Reactions of Silanes with Halogens: Chemiluminescent Products in the Ultraviolet–Visible Spectrum

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Abstract: The reactions of monosilane (SiH_4) and disilane (Si_2H_6) with Cl_2, F_2, and ClF have been studied. The monosilane–fluorine and disilane–fluorine systems are characterized by strong emission from the $A(^2\Sigma^+)$–$X(^2\Pi)$ transition of SiF, the $\tilde{A}(^2A_1)$–$\tilde{X}(^2A_1)$ transition of SiF_3, and the $A(^2\Delta)$–$X(^2\Pi)$ transition of SiH. Some evidence indicates the possible observation of the $a(^4\Delta)$–$X(^2\Pi)$ transition in SiH. By contrast, the principal emission spectrum in the monosilane–chlorine and disilane–chlorine reactions is the $^1A''$–$^1A'$ transition of HSiCl. A continuum emission feature may belong to $SiCl_2$ or $SiCl_3$. These results indicate specific reaction mechanisms which include both atomic and molecular halogen reacting with intermediate silylene (SiH_2) radicals and silicon atoms.

Many organic and inorganic hydrides react with halogens to give vibrationally excited hydrogen halides as products. Consequently, these systems have received attention as potential sources for infrared chemical lasers.[2] However, inorganic oxidation reactions are often highly exothermic and, as a result, produce a rich variety of electronically excited intermediates.[3] This suggests the study of gas-on-gas reactions, as an alternative to the presently favored metal–gas reactions,[4] as candidates for a visible chemical laser.

The complex nature of flame reactions enhances the possibility of observing new spectroscopic transitions.[5] In some cases, by identifying reaction intermediates from previously reported spectra, individual kinetic steps may be inferred. Alternatively, these reactions could be used to give a high flux of radicals, which are otherwise difficult to prepare in sufficient concentration, for subsequent kinetic and/or spectroscopic studies.

We report here the chemiluminescent spectra of the reactions of monosilane (SiH_4) and disilane (Si_2H_6) with F_2, Cl_2, and ClF. The monosilane–fluorine and disilane–fluorine reactions are characterized by an inner purple flame (emission by SiH* at 4150 Å) surrounded by a blue region (emission from SiF* at ~4375–4550 Å). The disilane–chlorine and monosilane–chlorine flame is green, as a result of emission from HSiCl*. In an earlier study of the monosilane–chlorine reaction, a green emission was observed and attributed to SiCl*.[2b] Our study definitely shows that the chemiluminescence is from HSiCl* and not from SiCl*.

The requirement that a single step be sufficiently exothermic to account for the observed chemiluminescence suggests the following reactions,

$$SiH_2 + F \rightarrow SiH^* + HF \tag{1}$$

$$SiH_2 + Cl_2 \rightarrow HSiCl^* + HCl \tag{2}$$

$$SiH + F_2 \rightarrow SiF^* + HF \tag{3}$$

$$Si + F_2 \rightarrow SiF^* + F \tag{4}$$

involving both atomic and molecular halogen. SiF* can be produced by both reactions 3 and 4. The experiments reported in this paper cannot distinguish between these exothermic reactions. It should be noted, however, that reaction 3 requires a four-center process which we do not expect to be competitive with reaction 4 if silicon atoms and SiH radicals are in comparable concentrations. The intermediates SiH_2, SiH, and Si must be formed by a series of stripping reactions which remove successive hydrogens and in the case of disilane also sever the weaker Si–Si bond.

Experimental Section

Reactions were carried out in a vacuum chamber at silane pressures of ~100 μ (a minimum pressure for "self-ignition" of the flame) and halogen pressures ranging from ~500 μ to a few Torr (an upper bound determined by the mechanical pumping speed). A concentric nozzle arrangement, depicted schematically in Figure 1, allows effusing silane gas to be bathed in excess oxidant and allows the reaction zone to be confined to a few centimeters in diameter. The fluorescence is focused onto the entrance slit of a 1-m Spex scanning spectrometer operated in first order with a Bausch and Lomb 1200 groove/mm grating blazed at 5000 Å. An RCA 1P28 photomultiplier is attached to the exit slit of the spectrometer. The photomultiplier current is measured using a Keithley 417 fast picoammeter whose output signal drives a recorder which provides a tracing of the spectrum.

Disilane was synthesized by reduction of hexachlorodisilane with lithium aluminum hydride ($LiAlD_4$, for the preparation of Si_2D_6) and purified by bulb-to-bulb distillation in vacuo.[6] Cl_2, the predominant impurity of ClF (K & K Laboratories, 90%) was removed by passing the ClF through a series of "u" traps cooled to −130 °C with an *n*-pentane slush. Cl_2 (Matheson V.H.P., >99.5%), F_2 (Allied, >98%), and silane (Matheson, semiconductor grade) were used without further purification. Several precautions were taken when using these reactive gases. Excess fluorine, which reacts destructively with mechanical pump oil, was removed by a trap, consisting of several trays containing soda lime, placed just after the reaction chamber. A more serious problem is the pyrophoric nature of the silanes.[2a] The danger of an explosion from unreacted silane was minimized by maintaining a constant flow of nitrogen gas at the exhaust vent of the mechanical pump.

Results

The reactions of mono- and disilane with fluorine and mono- and disilane with chlorine give distinctly different chemiluminescent products:

$$\begin{aligned} SiH_4 \text{ or } Si_2H_6 + F_2 \rightarrow\ & SiF\ A(^2\Sigma^+) - X(^2\Pi) \\ & SiH\ A(^2\Delta) - X(^2\Pi) \\ & SiF_3\ \tilde{A}(^2A_1) - \tilde{X}(^2A_1) \\ \text{and possibly } & SiH\ a(^4\Delta) - X(^2\Pi) \\ SiH_4 \text{ or } Si_2H_6 + Cl_2 \rightarrow\ & HSiCl\ \tilde{A}(^1A'') - \tilde{X}(^1A') \end{aligned}$$

and an unknown continuum extending from ~3035 to 4300 Å which may be attributed to a combination of $SiCl_2$ and $SiCl_3$—see discussion section.

For the reactions of silanes with F_2, all chemiluminescent features may be identified by comparison with previously reported emission spectra. Figures 2 and 3 show spectra attributed to SiH and SiF. In Figure 2 a well-resolved rotational structure allows an unambiguous assignment to the 0–0 band of the $A(^2\Delta)$-$X(^2\Pi)$ transition of SiH.[7,8] The spectrum of SiD[8] was observed for the reaction $Si_2D_6 + F_2$. The feature at 4195 Å cannot be attributed to the $^2\Delta$ state of SiH or to any other known emission spectrum. We find weak emission to the long wavelength side of this feature extending to the onset of the SiF features shown in Figure 3.

Consideration of the molecular electronic structure of SiH indicates that the $a(^4\Delta)$ state should lie slightly lower than the observed $A(^2\Delta)$ state. We postulate that the 4195 Å feature corresponds to Q branch structure for the $a(^4\Delta)$-$X(^2\Pi)$ transition and that the observance of this feature may result from a trend to strong spin-orbit coupling leading to emission from the $\Omega = \frac{3}{2}(^4\Delta_{3/2})$ and $\Omega = \frac{1}{2}(^4\Delta_{1/2})$ components to the ground state $\Omega = \frac{3}{2}(^2\Pi_{3/2})$ and $\Omega = \frac{1}{2}(^2\Pi_{1/2})$ components.

In the SiF emission studies, rotational structure was not resolved. The structure evident in Figure 3 corresponds to band head formation in the 0–0 sequence of SiF, $A(^2\Sigma^+)$-$X(^2\Pi_r)$. Transitions were assigned by comparison with calculated band head positions. The dominant branches were $^QR_{12}$ and R_2 for the $^2\Sigma^+$-$^2\Pi_{3/2}$ transition and R_1 and $^SR_{21}$ for the $^2\Sigma^+$-$^2\Pi_{1/2}$ transition. These were obtained by standard procedures,[9] using previously reported constants for the ground[10] and first excited[11] states of SiF. For all but two bands the calculated and measured head positions differed by less than 2 Å. For the $R_2(0,0)$ and $^SR_{21}(1,1)$ bands, head formation occurs at $J \sim 100$ where centrifugal distortion effects, not included in these calculations, become important. For these heads the measured positions exceed those calculated by 5–6 Å, in agreement with an estimate of the centrifugal distortion parameter from eq III,118 of ref 9. For the $^SR_{21}(0,0)$ branch, J head is approximately 275. Transitions $^SR_{21}(0,0)$ and $^QR_{12}$ for the (1,0) sequence are labeled by dashed lines in Figure 3 and correspond to previously reported band head positions.[12]

In addition to the bands assigned to SiF and SiH, we have observed an essentially continuous emission extending from ~2200 to 2750 Å. As Figure 4 shows, four distinct bands can be observed at the short wavelength edge of this feature. These features are attributed to the $\tilde{A}(^2A_1)$-$\tilde{X}(^2A_1)$ transition of SiF_3[13] as is the remainder of the continuum extending to longer wavelength. From the Deslandres scheme presented by Wang, Krishnan, and Margrave,[13] the resolved transitions correspond to emissions involving vibrational levels $(0,0,0,0 \rightarrow 0,v_2'',v_3'',0)$ where $v_3'' = 1$ and $v_2'' = 3, 4, 5,$ and 6. At longer wavelengths the above transitions are overlapped by the $(0,0,0,0 \rightarrow 0,v_2'',0,v_4'')$ emission features precluding resolution of distinct band structures. The remaining spectral features extending to longer wavelength are highly overlapped and, therefore, difficult to resolve.

Figure 5 shows emission from HSiCl*, observed for the reactions of both SiH_4 and Si_2H_6 with Cl_2. This radical has been characterized by its absorption and fluorescence spectra[14] and most of the vibrational transitions identified in Figure 5 correspond to previously reported assignments. Several new features have been identified in Figure 5. These were assigned using vibrational constants from ref 14. Because of the appearance of nominally forbidden rotational structure, the visible spectrum of HSiCl was originally envisioned as involving a triplet-singlet transition, $^3A''$-$^1A'$. However, no triplet splitting could be resolved. Later theoretical developments,[15,16] and an absorption study of the isovalent HSiI radical,[17] showed that an axis-switching mechanism leads to the same rotational selection rules. Consequently, the spectrum presented in Figure 5 is assigned as resulting from an $\tilde{A}(^1A'')$-$\tilde{X}(^1A')$ transition.

Reaction of Cl_2 with Si_2D_6 yields chemiluminescence from DSiCl.[14] The $A(^2\Sigma^+) \rightarrow X(^2\Pi_r)$ emission spectrum of SiCl occurs over approximately the same wavelength region as the visible spectrum of HSiCl.[18] However, no features attributable to SiCl were observed in spectra involving either disilane with chlorine or perdeuteriodisilane with chlorine.

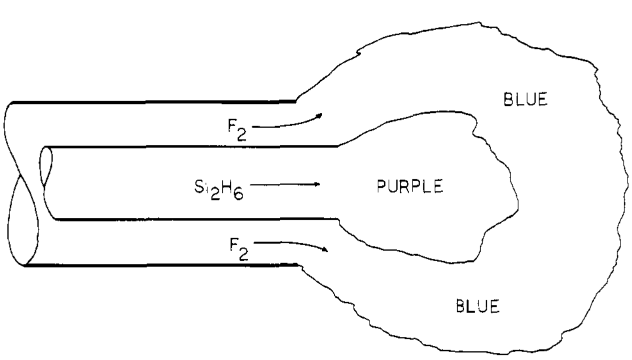

Figure 1. Schematic diagram of concentric nozzle showing the typical configuration for the silane–fluorine system.

A second feature in the spectrum observed in the monosilane and disilane–chlorine systems is a continuum emission extending over the range ~3035–4300 Å, with maximum intensity at ~3340 Å. An identical spectrum is observed for reaction with Si_2D_6. The attribution of this emission feature to SiCl seems unlikely, since its known spectrum[18] does not fall in this region. Spectroscopic information on $SiCl_2$ and $SiCl_3$ is sparse. Spectra in the range 3200–4700 Å, produced by discharge through $SiCl_4$, have been attributed to emission from $SiCl_2$.[19] $SiCl_2$ is reported to have maximum intensities at ~3275 and ~3970 Å, in contrast to a single maximum at ~3340 Å as observed in our systems.

In a further attempt to assign the spectrum in the region 3035–4300 Å, the emission spectrum by microwave electrodeless discharge in $HSiCl_3$ was observed. This resulted in a continuum identical with that observed previously. There was no evidence in the discharge for emission from HSiCl*; however, emission from the $^2\Sigma^+$ state of SiCl was observed. We believe that the observed feature is probably due to $SiCl_3$ although we cannot rule out $SiCl_2$ emission. If the emission is due to $SiCl_3$, then it is analogous to the observed SiF_3 system. In addition, based upon the work of Rao[20] and Wang et al.[13] we expect to observe, at best, a very weak $SiCl_2$ feature if the $SiCl_3$ feature is strong. In a high frequency electrodeless discharge of SiF_4 vapor Rao observed a weak system extending from 3645 to 4183 Å attributable to SiF_2 $(^3B_1$-$^1A_1)$. This system was observed when the conditions for excitation of the ultraviolet system (2100–2600 Å) recently attributed to SiF_3[13] were optimized for maximum intensity. The intensity of the Rao[20] bands appears to be weaker by a factor of 10 when compared to the ultraviolet SiF_3 system.

Discussion

In contrast to the analogous carbon systems, much less is known about the reactions and mechanisms of silicon radicals and intermediates.[21] By fingerprinting the excited intermediates, chemiluminescent reactions provide a method for studying the behavior of these transient species. In the reactions of mono- and disilane with chlorine, fluorine, and ClF, the identified products are di- or triatomic molecules containing a single silicon atom and at most one hydrogen atom. These reactions suggest a process occurring in two parts: a series of stripping reactions (HF or HCl formation), which remove successive hydrogens (reaction 5) and in the case of disilane also sever the comparatively weak Si–Si bond ($\Delta H \sim 50$ kcal/mol from ref 22). These stripping reactions are followed by reactions of intermediate silicon hydride species and silicon atoms. We believe that the intermediate silicon hydride species and silicon atoms are the immediate precursors to the observed chemiluminescence.

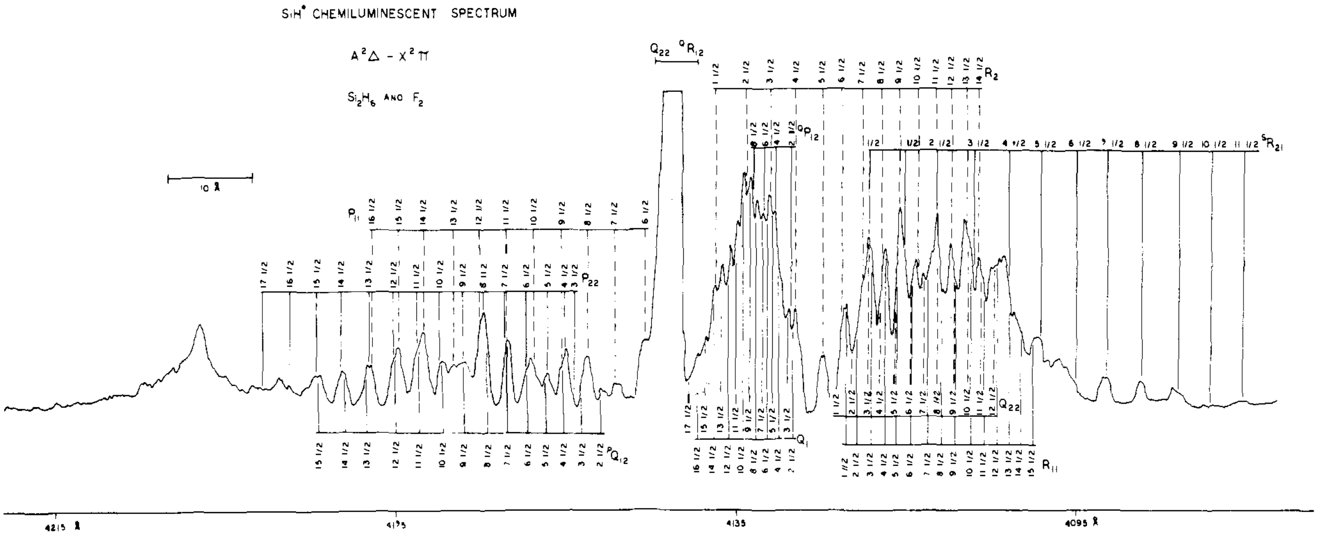

Figure 2. SiH* chemiluminescence spectrum showing partially resolved rotational resolution. Branch structure is labeled in the figure.

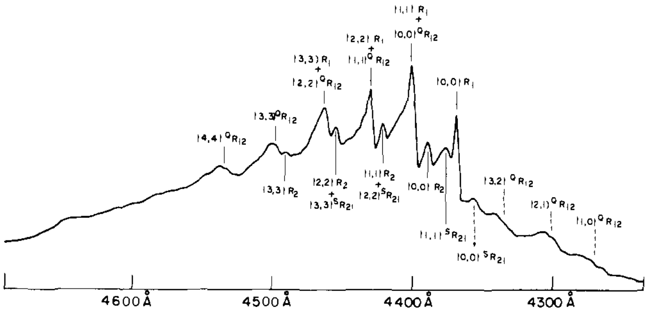

Figure 3. SiF* emission spectrum resulting from the A($^2\Sigma^+$)–X($^2\Pi$) transition. Band heads are identified by (v′,v″) labels.

$$SiH_4 + nX \rightarrow SiH_{4-n} + nHX \quad (5)$$

For reactants having little or no internal energy the observed HSiCl chemiluminescence must result from a reaction sequence exothermic by ≥65 kcal/mol.[23] The only reaction which meets this energy criterion is,

$$SiH_2 + Cl_2 \rightarrow HSiCl^* + HCl \quad (2)$$

for which ΔH is −78 kcal/mol. Two body radiative association processes of the type SiH + Cl → HSiCl* are probably unlikely since they usually require stabilization through third body collisions. In the absence of a third body, complexes formed in this manner are expected to be stable for only a few rotations,[24] a period much shorter than the time for radiative emission.

For those processes considered in this section, heats of reaction were determined using the tabulated bond energies found in ref 22. Bond energies have not been reported for HSiCl. D(HSi–Cl) and D(H–SiCl) were estimated semiempirically[25] using bond lengths from ref 22. The values used were respectively 91 and 65 kcal/mol.

The onset of the continuum feature observed for the mono- and disilane–chlorine reactions occurs at λ ~3035 Å, corresponding to approximately 95 kcal/mol. No single step, with the exception of two-body recombination, gives SiCl with sufficient energy to account for this chemiluminescence. If the chemiluminescence is due to $SiCl_3$ then the formation of this free radical must involve a complicated multibody process. Because of the uncertainty associated with the description of the molecular electronic structure of $SiCl_3$ and uncertainties in bond strengths of all species involved, the assertion of a mechanism for $SiCl_3$ formation is tenuous.

In spite of some complications, a comparison of the Cl_2 and F_2 reactions suggests that thermodynamics do play a determining role in these systems. Emission from SiH* and SiF* is observed for the mono- and disilane–fluorine reactions whereas the equivalent products are absent from the mono- and disilane–chlorine reactions. There are no chlorine atom reactions whose enthalpy of reaction to give SiH is ≥70 kcal/mol, the threshold energy for populating the A($^2\Delta$) state of SiH. By contrast, reaction 1 is exothermic by 77 kcal/mol, and, therefore, SiH emission is observed for the mono- and disilane–fluorine reactions. Only this step, reaction with fluorine atoms, proceeds with sufficient exothermicity.

$$SiH_2 + F \rightarrow SiH + HF \quad (1)$$

The observed emission from SiF* in the mono- and disilane–fluorine reactions can be accounted for by reaction 4[2b,26]

$$Si + F_2 \rightarrow SiF^* + F \quad (4)$$

which has an enthalpy of reaction of ~88 kcal/mol. An exoergicity of 75 kcal/mol is sufficient to account for the observed SiF* emission from vibrational levels $\nu' \leq 4$ (Figure 3). In contrast, the analogous reaction with chlorine has an exoergicity of ~40 kcal/mol, whereas, the first excited state of SiCl A($^2\Sigma^+$) lies at an energy in excess of 66 kcal/mol.[18]

$$Si + Cl_2 \rightarrow SiCl + Cl \quad (6)$$

Therefore, from thermochemical considerations, one does not expect emission from SiCl*. We must note, however, that the bond energies for SiCl show considerable uncertainty: D(Si–Cl) is 92 ± 15 kcal/mol according to ref 22 and 104 ± 12 kcal/mol according to ref 18. The absence of emission from SiCl suggests an upper limit of 96 kcal/mol for D(Si–Cl). The observed emission from SiF* in the reaction of silanes with ClF indicates a lower limit of 122 kcal/mol for D(Si–F).

Emission from HSiF was not observed in our reactions. In fact no emission or absorption spectra attributable to HSiF have been reported, whereas the spectra of HSiCl, HSiBr, and HSiI are known.[14,17] Assuming D(HSi–F) ≃ D(Si–F), a reaction analogous to eq 2 is exothermic by approximately 165 kcal/mol. This reaction might be expected to give HSiF chemiluminescence; however, any HSiF formed in this manner may dissociate prior to emission. Reactions using ClF instead of F_2 show that emission from HSiF is unlikely. For the mono- and disilane–ClF systems, eq 2 predicts the reactions,

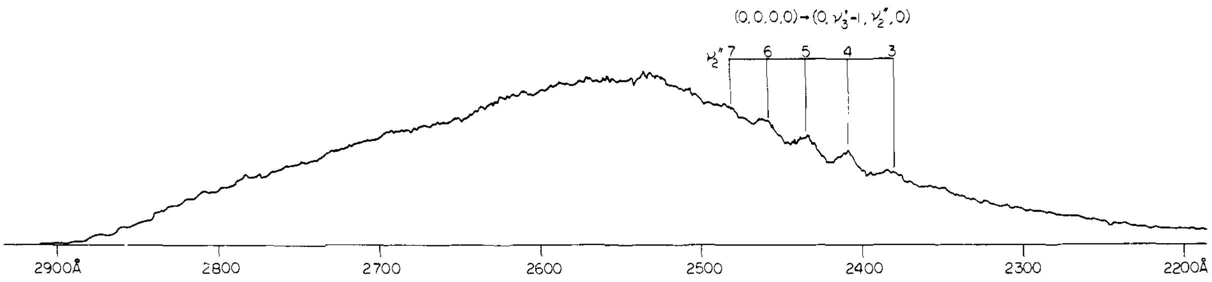

Figure 4. SiF$_3$* emission spectrum for the $\tilde{A}(^2A_1)$-$\tilde{X}(^2A_1)$ transition. Band head labels are given in the text.

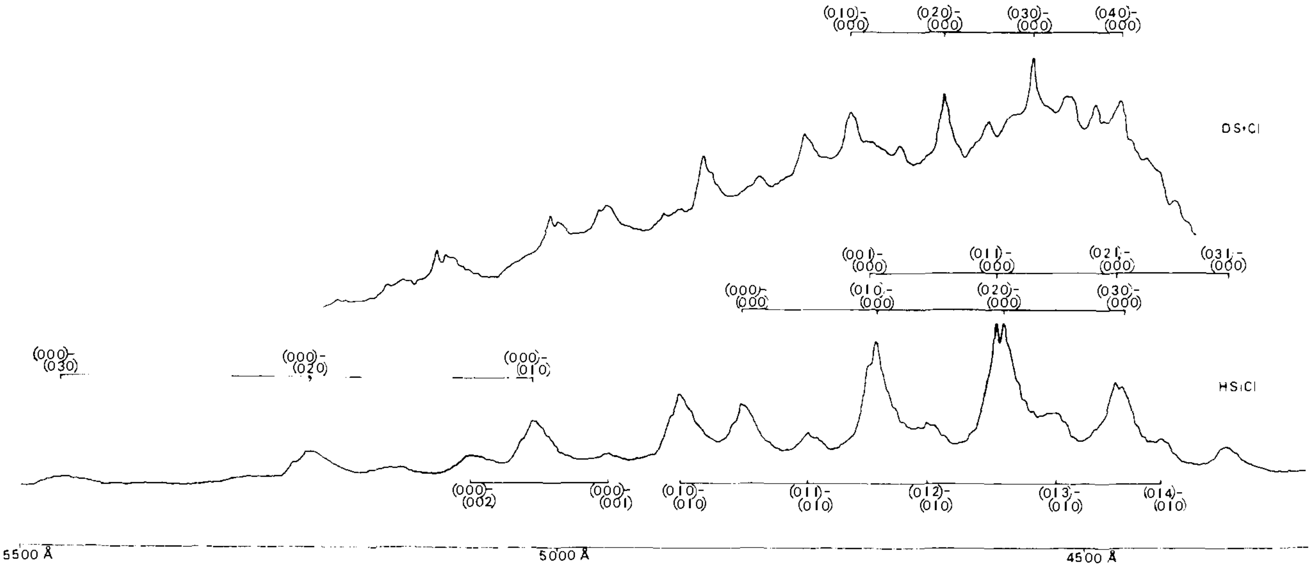

Figure 5. HSiCl* and DSiCl* emission from reaction of SiH$_2$ with chlorine. The observed transition corresponds to $\tilde{A}(^1A'') = \tilde{X}(^1A')$. Band heads are labeled $(v_1',v_2',v_3') - (v_1'',v_2'',v_3'')$ where v_1 denotes the symmetric stretch, v_2 denotes the bending mode, and v_3 denotes the asymmetric stretch.

$$SiH_2 + ClF \rightarrow \begin{cases} HSiCl + HF & (7) \\ HSiF + HCl & (8) \end{cases}$$

which release almost equal amounts of energy, $\Delta H \sim 110$ kcal/mol. An analysis of the chemiluminescence from the mono- and disilane-ClF systems shows only the products observed in the Cl$_2$ and F$_2$ reactions separately, and no features which can be attributed to HSiF.

Either HSiF is markedly less stable than HSiCl, HSiBr, and HSiI or the absence of HSiF chemiluminescence must be explained by kinetic and spectroscopic considerations and not by thermodynamics alone.

In summary, the chemiluminescent products from the reactions of monosilane and disilane with chlorine, fluorine, and ClF can be accounted for by differing reaction mechanisms. For the silane-chlorine systems,

$$SiH_2 + Cl_2 \rightarrow HSiCl^* + HCl \qquad (2)$$

whereas, for the mono- and disilane-fluorine mixtures

$$SiH_2 + F \rightarrow SiH^* + HF \qquad (1)$$

$$SiH + F_2 \rightarrow SiF^* + HF \qquad (3)$$

$$Si + F_2 \rightarrow SiF^* + F \qquad (4)$$

Reaction 4 is the expected source of SiF chemiluminescence; however, reaction 3 cannot be excluded. The above reactions are also consistent with the spectra observed from the reactions of monosilane and disilane with ClF.

We conclude that the observed chemiluminescence can be accounted for on the basis of thermodynamic arguments. The thermodynamic requirements are most often met by reactions giving rise to simultaneous hydrogen halide production. This is in accord with previous observations on similar systems.[2,26] The kinetics of these reactions and the absence of spectra from HSiF are interesting problems for future research.

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Complexation of Silver(I) with Thiourea and Tetramethylthiourea in Dimethyl Sulfoxide Solution as Studied by ^{13}C and ^{109}Ag Nuclear Magnetic Resonance Spectroscopy

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Abstract: A combination of ^{13}C and ^{109}Ag NMR spectroscopy has been used to study silver complexes of thiourea and tetramethylthiourea in dimethyl sulfoxide solution. The results are consistent with the presence of a variety of complex species for the concentrations used (approximately 1 M in silver ion with varying ligand concentrations) including highly aggregated forms. The combination of metal ion NMR and ^{13}C NMR appears to have general utility for the study of silver complexes, but instrumental improvements allowing for the study of solutions of lower concentrations are needed.

Increasingly, NMR spectroscopy is expanding beyond the study of "traditional" nuclei such as ^{1}H and, more recently, ^{13}C to include many other less common and, in many cases, more difficult nuclides.[1] For example, a number of metal nuclides have been examined in recent years with regard to possible information about solvation, ion pairing, and structure of organometallic compounds. Previous reports dealing with the silver nuclides, ^{109}Ag and ^{107}Ag, have been few, however.[2,3]

Metal complexes have also been studied in a variety of cases with ^{13}C NMR.[4] Carbon NMR has the potential of being especially informative about the binding site in an organic ligand, particularly if the interaction occurs through a functional group containing a centrally located carbon atom, such as a carbonyl group. It has already been used to study several silver complexes.[5] In a few cases, spin–spin coupling of the silver nuclei with carbon has been observed.[6] In general, however, the lability of most silver complexes averages such splittings to zero.

It appeared to us that the combined use of ^{13}C and ^{109}Ag NMR spectroscopy would offer a particularly powerful means of studying silver complexes in solution. The greatest problem to such an approach is the low inherent sensitivity of the ^{109}Ag nucleus (spin ½, natural abundance of 49%, NMR sensitivity relative to ^{1}H of 1.01×10^{-4} per nucleus, and very long relaxation times). Nevertheless, we have observed that ^{109}Ag spectra of usable quality can be obtained from solutions with 1 M Ag(I) concentrations with no more than a few hours of signal averaging;[7] ^{13}C spectra are now obtained easily for such solutions.

Although we hope eventually to be able to study a wide variety of silver complexes in concentrations of 0.1 M or lower, for the present time we have chosen to examine solutions containing 1 M silver nitrate in dimethyl sulfoxide (Me_2SO) with varying concentrations of thiourea and tetramethylthiourea. We made this choice for the following reasons: (1) thiourea and, presumably, tetramethylthiourea form complexes with silver(I) which have a variety of stoichiometries and high thermodynamic stabilities;[8-23] (2) crystal structures of isolated solids have been determined for some of these complexes;[24-25] (3) both thiourea and tetramethylthiourea are soluble up to at least 3 M with 1 M silver nitrate in dimethyl sulfoxide.

Dimethyl sulfoxide itself is believed to interact only weakly with silver(I), apparently through the oxygen atom.[26] Furthermore, since silver(I) is a "class b" metal,[27] one expects it to be only weakly solvated even in water. Solvent effects on the stability of the complexes may thus be relatively small, although presumably not completely negligible.[28] As a result, information about silver complexes obtained from Me_2SO solutions may be directly relevant to the properties of the same complexes in water.

This work was specifically designed to test the ability of NMR spectroscopy to reveal several types of information: (1) A determination of the binding site or sites in the organic ligand is important. (2) Specific information about the type of bonding between the ligand and the metal ion may be available from the NMR data in those cases where the empirical and/or theoretical correlations are far enough advanced for the types of systems of interest. For example, thiourea can act as both a bridging and terminal ligand with silver(I),[24,25] and the particular bonding involved in a given complex may be reflected in the NMR data. (3) The stoichiometries of the various complexes formed may also be found. In some cases, measures