}(\mathrm{CH_3}) \quad (19)$$

$$\mathrm{OO}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}{-}\mathrm{O}{-}\underline{\mathrm{Si}}(\mathrm{CH_3}) \xrightarrow{-\mathrm{CH_3},\,-\mathrm{O}} ((\mathrm{CH_3})_2\mathrm{Si{-}O})_3) \quad (20)$$

This rearrangement could also be the product of a surface reaction. The observation of ocatmethylcyclotetrasiloxane ($(((CH_3)_2Si{-}O)_4)$) as a “product” suggests a surface mechanism in which another $Si(CH_3)_2$ is added to the parent siloxane. The possibility of this occurring in the gas phase is remote due to the lower concentrations of the first generation reaction products.

The reaction mechanism for MD_2M is difficult to interpret due to the poor correlations between observed products’ concentrations vs. loss of MD_2M. Here again, surface reactions may play a role and cloud useful gas-phase mechanistic information.

CONCLUSION

The OH rate constants for hexamethyldisiloxane ($(CH_3)_3Si{-}O{-}Si(CH_3)_3$), octamethyltrisiloxane

$((CH_3)_3Si-O-Si(CH_3)_2-O-Si(CH_3)_3)$, and decamethyltetrasiloxane $((CH_3)_3Si-O-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_3)$ have been determined using the relative rate technique. The siloxane OH rate constants increase with additional lengthening of the siloxane backbone. Hexamethyldisiloxane, octamethyltrisiloxane, and decamethyltetrasiloxane react with OH with bimolecular rate constants of $1.32 \pm 0.05 \times 10^{-12}$ $cm^3molecule^{-1}s^{-1}$, $1.83 \times 0.09 \times 10^{-12}$ $cm^3molecule^{-1}s^{1}$, and $2.66 \pm 0.13 \times 10^{-12}$ $cm^3molecule^{-1}s^{-1}$, respectively. The OH rate constant for MM is in agreement with the values reported in the literature [3,4]. However, this is the first published report of the OH rate constant for both MDM and MD_2M. The reported OH rate constants yield atmospheric (1/e) lifetimes of 8.8, 6.3, and 4.3 days, for MM, MDM, and MD_2M, respectively.

The observed products of the OH + siloxane reactions have been used to propose the atmospheric mechanisms of MM, MDM, and MD_2M. For MM the major product observed is pentamethyldisiloxanol (MDOH, $HO-Si(CH_3)_2-O-Si(CH_3)_3$), but experiments done by Atkinson et al. [6] conclude that MDOH is a “second generation” product of water reacting with a siloxane ester product. Even though it may not be a direct product, due to the water in the atmosphere MDOH is most likely an important component in determining the atmospheric assessment of MM. Both MDM and MD_2M do not have such clearly defined mechanistic pathways. MDM’s major observed products were the two siloxane alcohols, MD_2OH and M_2TOH, but similarly to MDOH they are most likely “second generation” products. The observation of cyclic siloxanes during MDM and MD_2M product experiments highlights interesting molecular transformations.

This project was supported in part by Air Force contract F-08635-93-C-0020. The authors also wish to thank Majors Floyd Wiseman and Carolyn Vadnais for helpful comments, John Moore of Dow Corning Corporation for providing samples of the siloxanes, and Drs. Barry Arkles (Gelest Corporation), Grish Chandra (Dow Corning), and Cecil Frye (Dow Corning) for helpful discussions.

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