the higher energy $\sigma \rightarrow \sigma^*$ transition $A_g \rightarrow B_{2u}(^1B_{2u})$ is also predicted to be negative. These predictions lead to the order of these states reflected in the assignments of Table IV.

The spectra of the *trans*-$Au(CN)_2X_2^-$ ions also exhibit an intense high-energy band (band III for X = Cl^- and band IV for X = Br^- or I^-) that has no counterpart in the spectra of AuX_4^- and cannot be explained in terms of halide LMCT. For *trans*-$Au(CN)_2Br_2^-$ and *trans*-$Au(CN)_2Cl_2^-$ positive B_0 terms corresponding to these bands are observed in the MCD. These bands are tentatively assigned to $\pi(CN^-) \rightarrow \sigma^*$, LMCT involving the occupied π orbitals of the cyano ligands. In view of the intensities, the excited states are likely of B_{2u} symmetry ($1b_{2u}' \rightarrow 4a_g(x^2 - y^2)$) because σ–π mixing of the CN^- π orbital ($1b_{2u}$) with the halide σ orbital ($2b_{2u}$) via eq 3 would provide $\sigma \rightarrow \sigma^*$ character to the transition. The corresponding LMCT transition in $Au(CN)_4^-$ must occur at higher energy than for the *trans*-$Au(CN)_2X_2^-$ ions because no maxima or shoulders are observed below 5.2 μm^{-1}.[10] A red shift in CN^- LMCT for *trans*-$Au(CN)_2X_2^-$ is reasonable because the halide ligands are expected to be poorer σ donors than CN^-, resulting in a more stable σ^* orbital ($4a_g(x^2 - y^2)$ of Figure 1).

Bands in the spectra of $AuBr_4^-$ (band V at 5.05 μm^{-1} and also bands at 4.48 and 4.94 μm^{-1} in the MCD), *trans*-$Au(CN)_2Br_2^-$ (band V at 4.95 μm^{-1}), and *trans*-$Au(CN)_2I_2^-$ (bands V at 4.70 μm^{-1} and VI at 4.92 μm^{-1}) have not yet been assigned. These bands are all quite intense, characteristic of allowed transitions, but they cannot be interpreted within the LMCT model. They occur at high energy in a region where free halide ions are known to exhibit intense bands. For example Br^- in acetonitrile has intense bands with maxima at 4.59 μm^{-1} (ϵ 10700) and 4.93 μm^{-1} (ϵ 10600) while I^- has bands with maxima at 4.08 μm^{-1} (ϵ 16300) and 4.88 μm^{-1} (ϵ 22000).[22] These spectra are sensitive to the nature of the solvent and have been assigned to a process described as charge transfer to solvent (CTTS).[22-24] The spectra of the $AuBr_4^-$ and *trans*-$Au(CN)_2Br_2^-$ in water do show some differences from spectra in acetonitrile in this high-energy region, but difficulties due to hydrolysis cannot be ruled out entirely. Suppression of hydrolysis by adding excess halide ion obscures the changes of interest. The dissociation equilibrium for *trans*-$Au(CN)_2I_2^-$ likewise makes measurements in this region uncertain. However, on the basis of their energy and intensity, the high-energy bands in the halo Au(III) complexes are tentatively assigned as CTTS. The MCD for $AuBr_4^-$ and *trans*-$Au(CN)_2Br_2^-$ (band V in each case) is qualitatively consistent with that reported for Br^- CTTS in acetonitrile.[22]

The spectral assignments of the *trans*-$Au(CN)_2BrY^-$ ions given in Table IV are made by analogy to the *trans*-$Au(CN)_2X_2^-$ ions. The symmetry representations are given for their lower molecular symmetry (C_{2v}), but these representations are easily correlated with those of D_{2h}. The bands in these mixed-halo complexes are intermediate in energy between *trans*-$Au(CN)_2Br_2^-$ and *trans*-$Au(CN)_2Y_2^-$ (Y = Cl^-, I^-).

General Trends in LMCT Spectra. In terms of general trends among the halo Au(III) LMCT spectra, the characteristic energy shifts of corresponding bands in the order $Cl^- > Br^- > I^-$ are observed. This "hallmark" order of LMCT follows the stability of the occupied halide orbitals and depends to a lesser extent on differences in halide σ bonding, which affect the σ^* orbital stability. The energy shifts $Au(CN)_4^-$ > *trans*-$Au(CN)_2X_2^-$ > AuX_4^- for corresponding LMCT bands is also a feature of the Au(III) spectra and can be rationalized by the increase in stability of the σ^* orbital as the strong σ donor CN^- is replaced by a weaker σ-donor halide. When the $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ energy differences for AuX_4^- and *trans*-$Au(CN)_2X_2^-$ are compared, it is interesting that the energy difference between these two types of transitions is greater for AuX_4^- (1.31 μm^{-1} for Cl^- and 1.38 μm^{-1} for Br^-) than for *trans*-$Au(CN)_2X_2^-$ (1.13 μm^{-1} and 1.07 μm^{-1} for Br^-). The greater difference for AuX_4^- may reflect the σ–π intermixing between the halide σ- and π-bonding MO's ($1e_u$ and $2e_u$), which will serve to separate them. In contrast, the σ–π mixing in *trans*-$Au(CN)_2X_2^-$ involves mixing between the halide orbitals and more stable CN^- orbitals, which is likely less extensive and serves to destabilize both the σ and π halide orbitals. It must be admitted however that the differences are not large and may also reflect electron-repulsion differences between the two types of complexes.

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Registry No. $AuCl_4^-$, 14337-12-3; $AuBr_4^-$, 14337-14-5; *trans*-$Au(CN)_2Cl_2^-$, 39048-42-5; *trans*-$Au(CN)_2Br_2^-$, 30869-88-6; *trans*-$Au(CN)_2I_2^-$, 39043-93-1; *trans*-$Au(CN)_2BrCl^-$, 30869-89-7; *trans*-$Au(CN)_2BrI^-$, 86088-79-1.

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Photooxidation of Trichlorosilane in Silicon Tetrachloride

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Trichlorosilanol, Cl_3SiOH, was formed by low-pressure mercury-lamp photolysis of trichlorosilane, Cl_3SiH, and oxygen in silicon tetrachloride. This conversion was quantitative at low silane concentrations (200–2500 ppm) and was used to determine an infrared absorptivity at 3680 cm^{-1} of 102 ± 5 L/(mol cm) for Cl_3SiOH, a very reactive impurity in $SiCl_4$ that is unavailable in pure form. The high quantum efficiency (≥285) indicated a radical-chain pathway for the reaction. The hydroperoxide Cl_3SiOOH was not detected even under low-temperature photolysis where it should be thermally stable and was not likely to be a significant intermediate.

Introduction

The determination and removal of impurities from reactive compounds present interesting challenges in analysis and purification. The highly reactive and sensitive halides of silicon and germanium are used to fabricate optical waveguide glass fibers via the modified chemical vapor deposition (MCVD)

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process.[1] The desired high purity of these glasses requires the removal of metal and hydrogenic impurities from the halides. These halides also react vigorously with atmospheric moisture to yield hydroxyl-containing impurities, which can contribute to the introduction of undesirable hydroxyl groups during the high-temperature oxidative process used to form waveguide glasses. Thus, systematic studies of the determination, formation, and reactions of metal, hydrogenic, and hydroxyl impurities in various MCVD reagents are under way.[2]

The quantitative determination of metal[3] and hydrogenic impurities[4] in silicon tetrachloride, $SiCl_4$, has been accomplished by atomic absorption and infrared spectroscopy, respectively. The determination of trichlorosilanol, Cl_3SiOH, a particularly reactive species that is unavailable in pure form,[5] was accomplished recently by generating standard solutions, in situ, by the photooxidation of trichlorosilane, Cl_3SiH, in $SiCl_4$[5]. This photochemical generation of known quantities of an ordinarily unavailable compound enabled the experimental determination of its infrared extinction coefficient.

The photooxidation of Cl_3SiH to Cl_3SiOH proceeded quantitatively at ppm levels in relatively short time, although the photolyses were done at wavelengths greater than 250 nm, where the reactants, Cl_3SiH and O_2, and $SiCl_4$ have very low absorbances. In the present work, this photochemical reaction has been found to proceed via a radical-chain pathway that may be analogous to the photooxidation of hydrocarbons[7] and halocarbons.[8]

Experimental Section

Chemicals. Semiconductor grade $SiCl_4$ was obtained from various commercial sources and used without further purifications. High-purity Cl_3SiH (Alfa 99.8%), was distilled under nitrogen and a center fraction used. Hydrogen peroxide (FMC, 98%) was used without further purification. High-purity oxygen (Airco) was supplied in aluminum cylinders and contained less than 0.2 ppm of hydrocarbons. Oxygen, argon, and nitrogen were further dried by slow passage through a dry ice cooled copper coil trap or an Ascarite filter. All organic solvents were of the highest available commerical purity or freshly distilled under nitrogen prior to use.

Sample Preparation and Handling. To minimize atmospheric hydrolysis, all samples were handled and stored inside polyethylene glovebags filled with dry nitrogen. Samples were mixed or stored in Teflon bottles and transferred with glass Luer-Lok syringes and Teflon needles. Connections were made with Teflon tubing and valves. All glassware and plasticware were cleaned by rinsing in HF solution and distilled water and then dried in a vacuum oven at 120 °C for at least 4 h prior to use.

Infrared and Ultraviolet Analysis. Infrared spectroscopy was generally used to identify and monitor reactants and products. The infrared spectra were obtained with a Perkin-Elmer 421 spectrometer or 597 spectrophotometer, while purged with N_2 to protect the instruments. Liquid spectra were taken with 0.4 cm stainless steel cells equipped with Luer-Lok syringe tips for filling and silver chloride windows. Low-temperature spectra were taken by placing a 0.4-cm cell inside a low-temperature cell equipped with NaCl windows. The 0.4-cm cell was then filled while the larger cell was purged with argon, to avoid condensation on the cell windows.

Ultraviolet spectra were obtained on a Perkin-Elmer Model 330 ultraviolet–visible spectrophotometer. Liquid cells used were 1-cm path length and were sealed with Teflon valves.

Photooxidation of Cl_3SiH in $SiCl_4$. Room-temperature photolyses were done in cylindrical quartz cells, designed to allow a continuous flow of oxygen through the solution. The light source was two 50-W low-pressure mercury lamps with aluminum reflectors. The photolysis cell was mounted between the two lamps at 10 cm from each lamp to maintain a cell temperature of 24–26 °C. During photolysis, the cell was vented to the atmosphere through at charcoal–NaOH trap.

A solution of $SiCl_4$ containing 200–2500 ppm of Cl_3SiH was transferred to the cell under a nitrogen atmosphere, the cell connected to an oxygen line, and oxygen passed through at 3–5 mL/min. The course and extent of reaction was monitored by IR spectroscopy. Complete conversion of the silane occurred usually in 1.5–3 h with no visible precipitate. Blank runs of $SiCl_4$ alone indicated no observable photochemical changes.

Quantum Yield of Cl_3SiH Conversion. Due to the low absorption of the reactants, Cl_3SiH and O_2, and the solvent, $SiCl_4$, at 254 nm, only a lower limit of the quantum yield of Cl_3SiH conversion to Cl_3SiOH could be determined. The photon flux entering the cell (10 $cm^2 \times 3$ cm) was measured as 2.67×10^{-9} einstein/(s cm^2) with use of an Eppley wire-wound thermopile. The absorption of the solution, 2.4%, was estimated from that determined for 1 cm of pure $SiCl_4$. Therefore, 3.27×10^{-4} mol of Cl_3SiH was consumed after 30 min of photolysis and 1.15×10^{-6} einstein absorbed, giving a quantum yield of ≥ 285 based on light absorbed by $SiCl_4$.

Low-Temperature Photolysis of Cl_3SiH in $SiCl_4$. A 1 cm quartz cell was filled with solution under N_2 and placed in a Dewar cell equipped with quartz windows. The cell was cooled with N_2 gas to −50 to −60 °C. The cell was irradiated with light from a 700-W medium-pressure mercury lamp while an oxygen stream was passed through the cell. After 30 min, a sample was transferred to the apparatus used for low-temperature IR studies and a spectrum was quickly taken. About 25% of the Cl_3SiH was consumed while the SiOH band showed a similar increase. No other products were detected.

Photolysis of Cl_3SiH in the Presence of NO_2. A 500-mL glass bulb was evacuated and filled with a mixture of NO_2 and O_2. An O_2 stream was passed through the bulb and into a photolysis cell. The cell was irradiated with the 313 ± 10 nm output from a 2.5-kW Hg–Xe lamp and Schoeffel high-intensity grating monochromator. After 3 h of photolysis, IR spectra showed little or no change in SiH and SiOH bands.

Reaction of $SiCl_4$ and H_2O_2. A saturated solution of H_2O_2 in CCl_2 was prepared under nitrogen. The IR spectrum of this solution showed two bands in the OH stretching region at 3625 and 3550 cm^{-1} (~1:3) corresponding to H_2O and H_2O_2, respectively. When 2 mL of this solution was added to 5 mL of $SiCl_4$ at room temperature, the resulting IR spectrum showed a single OH band at 3680 cm^{-1} corresponding to SiOH. When the CCl_4 solution and $SiCl_4$ were cooled to −50 °C in a dry ice–acetone bath prior to mixing, the resulting IR spectrum showed OH bands at 3680 and 3535 cm^{-1} (2:1) in agreement with assignments for SiOH and SiOOH, respectively. Upon warming of the cell to room temperature, the 3535-cm^{-1} band (SiOOH) disappeared, while the 3680-cm^{-1} band (SiOH) increased in intensity.

Results

The facile and efficient conversion of Cl_3SiH by photooxidation allows the measurement of the infrared absorptivity of the OH stretch of the very reactive Cl_3SiOH. Figure 1 shows the infrared spectra of solutions before and after photolysis. The IR band at 2260 cm^{-1} (Cl_3SiH) is totally removed, and bands at 3680 and 965 cm^{-1} (Cl_3SiOH) increased in a similar manner. These bands as well as the lower frequency SiCl bands have been confirmed in matrix isolation studies as being characteristic of Cl_3SiOH.[9] At these concentration levels, Cl_3SiOH appears to be stable in $SiCl_4$, for at least

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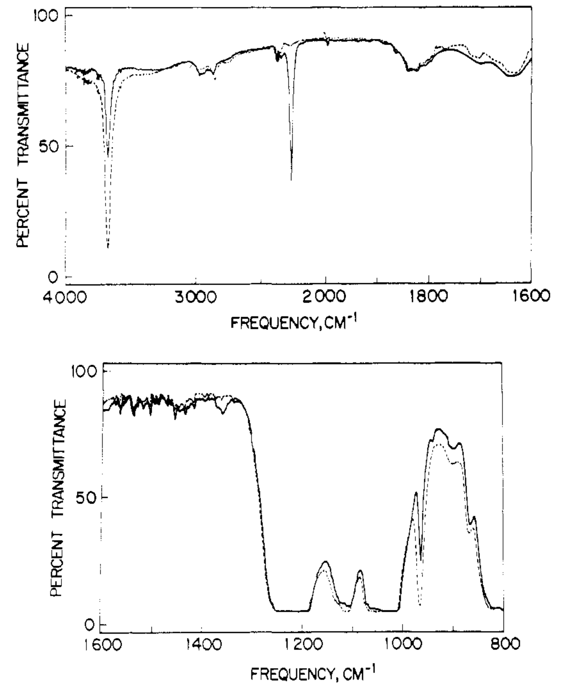

Figure 1. Liquid-phase infrared spectra of Cl_3SiH in $SiCl_4$ before (—) and after (---) 1.5 h of photooxidation at 254 nm.

several days. No further reaction via self-condensation (eq 1) or with $SiCl_4$ (eq 2) is observed. After several weeks or

$$Cl_3SiOH \rightarrow Cl_3SiOSiCl_3 + [H_2O] \quad (1)$$

$$Cl_3SiOH + SiCl_4 \rightarrow Cl_3SiOSiCl_3 + HCl \quad (2)$$

months, a noticeable buildup of $Cl_3SiOSiCl_3$, as evidenced by IR bands at 1870, 1735, and 1575 cm^{-1}, occurs. By the use of standard solutions of Cl_3SiH, the infrared absorptivity of the SiO–H stretch at 3680 cm^{-1} was determined to be 102 ± 5 L/(mol cm), in good agreement with the previously reported absorptivities of triphenylsilanol in CCl_4 of 160 L/(mol cm)[4] and of trimethylsilanol in CCl_4 of 127 L/(mol cm).[10]

The low absorbance and concentration of the reactants Cl_3SiH and O_2 at the primary wavelength output, 254 nm, of the mercury lamp used suggest that the reaction proceeds via a radical-chain mechanism. Figure 2 shows the short-wavelength UV absorption spectra of $SiCl_4$ and oxygenated $SiCl_4$. At 254 nm, the extinction coefficient, ϵ, of $SiCl_4$ is measured as 1.12×10^{-2} L/(mol cm).[11] The absorption of Cl_3SiH is expected to be similar.[12] Saturation with oxygen increases the absorption at 254 nm only slightly. The threshold of several absorption bands in oxygen is reported at 240–243 nm.[13] The remaining emission lines of the low-pressure mercury lamp at $\lambda < 250$ nm are expected to be about 10^{-4} as intense as the 254-nm line.[14] The quartz envelope of the lamp does not transmit light below 200 nm, ruling out the involvement of the 185-nm mercury line. It can be concluded that the primary wavelength initiating the reaction is at 254 nm.

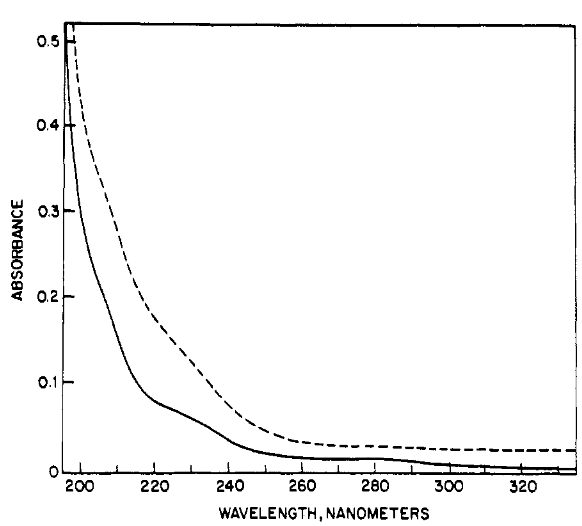

Figure 2. UV absorption of high-purity $SiCl_4$ after 5 min of degassing with argon (—) and after saturation with oxygen (---). The dashed curve has been displaced upward for comparison.

If it is assumed that the photooxidation is initiated primarily through light absorption of the solvent, $SiCl_4$, then a quantum yield can be estimated. On the basis of the cell's dimensions, the volume of solution, and an observed conversion of about 1000 ppm of Cl_3SiH in 30 min, the quantum yield is found to be ≥285, indicating a chain process.

In the photooxidation of chloroform, CCl_3H, which proceeds via radical-chain reaction, peroxides were detected as intermediates by chemical analysis.[8b,c] The hydroperoxide, Cl_3SiOOH, which can be formed from the low-temperature reaction of H_2O_2 and $SiCl_4$, has a distinct infrared OH frequency[15] and may be detected during the photooxidation of Cl_3SiH. Although Cl_3SiOOH appears to be stable only at low temperatures, similar to the case of Me_3SiOOH,[16] it was not detected by IR analysis during the photolyses run at −60 °C.

Attempts to initiate the photooxidation of Cl_3SiH by oxygen atoms, while other initiating steps were included, i.e., via photodissociation of NO_2 at 313 nm,[17] were unsuccessful. Although dissociation of NO_2 occurred at evidenced by the presence of NO, silanol was not detected. Preclusion of this expected reaction probably results from competing reactions of NO. It has been shown that the addition of NO to silane photolyses dramatically changes the observed reactions and products.[18] Experiments to test other suitable oxygen atom sources are being planned.

Discussion

Due to their low ultraviolet absorbances, the primary photochemistry of silanes and chlorosilanes has been studied mostly with vacuum-ultraviolet ($\lambda < 190$ nm) radiation or mercury sensitization. For Cl_3SiH, the primary reaction observed is Si–H bond cleavage.[19] The gas-phase photolysis yields hexachlorodisilane, and H_2 initially, by a nonchain process.[20] Prolonged photolysis yields a wider variety of perchlorosilanes, including dodecachloroneopentasilane.[21]

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Scheme I

$$SiCl_4 \xrightarrow{h\nu} Cl_3Si\cdot + Cl\cdot \tag{3}$$

$$Cl_3SiH \xrightarrow{h\nu} Cl_3Si\cdot + H\cdot \tag{4}$$

$$Cl_3SiH + Cl\cdot \rightarrow Cl_3Si\cdot + HCl \tag{5}$$

$$Cl_3SiH + H\cdot \rightarrow Cl_3Si\cdot + H_2 \tag{6}$$

$$Cl_3Si\cdot + O_2 \rightarrow Cl_3SiOO\cdot \tag{7}$$

$$2Cl_3SiOO\cdot \rightarrow 2Cl_3SiO\cdot + O_2 \tag{8}$$

$$Cl_3SiH + Cl_3SiO\cdot \rightarrow Cl_3Si\cdot + Cl_3SiOH \tag{9}$$

$$Cl_3SiH + Cl_3SiOO\cdot \rightarrow Cl_3Si\cdot + Cl_3SiOOH \tag{10}$$

$$Cl_3SiOOH \rightarrow Cl_3SiO\cdot + \cdot OH \tag{11}$$

$$Cl_3SiH + \cdot OH \rightarrow Cl_3Si\cdot + [HOH] \tag{12}$$

$$SiCl_4 + HOH \rightarrow Cl_3SiOH + HCl \tag{13}$$

$$2Cl_3Si\cdot \rightarrow Cl_3SiSiCl_3 \tag{14}$$

$$Cl_3Si\cdot \rightarrow Cl_3SiO\cdot \rightarrow Cl_3SiOSiCl_3 \tag{15}$$

$$2Cl_3SiO\cdot \rightarrow Cl_3SiOOSiCl_3 \tag{16}$$

$$Cl_3Si\cdot + H\cdot \rightarrow Cl_3SiH \tag{17}$$

$$Cl_3Si\cdot + Cl\cdot \rightarrow SiCl_4 \tag{18}$$

The trichlorosilyl radical is more stable and less reactive than alkyl silyl radicals because of increased delocalization of the unpaired electron.[22] Generally, silyl radicals are found to be less reactive than carbon- or oxygen-centered radicals, particularly in hydrogen abstractions.[23] Reported reactions of the trichlorosilyl radical include halide atom abstraction from alkyl halides[23,24] or halogens[23,25] and addition to olefins,[26] alkynes,[27] or acetone.[28] Radical-chain reactions can occur if another radical, capable of abstracting the relatively more weakly bonded Si–H, is present. For example, the light-initiated hydrosilylation of olefins by Cl_3SiH in solution is quantitative when *tert*-butyl peroxide is used as an initiator.[29] Emeleus and Welch[30] photolyzed and thermally exploded gaseous mixtures of Cl_3SiH and oxygen and found HCl, $(SiOCl_2)_4$, and the thermally unstable Cl_3SiOH.

On the basis of these observations and our experimental results, a radical-chain mechanism to account for the photooxidation of Cl_3SiH in $SiCl_4$ is shown in Scheme I.

Since a study of the kinetics of this reaction was not attempted, this mechanism is tentative and reflects the available experimental evidence at present. Initiation of the reaction is expected to occur by photodissociation of $SiCl_4$, the stronger light absorber, and to a much lesser extent, Cl_3SiH (steps 3 and 4). The radical, $Cl_3Si\cdot$, formed initially and in subsequent steps, is expected to be the chain carrier. This silyl radical reacts with molecular oxygen to form $Cl_3SiOO\cdot$ (step 7). The experimental observation of a predominant formation of Cl_3SiOH is best accounted for by a pathway proceeding through steps 8 and 9. The oxidation of $Cl_3C\cdot$ from the photolysis of chloral has been proposed to follow a pathway analogous to steps 7 and 8.[31] Reaction via steps 10–13 is expected to be very minor, since Cl_3SiOOH was not detected even under low-temperature photolyses. Additionally, such a pathway would require the conversion of one-third of the silane hydrogens to HCl. Some of the possible termination reactions by radical–radical combination are shown in steps 14–18.

In earlier studies on the photooxidation of chloroform, somewhat interesting and contrasting observations were made. An oxidizing intermediate, presumed to be Cl_3COOH, was detected while the intermediate alcohol, Cl_3COH, was assumed to decompose to HCl and Cl_2CO.[8,32] Similarly, the radical, $Cl_3CO\cdot$, is proposed to decompose to Cl_2CO and Cl.[31] The silanol, Cl_3SiOH, and siloxyl radical, $Cl_3SiO\cdot$, appear to be thermodynamically more stable than their carbon analogues because of silicon's disinclination to form multiple bonds.[33]

Ozone is known to react readily with silanes to form silanols and siloxanes.[34] A mechanism to be considered as an alternative to that proposed above is one including ozone as an intermediate formed by the photolysis below 240 nm and subsequent reactions of molecular oxygen. Ozone would then react directly with Cl_3SiH to form Cl_3SiOH and O_2.

Acknowledgment. I thank J. W. Mitchell and E. A. Chandross for useful and stimulating discussions and S. R. Nagel and H. D. Roth for gifts of chemicals. Professors J. Shirk and A. Shirk are gratefully acknowledged for communicating unpublished results.

Registry No. Cl_3SiH, 10025-78-2; $SiCl_4$, 10026-04-7; O_2, 7782-44-7; H_2O_2, 7722-84-1; Cl_3SiOH, 81323-72-0.

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