NIR investigation of the rarefied flame of dichlorosilane oxidation at low pressures and 293 K

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10.1070/MC2000v010n04ABEH001236

Electronically excited radicals HO_2 ($A^2A' - X^2A''$), vibrationally excited OH ($v = 2$–0), HCl ($v = 3$–0), combined vibrational bands of H_2O (0.823 μm) and H_2O_2 (0.854 μm) have been detected in the emission spectra of rarefied flame of dichlorosilane oxidation at 293 K and low pressures over the range 0.8–1.6 μm.

The application of thin SiO_2 films in integrated circuit processing[1] has evoked an increasing interest to the oxidation of silanes. Reacting with F_2 and Cl_2, silanes form vibrationally excited HF and HCl, which are of interest to infrared chemical lasers.[2,3] The synthesis of nanosized particles based on the branching chain processes involving inorganic hydrides is also of considerable interest.[4] The branching chain nature of dichlorosilane (DCS) oxidation has been established,[5] but the kinetic mechanisms have not been yet assigned. Radicals OH ($A^2\Sigma^+$),[6] SiO ($A^1\Pi - X^1\Sigma$), $SiCl_2$ (A^1B_1, $a^3B_1 - X^1A_1$),[7] and Cl atoms have been detected in DCS oxidation;[5] the overall reaction for a stoichiometric mixture obeys the equation[8] $SiH_2Cl_2 + O_2 \rightarrow SiO_2 + 2HCl$. The additives of SF_6 were found to act as an inhibitor on self-ignition and flame propagation in DCS + O_2 mixtures.[9]

The aim of this work was to detect vibrationally excited species in a rarefied flame of DCS oxidation and to elucidate the mechanism of action of SF_6 additives on this reaction by NIR emission spectroscopy.

The experiments were carried out under static conditions at 293 K and total pressures in the range of 2–15 Torr. A cylindrical quartz reactor (12 cm in height and 12 cm in diameter) had inlets for power supply and gas evacuation and optical windows. The ignition was provided by a rapidly heated nichrome wire coil placed at the centre of the reactor. The reactor was evacuated to 4×10^{-4} Torr before each experiment. The mixtures of DCS + O_2 and SF_6 (if necessary) were prepared prior to an experiment. The NIR emission was modulated on a frequency of 3.3 kHz and detected through a silicon filter with an FD-10 photodiode sensitive in the range 0.8–1.6 μm, supplied with high-frequency amplifiers. The resulting signal recorded by an oscilloscope was alternating (and symmetric about the x axis) with a frequency of 3.3 kHz. The intensity of emission J at a specified wavelength λ was defined as the mean of the maximum signal amplitudes for 5–7 ignitions in the ranges $\Delta\lambda = 0.005$ μm; the dependence of J on λ was constructed. A grating (300 slits per millimetre) monochromator was calibrated using CH_2Cl_2 absorption bands.[10] The spectral width of the slit was 0.005 μm. Visible emission was recorded with a UV–VIS photomultiplier; it was also used for the start-up of recording.

The NIR emission spectra of the initiated ignition of the mixtures 24% DCS + O_2 (thin solid curve) and 22% DCS + + 18% SF_6 + O_2 (thick solid curve) are shown in Figure 1(*a*). The $X^1\Sigma$ HCl transitions ($v = 3$–0, band centre 1.20 μm,[11] R- and P-branches), electronically excited HO_2 transition A^2A' – – X^2A'' ($v = 0$–0 at 1.43 μm, $v = 1$–1 at 1.48 μm[12]) and OH $X^2\Pi_i$ ($v = 2$–0, band centre 1.437 μm R-, Q- and P-branches[13]) are observed in the spectrum.

In the far-visible region [0.7–0.9 μm, recording by a photodiode without a silicon filter, Figure 1(*b*)] strong combined vibrational bands of H_2O^* ($\lambda = 0.823$ μm) and $H_2O_2^*$ ($\lambda = 0.854$ mm)[14] are observed. This emission is probably due to the following reactions of H and HO_2:

$$H + O_2 + H_2O = HO_2 + H_2O^* + 47\ \text{kcal mol}^{-1}$$

$$HO_2 + HO_2 = H_2O_2^* + O_2 + 33.5\ \text{kcal mol}^{-1}$$

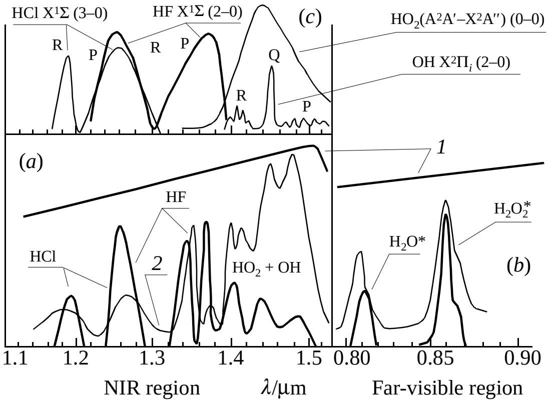

Figure 1 NIR emission spectra of rarified flames of DCS oxidation (intensities are given in arbitrary units): (*a*) thin solid line, a mixture of 23.5% DCS + O_2 in the NIR region; thick solid line, a mixture of 22% DCS + 18% SF_6 + O_2 in the NIR region; (*b*) thin solid line, a mixture of 22% DCS + 18% SF_6 + O_2; thick solid line, a mixture of 22% DCS + 18% SF_6 + O_2, $P = 3$ Torr, slit, 1 mm; (*1*) spectral sensitivity of an FD-10 photodiode; (*2*) background emission of an aerosol; (*c*) the NIR emission spectrum simulated according to refs. 11–13.

The emission of HF ($X^1\Sigma$) ($v = 2$–0, band centre 1.29 μm, R- and P-branches[15]) is observed in DCS oxidation in the presence of SF_6 [Figure 1(*a*), thick solid curve]. The emission intensity of HO_2 ($A^2A' - X^2A''$) and OH $X^2\Pi_i$ ($v = 2$–0) decreases in the range 1.34–1.51 μm. Therefore, the SF_6 additives efficiently quench electronically excited HO_2 radicals.

The mean temperature of combustion products (during the emission) can be estimated from the distribution of intensities of HCl $X^1\Sigma$ ($v = 3$–0) and HF $X^1\Sigma$ ($v = 2$–0) under the assumption that the rotational temperature T_r is close to the vibrational temperature T_e. Figure 1 suggests[11] that for HCl ($v = 3$–0) the rotational quantum number $j_{max} \sim 12$ and for HF ($v = 2$–0) $j_{max} \sim 8$, which correspond to the maximum emission intensity. From the relationship[11] $j_{max} \sim (kT/B_v)^{1/2}$, where k is the Boltzmann constant, B_v is the rotational constant ($B_{v=3} = 9.365$ or $B_{v=2} =$ $= 19.028$ cm^{-1} for HCl or HF, respectively[15]), we have $T_r \sim T_e \sim$ ~ 2000 K. This value is close to the experimental data.[9]

On the basis that HCl is the main stable final product[8,16] and using known values of the probabilities of vibrational transitions in emission equal to 0.0379 (HCl, $v = 3$–0) and 29.31 s^{-1} (HF, $v = 2$–0)[17] and estimates of H_2O^* and $H_2O_2^*$ (~10 s^{-1}),[18] we can assess the amount of the particles from the ratio between intensities in spectra [Figure 1(*a*)]. These fractions make up (relative to HCl) for HF ~ 0.2%; for H_2O^* and $H_2O_2^*$ ~ 4.5%. The estimated fraction of H_2O vapour is close to the calculated (~1.72 mol%)[19] equilibrium value in hot products of combustion of DCS + O_2 + 3.76N_2.

It was found[9] by high-speed schlieren cinematography that the ignition at the centre of reactor gives rise to propagation of a spherical flame. The spectra (Figure 1) makes up either the emission of final products from the volume of this sphere or the emission from a narrow zone of the propagating spherical front of a branching chain reaction. In this case, the temperature of final products is close to adiabatic with a specific heat of ~ 170 kcal mol^{-1}.[8,16] To estimate the contribution from either

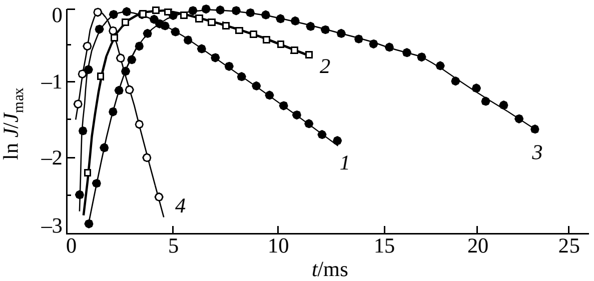

Figure 2 Kinetics of emission on initiated ignition: (*1*) 26.5% DCS + 7% $SF_6 + O_2$; (*2*) 23% DCS + 12% $SF_6 + O_2$; (*3*) 22% DCS + 18% $SF_6 + O_2$; (*4*) 22% DCS + 18% $SF_6 + O_2$; $P = 3$ Torr, 293 K. (*1*)–(*3*) Integral NIR emission (silicon filter), (*4*) integral visible emission (0.2–0.6 μm).

emitting areas to the total emission, the time dependence of J in the visible and NIR regions was examined.

These functions for the mixtures of similar composition in visible J_v (Figure 2, curve *4*) and NIR J_r (Figure 2, curves *1–3*) regions differ from one another. The time τ it takes for the attainment of J_v max is shorter than that for the attainment of $J_{r\,max}$. An estimation of the visible velocity U_v of the flame propagation till the moment of the attainment of $J_{v\,max}$ from Figure 2 ($V \sim R/\tau$, where R is the reactor radius) gives $U_v \sim$ ~ 20 m s^{-1}. This value is close to U_v measured by schlieren cinematography.[9] Thus, J_v (curve *4*) accounts for an intense reaction within the front of a branching chain process,[7] therewith J_r (curves *1–3*) accounts for further emission due to stable and slightly reactive final products. The characteristic times of decay of NIR emission are independent of the nature of the emitting species (HCl, HF, OH, HO_2). Therefore, Figure 1 represents the emission spectrum of combustion products from the volume.

It follows from curves *1–3* (Figure 2) that the time of occurrence of the excess vibrational excitation increases in the presence of SF_6, probably, due to the transfer of an excess of energy of SF_6 to the vibrational degrees of freedom of the products. Thus, SF_6 additives make an extra reservoir of vibrational energy. The fact that the kinetic curves of NIR emission of HCl, HF, OH and HO_2 have almost equal characteristic times of decay in the presence of SF_6 suggests that energy transfer to the vibrational modes of HCl, HF, H_2O and HO_2 occurs from the same energy reservoir. The heat losses by emission can be neglected because the probabilities of IR emission are low: *e.g.*, for HCl in the ground state $X^1\Sigma$ and $v = 1–0$, 2–0, 3–0, these values make up 33.9, 2.32 and 0.49 s^{-1};[17] for combined transitions of H_2O (101–000) and (111–000), 26.4 and 2.15 s^{-1}.[18] The losses can also occur through the emission of condensed particles (*e.g.*, SiO_2). However (Figure 1), the intensity of the background emission decreases, and the characteristic time of the decay of NIR emission increases in the presence of SF_6 (see ref. 7). The excess of energy is not also related to overheated SiO_2 particles, because SF_6 additives markedly reduce the amount of an aerosol formed.[9]

The characteristic times of deactivation were estimated. The rate constants of vibrational deactivation, from $v = 3,2,1$ to $v =$ = 2,1,0 for HCl and O_2 predominantly inherent in the gas at the end of the reaction make up about 10^{-14}–10^{-12} cm^3 s^{-1} over a range of 300–2000 K.[20] Thus, the characteristic times of V–V deactivation make up $\tau_{V-V} \sim 10^{-3}$–10^{-5} s at a pressure of 3 Torr. The V–T process requires 10^3–10^5 collisions per second; thus, we have $\tau_{V-T} \sim (10^3–10^5)/(10^{17}\times10^{-10}) = 10^{-5}–10^{-3}$ s at 2000 K.

Therefore, τ_{V-V} and τ_{V-T} are close to each other. If so and if the rate of V–T energy transfer is higher than the rate of cooling of the products through heat transfer to the wall, the characteristic time of decay of J_r (Figure 2) must be equal to the charasteristic time of cooling. The following relationship holds for the regular regime of cooling of a spherical gas volume in the absence of heat sources:[21]

$$(T - T_0) \sim \exp(-k_1^2 \alpha t), \qquad (1)$$

where k_1 is a minimum eigenvalue of the linear heat transfer equation, $k_1 = \pi/R$, $\alpha \sim D$ (diffusivity factor)[21] is the temperature conductivity. From (1), we have for the characteristic time of cooling τ_t

$$\tau_t^{-1} = k_1^2 D_0(T/T_0)^{1.7}(P/P_0) \qquad (2)$$

where D_0 is the diffusivity factor under standard conditions (300 K, 760 Torr) for combustion products, P and T are the pressure and temperature, respectively. For $T = 1500$ K, $D_0 = 1.6$ cm^2 s^{-1}; $P_0 =$ = 3 Torr, $R = 6$ cm, and τ_t^{-1} is ~220 s^{-1}. This value is really close to the experimental time ~200 s^{-1} (Figure 2, curves *1–3*). It means that either V and T degrees of freedom come to equilibrium, *i.e.*, $T_v = T$ or the time lag t before the beginning of cooling results from energy transfer from the reservoir of vibrational energy of the SF_6 additive. As can be seen in Figure 2, t increases as a fraction of SF_6 increases. Thus, SF_6 molecules passing through the front of a branching chain reaction would acquire the excess of energy over equilibrium. The transformation of this energy to heat energy occurs almost without losses. This is supported by the fact that the resulting degree of expansion of products is close to adiabatic[9,22] at different contents of SF_6 even with regard to a change in the overall heat capacity of final products C_p. However, a marked decrease in U_v in the presence of SF_6[9,22] (Figure 2, curves *3* and *4*) cannot be explained only by the thermal nature of flame propagation because of $U_v \sim C_p^{-1/2}$.[21]

Processes that may be responsible for the decrease in U_v in the presence of SF_6 are considered below. It is well known that in the presence of SF_6 the upper limit of the self-ignition of the $H_2 + O_2$ reaction[23] decreases because of the termolecular reaction $H + O_2 + SF_6 \rightarrow HO_2 + SF_6^{V-V}$ (the resulting HO_2 is slightly active). The SF_6 additives to $H_2 + O_2 + Ar$ flames over the temperature range 1300–1940 K react with H atoms.[24] The rate constant of $H + SF_6 \rightarrow HF + SF_5$ (chain termination) is $2\times10^{15}\times$ $\times\exp(-30000/RT)$ cm^3 mol^{-1} s^{-1}. SF_6 is also an efficient inhibitor in rich H_2–air flames,[25] leading to a marked decrease of U_v, therewith its thermal dissociation occurs only at $T > 1500$ K, since the S–F bond strength is ~60 kcal mol^{-1}.[26] The inhibitory effect of SF_6 on the propagation of the spherical $H_2 + O_2$ flame was observed previously.[14] It was found that the visible emission is caused by processes involving O and H atoms and OH radicals; the NIR emission with longer characteristic times is due to H_2O, H_2O_2 and HO_2, emitting at the resulting temperature of combustion. The H_2O formation is accompanied by the emission at $\lambda = 0.823$ μm, and HO_2 formation in the reaction $HO_2 + HO_2 \rightarrow$ $\rightarrow H_2O_2^* + O_2$, by the emission at $\lambda = 0.852$ μm[14] (Figure 1). These data suggest either the parallels between the impact of SF_6 on the reactions of H_2 and DCS oxidation or the influence of the chemical nature of the additive on U_v even when a considerable warming-up occurs. The influence is caused by a change in the rate of the termolecular chain termination $H + O_2 + M \rightarrow$ $\rightarrow HO_2 + M$ in the developing combustion.[24] Thus, the inhibitory effect of SF_6 is due to reactions providing the change-over from the active centre of reaction chains (namely, H atoms) to slightly active species: $H + SF_6 \rightarrow HF + SF_5$ or $HF^{V-V} + SF_5$; and $H + O_2 + SF_6 \rightarrow HO_2 + SF_6^{V-V}$. The latter reaction is also accompanied by the transfer of an excess of energy to SF_6 molecules.

We are grateful to V. V. Azatyan, corresponding member of the RAS, for many useful discussions.

This work was supported by the Russian Foundation for Basic Research (grant nos. 99-03-32250a and 00-03-32979a).

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Received: 29th November 1999; Com. 99/1563