

Kinetic Study of the Chemiluminescence Spectrum of Rarified Flame in Dichlorosilane Oxidation in the Near IR Region

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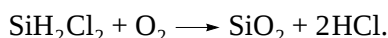
Received May 12, 2000

Abstract—Electronically excited $\text{HO}_2^{\bullet}$ radicals ($A^2A' - X^2A''$), $\text{OH}^{\bullet}$ radicals ($v = 2 - 0$), and HCl molecules ($v = 3 - 0$) are identified using the emission spectra at 0.8–1.6 μm in the rarefied flame in dichlorosilane combustion at 293 K and low pressures. The spectrum also contains the composite bands of the H_2O (0.823 μm) and H_2O_2 (0.854 μm) molecule vibrations. The maximum intensity of emission of these species is attained behind the front of the active chemical transformation, and the equilibrium between the vibrational and translational degrees of freedom is established in the region of the regular thermal regime of cooling. SF_6 additives act as a reservoir that accumulates the vibrational energy in developed ignition. The processes responsible for the inhibition of dichlorosilane oxidation by SF_6 additives are considered.

INTRODUCTION

Investigation of the mechanism of the combustion of silanes and their chlorine derivatives and the kinetics of the oxidation of these compounds under various conditions and at different gas-mixture compositions is of great scientific and practical interest. These processes are widely used in microelectronics to apply isolating and passivating layers of silicon dioxide in the integrated circuit of semiconductor instruments [1, 2]. Reacting with halogens, monosilane and its chlorine derivatives form vibrationally excited hydrogen halides [3, 4], which may be used as active media in infrared chemical and electron-discharge lasers [5, 6]. The development of the methods of synthesis of nanopowders based on the processes involving inorganic hydrides is of considerable interest [7, 8].

Studies of the combustion of silanes and their derivatives are also important for the theory of chemical transformation. The oxidation of these compounds occurs via the branched-chain mechanism [9, 10]. The electronically excited radicals $\text{OH}^{\bullet}$ ($A^2\Sigma^+$) [11], $\text{SiO}^{\bullet}$ ($A^1\Pi - X^1\Sigma$), $\text{SiCl}_2^{\bullet}$ ($A^1B_1 - X^1A_1$, $a^3B_1 - X^1A_1$) [12, 13], and chlorine atoms [10] were registered in the rarefied flame during dichlorosilane (DCS) oxidation. The IR spectrophotometric study [14] showed that the process in oxygen at $[\text{DCS}] < 50\%$ and low pressures may be described by the following overall equation:



The final products of DCS combustion in air under ordinary conditions over a wide range of initial DCS concentrations also include H_2O , chlorosilanes, and molecular hydrogen [15]. Certain hydrocarbons (e.g., C_2H_2 and C_2H_4) inhibit flame propagation in the DCS +

O_2 mixtures [9]. The SF_6 additives inhibit self-ignition and retard flame propagation in the $\text{DCS} + \text{O}_2$ mixtures [16]. At the same time, several main steps of this process, including chain propagation reactions, have not been identified yet. The retardation of ignition by water vapors and molecular nitrogen has not been explained even at such low pressures either, when termolecular reactions can be neglected [17].

The aim of this work was to determine the chemical nature of vibrationally excited species in the rarefied flame during DCS oxidation and to establish the mechanism of the inhibition of this reaction by the SF_6 additives.

EXPERIMENTAL

The experiments were conducted in a vacuum setup described elsewhere [14]. The reaction vessel was a quartz cylinder (diameter, 120 mm; height, 120 mm). The reactor was equipped with inlets for electrodes and gas supply and optical quartz windows. A fuel mixture prepared beforehand was fed from a by-pass volume into the reactor through a vacuum valve. The reactor was evacuated to 4×10^{-4} torr using 3NVR-1D forevacuum and N-01 oil-diffusion pumps. The residual pressure was measured with VIT-2 thermocouple-ionization and VDG-1 gas-discharge vacuum gages. The mixtures were prepared beforehand by admitting a required amount of DCS into oxygen (containing SF_6 additives if necessary) through a narrow capillary. Both oxygen and SF_6 were of reagent grade. The DCS purity was ~98% as determined by IR spectroscopy [14]. The reaction was initiated from outside and conducted under steady-state conditions at room temperature and 2–5 torr. Mixtures of the following composition were used: 23.5% $\text{DCS} + \text{O}_2$, 26.5% $\text{DCS} + 7\% \text{SF}_6 + \text{O}_2$, and

22% DCS + 18% SF₆ + O₂. A coil of Nichrome wire (diameter, 0.3 mm) was placed in the middle of the reactor for heating. Ignition was initiated by pulse heating of this coil with a condenser battery (capacitance, 3000 μF). Chemiluminescence in the visible region registered with a FEU-39 photomultiplier (spectral sensitivity, 0.2–0.6 μm) was used to start the registration system. An FEU signal was transmitted to the synchronization inlet and one beam of an S9-8 two-beam memory oscilloscope starting in a leading-phase mode. Emission during combustion was also registered at 0.7–1.9 μm using an MDR-3 monochromator (diffraction lattice, 300 stroke/mm) and silicon and quartz light filters. The spectral slit width was ~0.005 μm. The kinetic curves of the integral emission in the visible region and spectral emission upon single ignition were registered simultaneously at a fixed wavelength every Δλ = 0.005 μm. The monochromator was calibrated by the characteristic absorption bands of chloroform at 1.15, 1.21, 1.41, and 1.69 μm [18].

The system of emission registration included an FD-10 photodiode and a preamplifier equipped with field-controlled transistors and U3-29, V6-9, and U2-8 amplifiers connected in a series (the signal from the third one was transmitted to the S9-8 oscilloscope). The registration was performed by the alternating current with emission modulation by a mechanical interrupter operating at a frequency of 3300 Hz sufficient for ignition registration (the characteristic time of combustion was >3 ms, see below). The interrupter was placed in front of the inlet slit of the monochromator. The alternating signal was thus registered and its maximal value was determined as the arithmetic mean for 5–7 ignitions. Using these data and the maximal signal intensity on the kinetic curve for each wavelength λ, the emission intensity vs. λ curve was plotted. The reproducibility of the maximal emission intensity in each separate ignition was ~15%. Figure 1 presents the optical scheme of the setup. Under the operating conditions, the spectral slit width was ~35 cm⁻¹ at λ = 1.2 μm. This value is comparable with the distance between separate vibrational-rotational lines of HCl (3–0) and HF (2–0). For HF (2–0) near the *P* and *R* branches, this distance is ~50 and 30 cm⁻¹, respectively. For HCl (3–0), this distance is still shorter because of the lower rotational constant B_e [19, 20]. The Doppler line width under these conditions (~2000 K) is ~0.045 cm⁻¹. Therefore, the experimental spectra are represented as solid lines (like the spectra of unresolved rotational structure).

Before each run, the reactor was evacuated for 5 min at a residual pressure of 4 × 10⁻⁴ torr. To remove the deposits of solid products from the surface of the optical windows, the latter were polished after every 15 ignitions. This was a routine procedure because the deposition of the SiO₂ aerosol on the windows had virtually no effect on the signal registered in the near IR region.

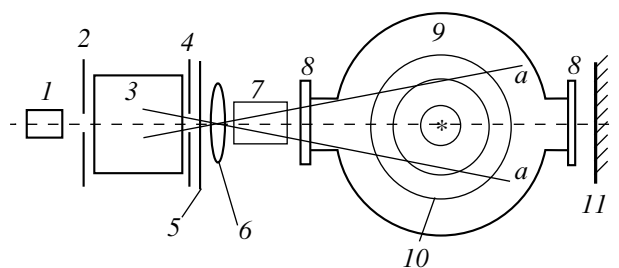
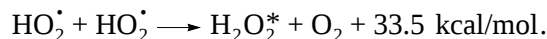
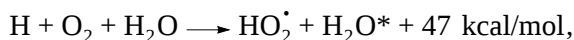


Fig. 1. Optical scheme of the experimental setup: (1) photodiode, (2) outlet slit of monochromator, (3) monochromator, (4) inlet slit of monochromator, (5) light filter, (6) condenser, (7) collimator, (8) optical windows, (9) reaction vessel, (10) spherical flame front, (11) reflecting mirror (Au), and (a-a) visual field of the registration system.

RESULTS AND DISCUSSION

Figure 2a presents the emission spectra in the near IR region for the initiated self-ignition of the 23.5% DCS + O₂ (spectrum 1) and 22% DCS + 18% SF₆ + O₂ (spectrum 2) mixtures. The vibrational-rotational bands of HCl in the X¹Σ state (ν = 3–0, where ν is the vibrational quantum number; band center, 1.198 μm; *R* and *P* branches [19, 20]) are observed in the near IR region (Fig. 2). A band system corresponding to both the electron transition of HO₂^{*} (A²A' – X²A''), transitions ν = 0–0 at 1.43 μm, ν = 1–1 at 1.48 μm [21]) and the vibrational transition of OH^{*} (X²Π_i, ν = 2–0 transition; band center, 1.437 μm; *R*, *Q*, and *P* branches [22, 23]) is registered at 1.34–1.51 μm.

The intense composite emission bands of the H₂O* (λ = 0.823 μm) and H₂O₂* (λ = 0.854 μm) molecule vibrations are observed in the far visible region at 0.7–0.9 μm using an FD-10 detector without silicon light filter [24, 25]. These bands can be attributed to the following recombination reactions between H and HO₂^{*}:



During the combustion of mixtures with the SF₆ additives (Fig. 2a, spectrum 2), an additional HF X¹Σ band (ν = 2–0 transition; band center, 1.29 μm; *R* and *P* branches) is observed [19, 20]. The emission intensity of HO₂^{*} (A²A' – X²A'') and OH^{*} X²Π_i (ν = 2–0) in the band system at 1.34–1.51 μm dramatically decreases. This suggests that the SF₆ additives efficiently quench electronically excited HO₂^{*} radicals.

Assuming that the rotational temperature *T_r* is equal to the translational temperature *T_t*, one can estimate the average temperature of the combustion products during emission registration from the distribution of the emis-

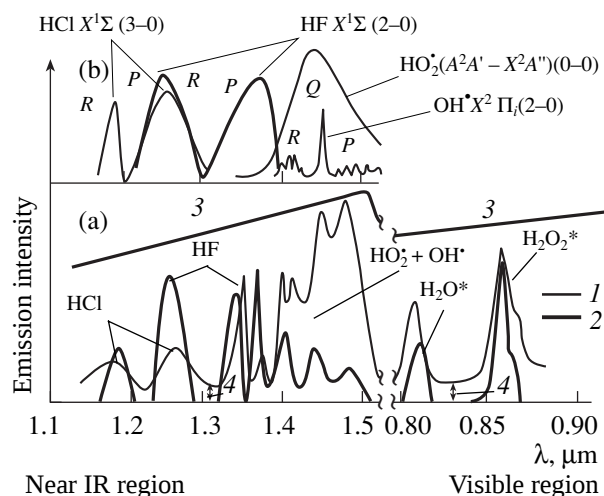


Fig. 2. (a) Emission spectra of the rarefied flame during DCS oxidation: (1) 23.5% DCS + O₂; (2) 22% DCS + 18% SF₆ + O₂; (3) spectral sensitivity of an FD-10 photodiode [45]; (4) aerosol background; (*T* = 300 K; *P* = 3 torr; slit, 1 mm; and (b) emission spectra in the near IR region of the HCl and HF molecules and HO₂[•] and OH[•] radicals [20, 21, 23, 26, 29]. The intensity distribution for the *R* and *P* branches is qualitative.

sion intensities of the vibrational-rotational bands of HCl ($\nu = 3-0$) and HF ($\nu = 2-0$). Taking into account the data of [19, 20] and the experimental error in the spectral intensity of the vibrational-rotational transitions of HCl and HF, we found from Fig. 2 that the rotational quantum numbers $j_{\max} \sim 10 \pm 2$ and ($\nu = 2-0$) $j_{\max} \sim 7 \pm 1$ correspond to the maximum band emission for HCl ($\nu = 3-0$) and HF ($\nu = 2-0$). From the relation $j_{\max} \sim (kT/2B_e)^{1/2}$ [19], where k is the Boltzmann number and B_e is the rotational constant ($B_{\nu=3} = 9.365 \text{ cm}^{-1}$ for HCl and $B_{\nu=2} = 19.028 \text{ cm}^{-1}$ for HF [26]), we obtained that $T_r \sim T_t = (1700-3900) \text{ K}$. This suggests that combustion occurs under nearly adiabatic conditions.

Taking into account that HCl is the main stable final product [27] and using the available probabilities of the vibrational transitions during ignition (the Einstein coefficients) equal to 0.0379 s^{-1} (HCl, $\nu = 3-0$) and 29.31 s^{-1} (HF, $\nu = 2-0$) [28-30] and the estimates for H₂O^{*} and H₂O₂^{*} equal to $\sim 10 \text{ s}^{-1}$ [31], we assessed the number of these species (with respect to HCl) equal to $\sim 0.2\%$ for HF and $\sim 4.5\%$ for H₂O and H₂O₂^{*}. The estimated concentration of water vapors is close to its calculated equilibrium value [27, 32] in the hot products of DCS + O₂ + 3.76 N₂ mixture combustion equal to $\sim 1.72 \text{ mol } \%$.

Using rapid schlieren photography, we observed earlier [16] spherical flame propagation if emission was initiated in the middle of the reaction vessel. Thus, the spectrum registered (see Fig. 2) may be related to the emission of the final combustion products from the bulk of the sphere and the emission from the narrow

zone of the propagating spherical flame (the regions of the intensive chemical transformation, see Fig. 1). In this case, the temperature of the combustion products is close to the adiabatic one, and the reaction heat is $Q \sim 170 \text{ kcal/mol}$ [14, 27]. To estimate the contribution of each component to the overall emission, we registered the kinetics of the integral emission J in the visible (J_{vis}) and near IR spectrum regions (J_{IR}) (Fig. 3).

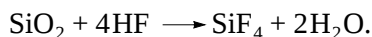
The kinetic curves of the emission intensity for the mixtures of the same composition in the visible (Fig. 3, curve 4) and near IR (Fig. 3, curve 2) regions differ widely from each other: the $J_{\text{vis}}^{\max}$ value is attained earlier (time τ) than $J_{\text{IR}}^{\max}$. The observed rate of flame propagation U before the attainment of the $J_{\text{vis}}^{\max}$ value ($U \sim R/\tau$, where R is the reactor radius) was estimated from Fig. 3 to be $U \sim 20 \text{ m/s}$, which is close to its experimental value measured by rapid schlieren photography [16]. This indicates that the J_{vis} value (Fig. 3, curve 4) reflects the active chemical transformations in the branched-chain reaction [12, 24], whereas the J_{IR} value (curves 1-3) characterizes further emission in the resulting stable and inert reaction products. The shape of the kinetic curves of the spectral ignition in the IR region is virtually independent of emitter (HCl, HF, H₂O, or HO₂[•]) to which a kinetic curve refers. Therefore, Fig. 2 illustrates the ignition spectrum of the combustion products in the bulk of the reactor. Comparison of the kinetic curves (Fig. 3, curves 1-3) shows that the SF₆ additives cause an increase in the lifetime of the vibrationally excited states (the existence of the relatively constant $J_{\text{IR}}^{\max}$ values). This can be attributed to the transition of the excess internal energy of the SF₆ molecules to the vibrational degrees of freedom of the combustion products. In other words, the addition of SF₆ to the fuel mixture results in the formation of an additional reservoir for the vibrational energy. That is why the energy amount from the vibrational levels of the SF₆ molecules is close for some time to the energy of heat loss during emission and heat exchange with the reactor walls.

The Mache effect [26, 33] also influences the region of stable $J_{\text{IR}}^{\max}$ values due to heat release in the bulk of the reactor during the adiabatic compression of the combustion products upon the complete combustion of the fuel mixture. An increase in the SF₆ concentration in the mixture causes a noticeable retardation of flame propagation [16] and, hence, a decrease in the contribution of the Mache effect because of an increase in the heat loss through the wall as combustion continues. However, the region of the relative stability of the $J_{\text{IR}}^{\max}$ values enlarges with an increase in the SF₆ concentration in the fuel mixture (Fig. 3, curves 1-3). This suggests that the contribution of the Maucher effect to the

heat capacity of the combustion products is negligible and can be neglected.

The fact that the kinetic curves of the spectral emission for HCl, HF, H₂O, and HO₂[•] in the IR region exhibit the same characteristic times of the intensity decrease and increase upon SF₆ addition to the reaction mixture suggests that the energy is transferred to the vibrational modes of these species from the same energy reservoir supported by the SF₆ additives. The heat loss for emission can also be neglected because of the low probabilities of emission in the IR region. For example, these probabilities are 33.9, 2.32, and 0.0379 s⁻¹ for HCl in the ground state X¹Σ and the 1–0, 2–0, and 3–0 transitions, respectively [28, 30] and 26.4 and 2.15 s⁻¹ for the composite transitions of the vibrationally excited water molecules (101–000) and (111–000), respectively [31].

The heat loss may also be due to the emission of condensed species (for example, silane dioxide). However, upon SF₆ addition, the continuous emission disappears (see Fig. 2 and [12]), whereas the time interval, during which IR emission is registered, is prolonged. Additional energy can also be attributed to the presence of overheated condensed species of silicon dioxide and the energy liberated in the recombination of the active sites of the chain reaction on the surface of the forming new phase. Although SF₆ consumes some part of energy released in phase formation [32], its additives cause a dramatic decrease in the overall amount of aerosol produced by ignition [34] via the reaction



Therefore, the vibrational energy of the sulfur hexafluoride molecules is higher than the equilibrium value until the $J_{\text{IR}}^{\text{max}}$ values remain virtually unchanged. Then, a regular cooling regime is observed (see below) characterized by the energy equilibrium between the vibrational and translational degrees of freedom of the reaction products.

Let us estimate the characteristic times of deactivation due to the vibrational relaxation in the gas phase. For the HCl and O₂ molecules, which are the main gaseous reaction products, the rate constants for the vibrational deactivation (the V–V exchange) from the $\nu = 3, 2, 1$ to the $\nu = 2, 1, 0$ levels, respectively, are 10⁻¹⁴–10⁻¹² cm³/s at 300–2000 K [35]. Hence, the characteristic times of the vibrational–vibrational relaxation for 3 torr τ_{V-V} are nearly 10⁻³–10⁻⁵ s. The relaxation of the vibrational energy to the translational energy (the V–T exchange) requires 10³–10⁵ collisions per second and $\tau_{V-T} = 10^{-5}$ –10⁻³ s at 2000 K. This suggests that the τ_{V-V} and τ_{V-T} values are comparable. In this case, if the rate of the V–I exchange is higher than the rate of cooling the combustion products during heat exchange with the reactor walls, the characteristic time of the dip of the kinetic curve J_{IR} from the data of Fig. 3 should coincide with time of cooling the reaction products. For the regular

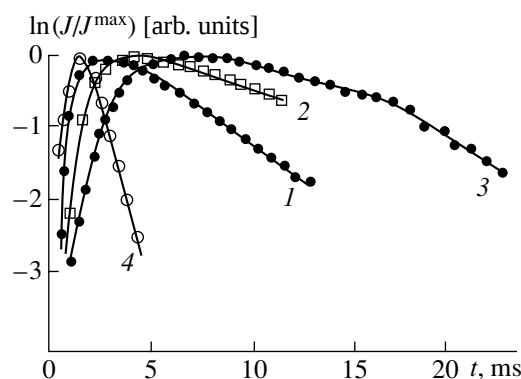


Fig. 3. Kinetics of emission during initiation ignition: (1) 23.5% DCS + O₂; (2, 4) 26.5% DCS + 7% SF₆ + O₂; and (3) 22% DCS + 18% SF₆ + O₂. $P = 3$ torr, 293 K. (1, 3) Integral emission in the near IR region, and (4) integral emission in the visible region.

thermal regime of the cooling a spherical gas volume from T to T_0 (T_0 is the wall temperature) in the absence of heat release in the volume, Frank-Kamenetskii derived the following relation [36]:

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

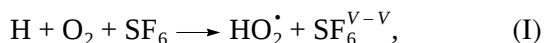
where k_1 is the minimal eigenvalue of the thermal conductivity linear equation, $k_1 = \pi/R_0$, R_0 is the reactor radius, and α is the coefficient of temperature conductivity. Assuming that the α value is equal to the diffusion coefficient D [36] and taking into account Eq. (1), one can determine the characteristic time of cooling τ as

$$\tau^{-1} = k_1^2 D_0 (T/T_0)^{1.5} (P/P_0), \quad (2)$$

where D_0 is the diffusion coefficient [37] under ordinary conditions (300 K, 760 torr) for the combustion products, and P and P_0 are the pressures corresponding to the temperatures T and T_0 , respectively. Assuming that $T = 1500$ K for the beginning of the regular thermal regime of cooling, $D_0 = 1.6$ cm²/s, $P_0 = 3$ torr, and $R_0 = 6$ cm, we obtain the characteristic time of cooling $\tau^{-1} \sim 210$ s⁻¹. This value is close to the experimental one equal to ~ 200 s⁻¹ (Fig. 3, curves 1–3). Our finding suggests that the equilibrium between the vibrational and translational degrees of freedom, that is, $T_v = T_v$ is established in the region of the regular regime of cooling. Therefore, the time of the establishment of the V–V and V–T equilibria is shorter than the time of cooling the reaction products. This also indicates that a delay in cooling (the time interval corresponding to the region of the relatively constant $J_{\text{IR}}^{\text{max}}$ values (Fig. 3)) is due to the relaxation of the energy of the vibrational reservoir of added SF₆. After combustion, the concentration of the vibrationally excited molecules increases, and its relative increase is proportional to the SF₆ concentration. The delay in cooling also increases with an increase in the concentration of sulfur hexafluoride

(Fig. 3). Therefore, the SF₆ molecules, passed the chemical reaction front during spherical flame propagation, accumulate an overequilibrium content of the vibrational energy, which is further transformed into the thermal energy of combustion products without noticeable loss. This is also confirmed by the fact that the final degree of expansion of the combustion products is close to the adiabatic one [16, 38] at various SF₆ concentrations with due regard to the overall heat capacity of the combustion products C_p . At the same time, a dramatic decrease in the apparent rate of flame propagation U in the presence of SF₆ [16, 38] (Fig. 3, curves 1 and 4) can barely be explained by the thermal nature of flame propagation because $U \sim C_p^{-1/2}$ and variations in the diffusion coefficient of the active sites in the mixtures with SF₆ additives [33] (see Appendix).

Let us consider some possible processes responsible for a decrease in the U value in the presence of sulfur hexafluoride. It is known that SF₆ additives cause a decrease in the second self-ignition limit in the H₂ + O₂ reaction [39], thus stabilizing the inert HO₂[•] radicals formed in the process



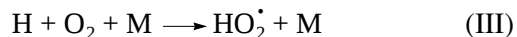
where SF₆^{V-V} is a vibrationally excited species.

The SF₆ molecules added to the H₂ + O₂ + Ar flames react with hydrogen atoms at 1300–1940 K with the rate constant $k = 2 \times 10^{15} \exp(-(30 \pm 5)/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (the activation energy is expressed in kcal/mol) [40]. In this case, the reaction



with the above rate constant is a chain termination reaction. The SF₆ molecules also dramatically inhibit combustion in the flames that are rich in hydrogen and air [41]. SF₆ virtually does not dissociate under these conditions. Dissociation only occurs at $T > 1500 \text{ K}$ because the S–F bond energy in this molecule is $\sim 600 \text{ kcal/mol}$ [42]. Abid *et al.* [24] also found that sulfur hexafluoride additives inhibited the propagation of the spherical H₂ + O₂ flame. Chemiluminescence in the visible region with the characteristic time, which is of the same order as the time of ignition, is due to the processes involving the O, H, and OH[•] radicals, whereas chemiluminescence in the near IR region with much longer characteristic times may be caused by the H₂O, H₂O₂ and HO₂[•] species, which emit at the finite combustion temperature. Water formation is accompanied by emission with $\lambda = 0.823 \mu\text{m}$, whereas hydrogen peroxide formation during the recombination $\text{HO}_2^\bullet + \text{HO}_2^\bullet \longrightarrow \text{H}_2\text{O}_2^* + \text{O}_2$ is accompanied by emission with $\lambda = 0.852 \mu\text{m}$ [24, 25] (cf. Fig. 2). These data suggest that the SF₆ additives have a similar effect on hydrogen and dichlorosi-

lane oxidation and that the rate of flame propagation depends on their chemical nature. The latter is due to a change in the rate of termolecular termination of the reaction chains via the reaction



under the conditions of developed combustion. Note also that the SF₆ molecules can participate in chain termination involving charged species during DCS combustion [17].

Reaction (III) also plays a critical role in hydrocarbon combustion in mixtures that are poor or insufficiently enriched in fuel [43]. Note that the thermal dissociation of fuel during the combustion of hydrocarbons (and inorganic hydrides) is a relatively rapid process resulting in the formation of hydrogen atoms and other chain carriers [43]. The thermal decomposition of DCS also results in H₂ formation under certain conditions [15, 27, 44], that is, the main elementary reactions of hydrogen oxidation should play a significant role in developed combustion at temperatures approaching 2000 K.

In this work, we found experimentally that the addition of SF₆ to the DCS + O₂ fuel mixture results in both the formation of the HF molecules and the deactivation of electronically excited HO₂[•] radicals ($A^2A' - X^2A''$). These findings indicate that the inhibition of flame propagation in this reaction system by sulfur hexafluoride additives should be due to reactions (I) and (II) resulting in the replacement of the active centers of reaction chains by inactive centers. In this case, reaction (I) is accompanied by energy transfer to the vibrational degrees of freedom of the sulfur hexafluoride molecules.

ACKNOWLEDGMENTS

We thank V.V. Azatyan for fruitful discussions. The work was supported by the Russian Foundation for Basic Research (project nos. 99-03-32250 and 00-03-32979).

APPENDIX

Let us show that variations in the coefficient of mutual diffusion in the DCS + O₂ mixtures in the presence of the SF₆ additives (up to 10%) cannot cause an increase in the lower self-ignition limit [16].

To determine the coefficients of mutual diffusion in a mixture, one should know the self-diffusion coefficients of the mixture components. $D_{\text{O}_2} = 0.18 \text{ cm}^2/\text{s}$ for O₂ under ordinary conditions [35]. The self-diffusion coefficients for SF₆, DCS, and O₂ can be estimated from the equation [45]:

$$D = V/(3\sqrt{2}n\sigma), \quad (3)$$

where V is the average rate of molecules; n is the number of molecules in cm^3 ($2.69 \times 10^{19} \text{ cm}^{-3}$ under ordinary conditions); and $\sigma = \pi d^2/4$, where d is the collision diameter. The d value was determined from the equation $d = (9.26 \times 10^{-9})b^{1/3}$ [35], where b is the correction to the volume in van der Waals equation equal to $b_{\text{SF}_6} = 88.1 \text{ cm}^3/\text{mol}$, $b_{\text{DCS}} = 107.8 \text{ cm}^3/\text{mol}$, and $b_{\text{O}_2} = 31.6 \text{ cm}^3/\text{mol}$. The D values obtained with due regard to the experimental D_{O_2} value under ordinary conditions were $D_{\text{DCS}} = 0.045 \text{ cm}^2/\text{s}$ and $D_{\text{SF}_6} = 0.043 \text{ cm}^2/\text{s}$. Taking into account that $D_{\text{DCS}} \sim D_{\text{SF}_6}$, the mutual diffusion coefficients can be estimated by the Blomck equation [35]:

$$D_{\text{AB}}^{-1} = f_{\text{A}}/D_{\text{A}} + f_{\text{B}}/D_{\text{B}}, \quad (4)$$

where f_{A} and f_{B} are the molar fractions of A and B, and D_{A} and D_{B} are the self-diffusion coefficients of A and B under ordinary conditions. For the 10% DCS + O_2 and 10% DCS + 4% SF_6 + O_2 mixtures, the D_{AB} coefficients are 0.14 and 0.13 cm^2/s , respectively. Hence, the relative change in the diffusion coefficient is $\sim 8.5\%$, which is insufficient for a 1.5-fold increase in the lower self-ignition limit even in the diffusion-controlled termination of the reaction chains.

REFERENCES

1. Cze, S., VLSI Technology, New York: Murray Hill, 1981, vol. 1.
2. Till, W.C. and Luxon, J.T., *Integrated Circuits. Materials, Devices and Fabrication*, Prentice Hall: Englewood Cliffs, 1982.
3. Conner, C.P., Stewart, G.W., Lindsay, D.M., and Gole, S.H., *J. Am. Chem. Soc.*, 1977, vol. 99, no. 8, p. 2540.
4. Chesnokov, E.N., *Khim. Fiz.*, 1992, vol. 11, no. 9, p. 1202.
5. Chesnokov, E.N., *Doctoral (Phys.-Math.) Dissertation*, Novosibirsk: Inst. of Chem. Phys., 1999.
6. Velikanov, S.D., Zapol'skii, A.F., and Frolov, Yu.N., *Kvant. Electron.*, 1997, vol. 11, no. 1, p. 11.
7. Khairutdinov, R.F., *Usp. Khim.*, 1998, vol. 67, no. 2, p. 125.
8. Aivazyan, R.G., Azatyan, V.V., Kalachev, V.I., and Rubtsov, V.I., *Fiz. Gor. Vzryva*, 1994, vol. 30, no. 4, p. 85.
9. Karmazin, M.V., Kochubei, V.F., and Senyuta, T.B., *Mater. IX Vsesoyuz. simp. po goreniyu* (Proc. IX All-Union Symp. on Combustion), Suzdal, 1989, p. 20.
10. Vartanyan, A.A., *Cand. Sc. (Chem.) Dissertation*, Chernogolovka: Inst. of Structural Macrokinetics, 1991.
11. Azatyan, V.V., Vartanyan, A.A., Kapkanov, V.A., and Temchin, S.M., *Kinet. Katal.*, 1991, vol. 32, no. 2, p. 511.
12. Rubtsov, N.M., Tsvetkov, G.I., and Chernysh, V.I., *Kinet. Katal.*, 1997, vol. 38, no. 4, p. 498.
13. Rubtsov, N.M., Tsvetkov, G.I., and Chernysh, V.I., *Kinet. Katal.*, 1998, vol. 39, no. 3, p. 330.
14. Rubtsov, N.M., Ryzhkov, O.T., and Chernysh, V.I., *Kinet. Katal.*, 1995, vol. 36, no. 5, p. 645.
15. Aivazyan, R.G., Azatyan, V.V., Kalachev, V.I., and Sinel'nikova, T.A., *Kinet. Katal.*, 1995, vol. 36, no. 2, p. 186.
16. Karpov, V.P., Rubtsov, N.M., Ryzhkov, O.T., et al., *Khim. Fiz.*, 1998, vol. 17, no. 4, p. 73.
17. Aivazyan, R.G., *Kinet. Katal.*, 1997, vol. 38, no. 1, p. 195.
18. Kustanovich, I.M., *Spektral'nyi analiz* (Spectral Analysis), Moscow: Vysshaya Shkola, 1967.
19. Bauwell, C.N., *Fundamentals of Molecular Spectroscopy*, London: McGraw Hill, 1983.
20. Kuipers, G.A. and Smith, D.F., *J. Chem. Phys.*, 1955, vol. 25, no. 2, p. 275.
21. Becker, K.H., Fink, H.H., Langen, P., and Schurath, U., *J. Chem. Phys.*, 1974, vol. 60, no. 11, p. 4623.
22. Garvin, D., Broida, H.P., and Kostkowski, H.J., *J. Chem. Phys.*, 1960, vol. 38, no. 10, p. 1742.
23. Charters, P.E. and Polanyi, J.C., *Can. J. Chem.*, 1960, vol. 38, no. 10, p. 1742.
24. Abid, M., Wu, J.S., Lin, J.B., et al., *Combust. Flame*, 1999, vol. 116, no. 3, p. 348.
25. Gardiner, M.C., *J. Phys. Chem.*, 1982, vol. 86, no. 6, p. 1429.
26. Radtsig, A.A. and Smirnov, B.M., *Spravochnik po Atomnoi i Molekulyarnoi Fizike* (Handbook of Atomic and Molecular Physics), Moscow: Atomizdat, 1980.
27. Britton, L.F., *Plant Operations Progress*, 1990, vol. 9, no. 1, p. 16.
28. Cashion, J.K. and Polanyi, J.C., *J. Chem. Phys.*, 1961, vol. 35, no. 2, p. 600.
29. Herbelin, J.M. and Emanuel, G., *J. Chem. Phys.*, 1974, vol. 60, no. 2, p. 689.
30. Cashion, J.K. and Polanyi, J.C., *Proc. R. Soc. A* (London), 1960, vol. 258, p. 529.
31. Burch, D.E., Gryvnak, D.A., Patty, R.R., and Bartly, C.E., *J. Opt. Soc. Am.*, 1969, vol. 59, no. 3, p. 267.
32. Aivazyan, R.G., Azatyan, V.V., Kalachev, V.I., et al., *Fiz. Gor. Vzryva*, 1994, vol. 35, no. 1, p. 77.
33. Zel'dovich, Ya.B., Barenblatt, G.I., Librovich, V.B., and Makhviladze, G.M., *Matematicheskaya teoriya goreniya i vzryva* (Mathematical Theory of Combustion and Explosion), Moscow: Nauka, 1980.
34. Karpov, V.P., Chernysh, V.I., Rubtsov, N.M., and Temchin, S.M., *Proc. XIX Int. Symp. on Combustion Processes*, Czestochova, 1995, p. 22.
35. *Fizicheskie velichiny: Spravochnik* (Physical Values: A Handbook), Grigor'ev, I.S. and Meilikhov, E.Z., Eds., Moscow: Energoatomizdat, 1991.

36. Frank-Kamenetskii, D.A., *Diffuziya i teploperedacha v khimicheskoi kinetike* (Diffusion and Heat Transfer in Chemical Kinetics), Moscow: Nauka, 1967.
37. Eremin, E.I., *Osnovy khimicheskoi kinetiki* (Foundations of Chemical Kinetics), Moscow: Vysshaya Shkola, 1976.
38. Karpov, V.P., Rubtsov, N.M., Tsvetkov, G.I., and Chernysh, V.I., *Khim. Fiz.*, 2000, vol. 19, no. 8, p. 74.
39. *Khimicheskaya kinetika i tsepnye reaktsii* (Chemical Kinetics and Chain Reactions), Kondrat'ev, V.N., Ed., Moscow: Nauka, 1966.
40. Fenimore, C.P. and Jones, G.W., *Combust. Flame*, 1964, vol. 13, no. 3, p. 231.
41. Miller, D.R., Evers, R.L., and Skinner, G.B., *Combust. Flame*, 1963, vol. 7, no. 2, p. 137.
42. *Handbook of Chemical Lasers*, Fross, R.W.F. and Bott, J.F., Eds., New York: Wiley, 1976.
43. *Combustion Chemistry*, Gardiner, W.C., Ed., New York: Springer, 1984.
44. Aivazyan, R.G., Dzhabiev, T.S., and Kir'yakov, N.V., *Kinet. Katal.*, 1995, vol. 36, no. 2, p. 179.
45. Levshina, E.S. and Novitskii, P.V., *Elektricheskie izmereniya fizicheskikh velichin* (Electrical Measurements of Physical Values), Leningrad: Energoatomizdat, 1983.