Kinetics and Catalysis, Vol. 44, No. 1, 2003, pp. 20–27. Translated from Kinetika i Kataliz, Vol. 44, No. 1, 2003, pp. 26–34.
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Branched-Chain Reaction of Dichlorosilane Chlorination in the Presence of Inhibiting and Deactivating Additives

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Received June 6, 2002

Abstract—Dichlorosilylene ($SiCl_2$) was identified along with SiHCl radicals in the chlorination reaction of dichlorosilane at low pressures and 293 K. The inhibiting effect of propylene additives (>4 vol %) on the self-ignition of dichlorosilane mixtures with molecular chlorine was found. In the presence of a chemically inert additive of SF_6 (>45%), the inhibiting effect was dramatically increased; this fact is an indication that energy factors play an important role. The absence of a isothermal flame propagation regime under experimental conditions suggests that chain branching occurs in a reaction whose rate is a linear function of the concentration of active centers. A kinetic mechanism was proposed, which includes the participation of silylenes in the branching process with the formation of excited states. This mechanism qualitatively describes the experimentally observed behavior.

INTRODUCTION

It is well known that the chlorination reactions of inorganic hydrides (monosilane [1], dichlorosilane (DCS) [2], phosphine [3], and germane [4]) and hydrocarbons [5], as well as the reaction of monosilane with nitrogen trichloride (NCl_3) [6], are branched-chain processes (BCPs). The behavior of BCPs depends on competition between chain branching and chain termination reactions; because of this, the kinetics of ignition is highly sensitive to the state of the surface that is in contact with reactants and to the presence of small additives of inhibitors and promoters [7, 8]. Because material branching, which is accompanied by an increase in the number of free valences, is improbable in the course of chlorination, one would expect chain branching to occur by a mechanism including the participation of excited intermediate species in chain propagation. Energy branching (EB), which occurs with the participation of electronically excited species, was found in the branched-chain process of the thermal decomposition of NCl_3 [9, 10]. EB in reactions with the participation of vibrationally excited species was found in the fluorination of molecular hydrogen and partially fluorinated hydrocarbons [11]. However, fluorination reactions are more exothermic than chlorination. Moreover, the energy of the first vibrational quantum of an HF molecule is higher than that of an HCl molecule. In the fluorination reactions of hydrocarbons, EB occurs if the energy released in an elementary step is sufficient for the subsequent unimolecular decomposition of the product of this step. For example, the following branching mechanism was proposed for the reaction CH_2F_2 + F_2: $^{\bullet}CF_2H + F_2 \longrightarrow CHF_3^* + F$; $CHF_3^* \longrightarrow :CF_2 + HF$ [11] (excited molecules are marked with asterisks). Analogous reaction sequences were proposed for the chlorination of 1,1-difluoroethane [5], the chlorination of monosilane [1], and the pyrolysis of chlorine-substituted silanes [12]. Note that carbenes and silylenes, respectively, play an important role as reaction chain carriers in the proposed mechanisms. In the mechanism proposed by Swihart and Carr [12], the reactions of chlorine-substituted silylenes with parent chlorosilane to form disilanes play an important role. Based on *ab initio* calculations, it was postulated that the following chain unit with EB occurs in the pyrolysis of DCS (the energetics of this process was reported in [12]):

$$\begin{gathered}
:SiHCl + SiH_2Cl_2 \longrightarrow HCl_2SiSiH_2Cl^*,\\
HCl_2SiSiH_2Cl^* \longrightarrow HCl_2SiSiCl + H_2,\\
HCl_2SiSiCl \longrightarrow Cl_2SiSiHCl \longrightarrow :SiCl_2 + :SiHCl,\\
HCl_2SiSiH_2Cl^* \longrightarrow \text{deactivation}.
\end{gathered} \qquad \text{(I)}$$

Note that the rate constant of the reaction :SiHCl + $SiH_2Cl_2 \longrightarrow$ products was measured to be equal to 5×10^{-15} cm^3/s [13] at 293 K.

It is well known that the reactions of olefins with silylenes are very fast [13]. The rate constants of the reactions $:SiH_2 + C_3H_6 \longrightarrow$ products and $:SiCl_2 + C_3H_6 \longrightarrow$ products are 10^{-10} and 5×10^{-13} cm^3/s, respectively. Safarik *et al.* [13] found that reactivity in the silylene series continuously decreases on going to chlorine-substituted silylenes; consequently, the rate constant of the reaction $:SiHCl + C_3H_6 \longrightarrow$ products lies between the above values for $:SiH_2$ and $:SiCl_2$. Because emission at 420–550 nm, which is characteristic of :SiHCl (A^1B_1–X^1A_1) [2], was observed in the BCP of DCS chlorination, it is expected that olefins (such as propylene) will inhibit this BCP. The detection of an inhibiting effect in the presence of olefin additives will serve as an argument for the importance of silylene reactions as reaction chain carriers in this process. Moreover, if inhibition takes place, homogeneous self-ignition in the reaction volume can be studied because the self-ignition of a mixture of pure DCS and Cl_2 at 293 K and a total pressure higher than 2 kPa occurs almost immediately after mixing (the induction period τ_i is <300 ms) [2].

The aim of this work was (a) to identify chlorine-substituted silylenes in the chlorination reaction of dichlorosilane and to examine the effects of propylene added as an inhibitor and of SF_6 as a deactivator on the BCP in order to reveal the role of silylenes and excited species in branching and (b) to examine the possibility of a isothermal flame regime, which is an indicator of quadratic chain branching in BCPs.

We used the ignition delay method, which is based on an expansion of the self-ignition area of an inhibited mixture with the consumption of an inhibitor [14, 15]. The dependence of the self-ignition limits on the inhibitor content of the reaction mixture was given by Azatyan [16]. Azatyan [16] also found that a combustible mixture enters the self-ignition area when the inhibitor concentration becomes equal to a certain critical value z_{crit}. The ignition delay time τ_c, that is, the time interval after which the combustible mixture containing an inhibitor ignites spontaneously, is combined of the time τ required to reach the boundary of the self-ignition area (self-ignition delay) and the induction period τ_i. That is, $\tau_c = \tau + \tau_i$. Relationships derived in this work are true for $\tau \gg \tau_i$ or $\tau_c \cong \tau$. Evidently, in case of the participation of excited intermediates in a chain unit, the addition of an effective deactivator provides additional termination of reaction chains on the molecules of this additive to affect the value of τ.

We illustrate below that the dependence of τ on the concentrations of initial reactants in the presence of both an inhibitor and a deactivator is fundamentally different from the dependence in the presence of only an inhibitor by the example of a generalized model of a BCP with EB. Because the mechanism of DCS chlorination is unknown, the model must include chain generation, propagation, EB, and termination on inhibitor (In) and deactivator (M) molecules:

$$Y_1 \longrightarrow 2Y_2, \quad (k_0) \quad \text{termination},$$

$$Y_1 + Y_3 \longrightarrow Y_2 + \text{products}, \quad (k_1)$$

chain generation,

$$Y_2 + Y_0 \longrightarrow Y_4^* + \text{products}, \quad (k_2)$$

formation of an excited species,

$$Y_3 + \text{In} \longrightarrow \text{chain propagation}, \quad (k_3), \qquad \text{(II)}$$

$$Y_4^* \longrightarrow 2Y_3, \quad (k_4)$$

liner branching (EB),

$$Y_4^* + \text{M} \longrightarrow \text{deactivation}, \quad (k_5),$$

$$Y_2 + \text{In} \longrightarrow \text{chain propagation}, \quad (k_6).$$

Here, Y_0 and Y_1 are the initial reactants, for example, fuel and an oxidant; Y_2 and Y_3 are active centers; and Y_4^* is the excited species whose unimolecular decomposition is responsible for chain branching. Let us assume that the pressure of the mixture is $P \gg P_1$, where P_1 is the lower limiting pressure (for the reaction DCS + Cl_2, P_1 is as low as ~45 Pa at DCS : Cl_2 = 1 : 1 [2]). In this case, heterogeneous chain termination can be ignored [14, 15]. The consumption of initial reactants during the delay time can be neglected, and the concentrations of intermediate products can be considered steady-state concentrations [14, 15]. Then, let $d[Y_i]/dt = 0$ (i = 0, 3, 4), $[Y_1]_0 = [B]$, and $[Y_0]_0 = [A]$. Substituting $y = [Y_2]/[B]$, $x = [Y_3]/[B]$, $u = [Y_4]/[B]$, $A = Y_0/[B]$, $z = [In]/[B]$, and $p = [M]/[B]$ into the corresponding rate equations, for the steady-state concentrations of Y_2, Y_3, and Y_4, we obtain

$$2k_0/(k_1[B]) + x - k_2y[A]/k_1 - k_6yz/k_1 = 0, \qquad (1)$$

$$-x + 2k_4u/(k_1[B]) - k_3xz/k_1 = 0, \qquad (2)$$

$$k_2y[A]/k_1 - k_4u/(k_1[B]) - k_5up/k_1 = 0. \qquad (3)$$

Determining u from Eq. (3), substituting it into Eq. (2), and inserting $h = k_4/(k_4 + k_5p[B])$, we have

$$-x + 2k_2hy[A]/k_1 - k_3xz/k_1 = 0. \qquad (4)$$

It is evident that the parameter h varies from 1 to 0 with an increase in the dimensionless deactivator concentration p. Equation (4) suggests that, if in an experiment the deactivator concentration is such that h is as high as 0.5, chain branching does not take place. Therefore, at $h > 0.5$, ignition delays and self-ignition do not occur. Let us assume that the initial mixture always contains 8% In with respect to A. Then, $[A] = z/0.08$. Determining x and y from Eqs. (1) and (4), we obtain

$$x = -4k_0(2k_1 + k_3z)/(z[B](50hk_1k_2 - 25k_1k_2 - 25zk_2k_3 - 2k_6k_1 - 2zk_6k_3)),$$

$$y = -2k_0(50hk_2 + 25k_2 + 2k_6)/([B](50hk_1k_2 - 25k_1k_2 - 25zk_2k_3 - 2k_6k_1 - 2zk_6k_3)).$$

If the denominator of these equations is equal to zero, x and y tend to infinity; that is, self-ignition occurs. Then, z_{crit} is determined by the equality $z_{crit} = k_1(50hk_2 + 25k_2 + 2k_6)/(k_3(25k_2 + 2k_6))$. We divide the equation $d[In]/dt = -k_6Y_2[In] - k_3Y_3[In]$, which determines the rate of inhibitor consumption, by $[B]^2$:

$$dz/dt = -[B](k_6yz + k_3xz). \qquad (5)$$

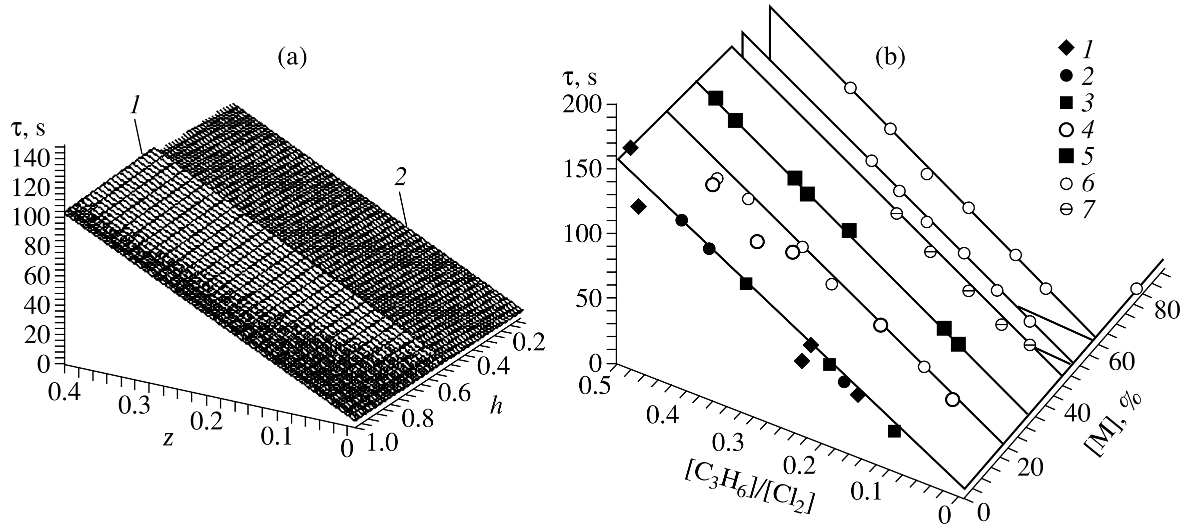

Fig. 1. (a) Self-ignition delay time (τ) as a function of the relative concentration of an inhibitor (*z*) or a deactivator (*h*) calculated in terms of generalized model (II) for the cases when (*1*) EB occurs and (*2*) deactivation does not occur ($h = 1$). The values of parameters are as follows: $B = 5 \times 10^{16}$ cm^{-3}, $k_0 = 2 \times 10^{-3}$ s^{-1}, $k_1 = 10^{-12}$ cm^3/s, $k_2 = 10^{-14}$ cm^3/s, $k_3 = 10^{-12}$ cm^3/s, and $k_6 = 10^{-11}$ cm^3/m. (b) Experimental dependence of the self-ignition delay time (τ) on the ratio $[C_3H_6]/[Cl_2]$ and the deactivator (M) (*1–5, 7*) SF_6 or (*6*) Kr in reactor I for the initial mixtures of the following compositions: (*1*) Cl_2 (0.20 kPa) + a mixture of DCS + 8% C_3H_6; (*2*) Cl_2 (0.28 kPa) + a mixture of DCS + 8% C_3H_6; (*3*) Cl_2 (0.12 kPa) + a mixture of DCS + 8% C_3H_6; (*4*) Cl_2 (0.20 kPa) + a mixture of DCS + 6.4% C_3H_6 + 20% SF_6; (*5*) Cl_2 (0.20 kPa) + a mixture of DCS + 5.4% C_3H_6 + 32% SF_6; (*6*) Cl_2 (0.20 kPa) + a mixture of DCS + 8% C_3H_6 + 20, 50, or 60% Kr or Cl_2 (0.20 kPa) + a mixture of DCS + 80% Kr; (*7*) Cl_2 (0.20 kPa) + a mixture of DCS + 4.5% C_3H_6 + 45% SF_6.

Let us substitute x and y into Eq. (5) and integrate Eq. (5) with respect to z between the limits from z to z_{crit} and with respect to t between the limits from 0 to τ to obtain the expected experimental dependence of τ on z and h. Figure 1a illustrates the results. The chosen values of rate constants were close to those of the corresponding reactions of silylenes [13], which are assumed to be chain carriers (for example, $k_2 = 10^{-14}$ cm^3/s, whereas the published value is 5×10^{-15} cm^3/s [13]). It can be seen in Fig. 1a that the linear dependence of τ on [In]/[B] is expected; the slope of this function is determined by the value of k_0 [14, 15]. Plot *1* in Fig. 1a indicates that at $h < 0.5$ (i.e., in the presence of a deactivator) ignition delays were absent over a wide range of [In]/[B]. This effect did not occur in the absence of an effective deactivator ($h = 1$) (Fig. 1a, plot *2*). For simplicity, we ignored the possible occurrence of material branching along with EB in the generalized model under consideration. However, it is easy to demonstrate that the inclusion of the material branching reaction $Y_0 + Y_2 \longrightarrow 3Y_3$ ($k \sim k_2$) into scheme (II) results in the disappearance of ignition delays at $h < 0.25$; that is, the critical character of the dependence of τ on h is retained. This result was supported by the numerical integration of the system of non-steady-state rate equations that correspond to mechanism (II). Thus, the above consideration predicts a critical character of the dependence of τ on deactivator concentration in the presence of both an inhibitor and a deactivator.

EXPERIMENTAL

The experiments were performed under static conditions at 293 K and a total pressure of 0.27–2.00 kPa using the setup described in [17]. Three types of cylindrical quartz reactors with different *S*/*V* ratios were used (reactor I 15 cm in length and 3 cm in diameter, reactor II 15 cm in length and 12 cm in diameter, and reactor III 80 cm in length and 4 or 2 cm in diameter). The reactors had gas inlets and diametrically opposite optical quartz windows. Chlorine was initially allowed to bleed into evacuated reactors I and II up to the required pressure (0.07–0.40 kPa). Next, a mixture of DCS + C_3H_6 + SF_6 or Kr (if necessary) was added to a total pressure of 0.40–2.00 kPa. The value of τ was determined as the interval from this instant in time to a dramatic decrease in the concentration of Cl_2, which corresponded to self-ignition, which was also easily observed visually. Mixtures containing SF_6 were studied simultaneously with mixtures containing the same amount of Kr in place of SF_6. The mixtures of DCS + (3–8)% C_3H_6 + (20–80)% SF_6 or (20–80)% Kr, as well as analogous mixtures without C_3H_6, were prepared before the experiments. Flame propagation was studied in reactor III. Chlorine was allowed to bleed into the reactor, and then a prepared combustible mixture containing the inhibitor was added. Flame propagation was initiated by a heater made of several coils of Nichrome wire 0.3 mm in diameter. A 3000-μF capacitor bank was discharged through this wire in a pulse mode. The flame run was detected with a multichannel light guide and a FEU-71 photomultiplier tube, a signal from which was supplied to an S9-8 two-beam storage oscilloscope.

The concentration of Cl_2 was measured by the absorption at a wavelength of 300 nm. The spectroscopic measurements at 200–680 nm were performed with the use of a high-aperture (aperture of 1 : 4.5) VM-25 diffraction monochromator (Germany). Two photomultiplier tubes (FEU-71 and FEU-39) were used, whose signals were supplied to both beams of S9-8. In emission kinetics measurements at a given wavelength, the signal from FEU-39 was supplied to the synchronization input, whereas the signal from FEU-71 was supplied to a beam of S9-8, which was turned on in go-ahead mode. The light absorption in the ultraviolet region of the spectrum was measured with the use of a DVS-25 mercury–hydrogen lamp with a continuous emission spectrum in the region 200–320 nm. Radiation from the lamp passed through a quartz collimator and a reactor, and it was focused with a condenser on the entrance slit of a monochromator. Radiation was detected with a FEU-71 photomultiplier tube or an OSA-500 optical spectra analyzer (see below). In the case of using the photomultiplier tube, an ac measurement circuit was used with radiation modulation with a mechanical chopper at a frequency of 500 Hz and U3-29 and V6-9 amplifiers placed in series and an U2-8 synchronous detector. The chopper was arranged before the entrance slit of the monochromator. The resulting constant signal was recorded using an Endim 620.02 plotter.

Flame emission spectra were measured with the use of an OSA-500 optical spectra analyzer (Germany). The resolving power of the optical system was 0.4 nm per channel. The required number of spectral scans (1 scan = 500 channels in 32 ms) was stored in the memory of the OSA-500 computer. In the course of combustion, emission in the region 0.7–1.9 μm was also measured with the use of an MDR-3 monochromator (diffraction grating with 300 lines/mm) and a silicon light filter (in the region 1.1–1.9 μm). The spectral slit width was ~0.005 μm. The kinetic curves of spectral radiation were measured with a single ignition at a fixed wavelength with $\Delta\lambda = 0.005$ μm. The monochromator was calibrated using the characteristic absorption bands of chloroform at wavelengths of 1.15, 1.21, 1.41, and 1.69 μm [18]. The radiation detection system consisted of an FD-10 photodiode, which is sensitive over the range 0.7–1.9 μm; a field-effect transistor amplifier; and U3-29, V6-9, and U2-8 amplifiers placed in series. The signal from the last-named amplifier was supplied to S9-8. An ac measurement circuit with radiation modulation with a mechanical chopper at a frequency of 3300 Hz, which is sufficient for measuring the kinetics of ignition (characteristic time of combustion >10 ms [2]), was used. The chopper was also arranged before the entrance slit of the monochromator. Thus, as a result, a variable signal was detected; the maximum value of this signal was determined as the arithmetic mean of maximum values for five to seven ignitions. Based on these data on kinetic curve maximums, the intensity of radiation was plotted as a function of wavelength for each λ. The reproducibility of the maximum radiation intensity in each individual ignition was ~15%.

The Kr, Cl_2, SF_6, C_3H_6, and H_2 gases were of chemically pure grade; the purity of DCS was monitored by IR spectrophotometry [17]. The reactor was pumped out to 0.4 Pa using a 2NVR-5D fore pump and an N-01 oil-diffusion pump. The residual pressure was measured with a VIT-2 thermocouple ionization vacuum gauge and a VDG-1 gas-discharge vacuum gauge. The reactor was pumped out for 5 min at a residual pressure of 0.4 Pa before each experiment. The change in the total pressure on self-ignition and flame propagation (reactors II and III) was measured by a 6P19S mechanotron with an intrinsic frequency of 300 Hz.

RESULTS AND DISCUSSION

Optical Spectra

According to Rubtsov *et al.* [2], the mixtures of DCS and Cl_2 in reactors I and II were self-ignited almost immediately after mixing at total pressures higher than 2 kPa. At the same time, in the presence of an additive of $[C_3H_6] > 4\%$, ignition delays for longer than 5 s were observed, whereas the induction period was <300 ms without additives (see above). Therefore, C_3H_6 is an inhibitor of the reaction of DCS chlorination, and $\tau \gg \tau_i$ under the conditions of this study. Thus, at $[C_3H_6] > 4\%$, the reactants can be considered well mixed; that is, homogeneous self-ignition occurs over the reactor volume in the presence of C_3H_6.

Figure 2 demonstrates the oscillograms of the combined detection of chemiluminescence at 470 nm (curve *1*) and 1.28 μm (curve *2*) and light absorption at 300 nm (curve *3*). The visible radiation maximum coincides in time with the maximum rate of chemiluminescence buildup at 1.28 μm. As can be seen in the kinetic curve of light absorption, two intermediates are formed in self-ignition. The spectrum of the long-lived product was a continuous structureless band at 270–480 nm with a maximum at 320 nm; it was observed only at $[DCS]/[Cl_2] \le 1$. Data on the nature of this spectrum are absent from the literature. Figure 3 demonstrates the UV spectrum of the short-lived product and the chemiluminescence spectrum in the visible region. As can be seen in Fig. 3, the observed emission spectral bands belong to the monochlorosilylene radicals :SiHCl (A^1B_1–X^1A_1), and the absorption bands belong to the dichlorosilylene radicals $:SiCl_2$. The assignment of spectra was performed in accordance with published data [19, 20].

Thus, silylenes were directly detected in the course of chain combustion. In this case, it was found that C_3H_6 is an effective inhibitor of the BCP of dichlorosilane chlorination. Therefore, propylene molecules react with chain

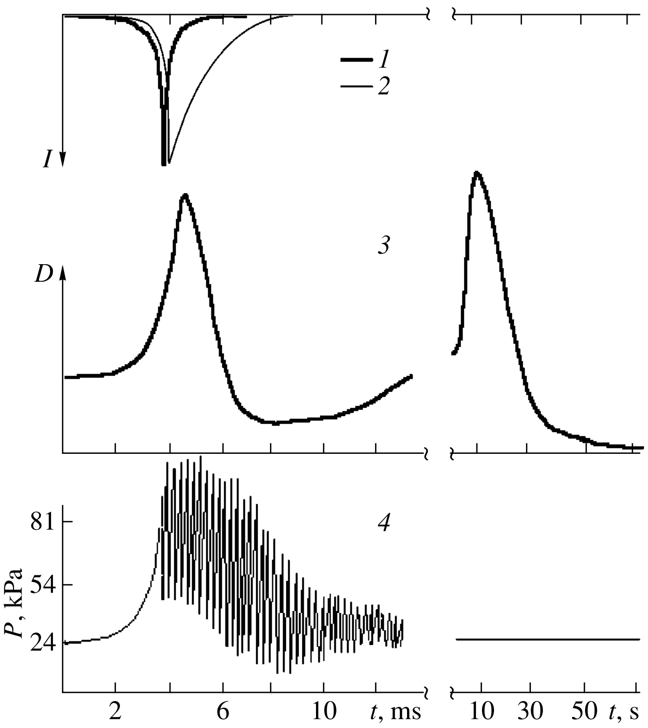

Fig. 2. Kinetic curves of chemiluminescence at a wavelength of (*1*) 470 nm or (*2*) 1.28 μm, (*3*) light absorption at 300 nm, and (*4*) total pressure in the self-ignition of a mixture of Cl_2 (0.13 kPa) and DCS + 8% C_3H_6 (0.13 kPa). Reactor II. Curve *4* exhibits the inherent vibrations of the mechanotron (300 Hz) under the action of a chain-thermal explosion.

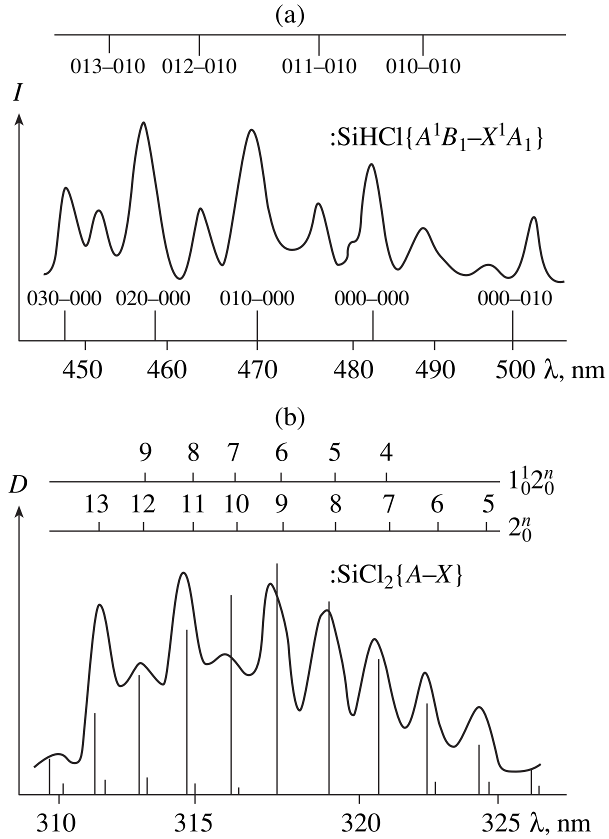

Fig. 3. Experimental spectra of (a) the luminescence of :SiHCl (A^1B_1–X^1A_1) and (b) the UV absorption of :$SiCl_2$ (10 scans; 10 accumulations; Cl_2 (0.20 kPa) + (DCS + 8% C_3H_6) (0.20 kPa); reactor II). The assignment of the spectra corresponds to the published data [19, 20]. The figures show vibrational modes for each band.

carriers, which participate in chain unit propagation [14, 16]. As noted above, the reactions silylene + $C_3H_6 \longrightarrow$ chain termination (10^{-10}–5×10^{-13} cm^3/s) [13] occur at high rates. Consequently, based on published data, we can assume that these reactions are responsible for the inhibiting effect of propylene. The experimental results given below will be considered within the framework of this assumption taking into account conceivable reaction set (I).

The emission spectrum in the near-infrared region (NIR) contains two intense bands at 1.28 and 1.42 μm. We failed to determine the nature of these bands based on published data. However, it should be noted that the effects of SF_6 additives on the intensity of NIR emission in the BCPs of DCS chlorination and oxidation were significantly different. As distinct from DCS oxidation, vibrational energy transfer from vibrationally excited BCP products to SF_6 additive molecules was absent from the chlorination; in contrast, SF_6 effectively quenched these emission bands. This quenching may be associated with the deactivation of excited species formed in the BCP in a process analogous to the fourth reaction from set (I). In the presence of molecular hydrogen in amounts of 50–100% with respect to Cl_2, the intensities of emission at NIR band maximums also noticeably decreased. A conceivable reason for this phenomenon is considered below. Moreover, in the combustion of DCS + O_2 mixtures with SF_6 additives, the emission band of HF $X^1\Sigma$ (v = 2–0) [21], which is due to the reaction H + $SF_6 \longrightarrow$ HF (v = 0, 1, 2) + SF_5, appeared in the spectrum, whereas this did not occur in the case of DCS + Cl_2 with SF_6 additives. Therefore, in contrast to DCS oxidation, hydrogen atoms do not play an important role as chain carriers in the BCP of DCS chlorination.

Flame Propagation

Branching in BCPs can occur by linear and quadratic mechanisms. In the former case, the rate of branching is a linear function of the concentration of an active center that participates in the reaction. In the latter case, a nonlinear branching reaction occurs, in which the number of free valences increases in the interaction of active centers with one another. In the latter case, a isothermal flame is observed in the BCP. This flame is a chemical reaction front, which stationarily

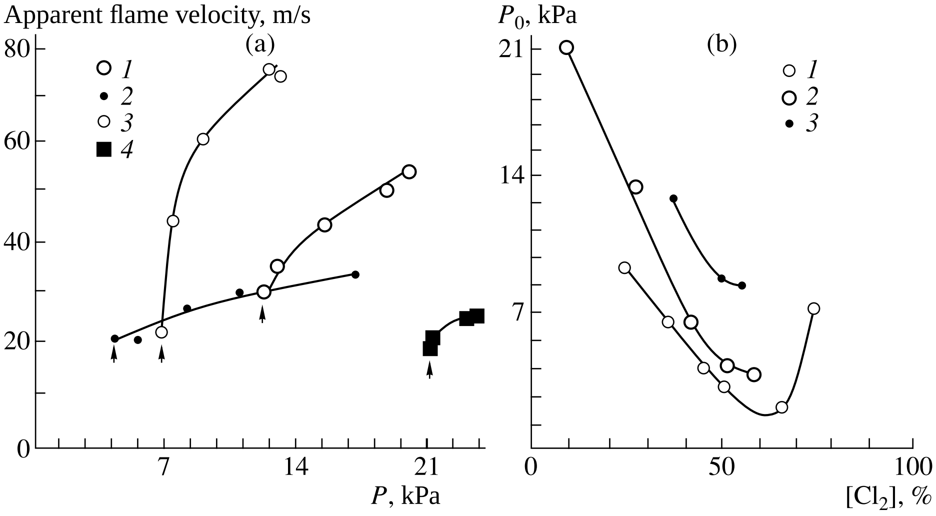

Fig. 4. Apparent velocities and concentration limits of chain-thermal flame propagation in the BCP of DCS chlorination. The results were treated using the least-squares technique. (a) The dependence of the apparent velocity of flame propagation on the total pressure at the following $[Cl_2]/[DCS]$ ratios (10% C_3H_6 in DCS; reactor diameter of 2 cm): (*1*) 1/3, (*2*) 4/2, (*3*) 5/2, and (*4*) 6/1. Arrows indicate pressures at which a stationary regime of flame propagation changed to a decaying regime. (b) The dependence of the concentration limits of flame propagation on the reactor diameter and the inhibitor concentration: (*1*) 10% C_3H_6 in DCS; diameter, 4 cm; (*2*) 10% C_3H_6 in DCS; diameter, 2 cm; and (*3*) 15% C_3H_6 in DCS; diameter, 2 cm.

propagates in space. In this case, heat generation is low so that the temperature can be considered constant and self-heating is insufficient to bring the reaction mixture to the area of self-ignition. The rate of this flame depends on the diffusion of the active centers of reaction chains to the unreacted mixture. The experimental observation of isothermal flame propagation serves as unambiguous evidence for the occurrence of nonlinear branching in the system [8]. The possibility of isothermal flame occurring was studied in reactors III. Because pure reactants interact almost instantaneously upon mixing, we used the found inhibiting effect of propylene additives, which cause ignition delays. After introducing the reactants into reactor III as described above, the mixture was stirred for the time $(\tau - 10)$ s, that is, immediately before the entry of the combustible mixture into the self-ignition area, when the inhibitor content of the combustible mixture became low. Next, an initiating pulse was supplied at the end of the vessel. In all of the experiments, only chain-thermal flames accompanied by characteristic sounds and pressure jumps, which were detected with the use of a mechanotron, were observed. For each concentration, a pronounced lower limit of flame propagation in terms of the total pressure (P_0) was observed, below which always only a diminishing flame was detected. The apparent flame velocities were 15–70 m/s (Fig. 4). We found previously that the number of moles remained unchanged in the BCP of DCS chlorination; thus, the pressure jump was due to self-heating. Figure 4 demonstrates the results of measuring the velocities of flame propagation (apparent velocities) and the concentration limits of flame propagation. Previously [22], it was found that two modes of flame propagation occur in BCPs with nonlinear branching; these modes correspond to chain-thermal and isothermal regimes. In this case, a chain-thermal regime changes to an isothermal stationary regime as the total pressure or fuel concentration is decreased. Consequently, with the occurrence of quadratic branching, stationary flame propagation will be observed at the total pressure $P < P_0$, which is not accompanied by a pressure jump. Thus, the detection of a stationary flame front at $P < P_0$ would serve as evidence for the occurrence of a isothermal flame. However, as mentioned above, this regime of combustion was not detected: the flame propagation was always slowed down below P_0. Therefore, as distinct from the oxidation reactions of silanes, nonlinear branching in the silane chlorination mechanism at 293 K is insignificant.

Self-Ignition Delays

We found that the values of τ measured in reactor I increased with the $[C_3H_6]/[DCS]$ ratio at a constant concentration of molecular chlorine. In this case, we also found that τ is independent of the total pressure, whereas it depends on only the ratio of the sum of the initial concentrations $[DCS] + [C_3H_6]$ to the initial concentration $[Cl_2]$. Thus, because in each set of experiments on measuring τ the $[DCS]/[C_3H_6]$ ratio was kept constant (the mixtures of DCS with the inhibitor were prepared beforehand as described above), the measured values of τ only depend on the concentration ratio between the inhibitor and molecular chlorine. Figure 1b demonstrates the experimental results. The data were

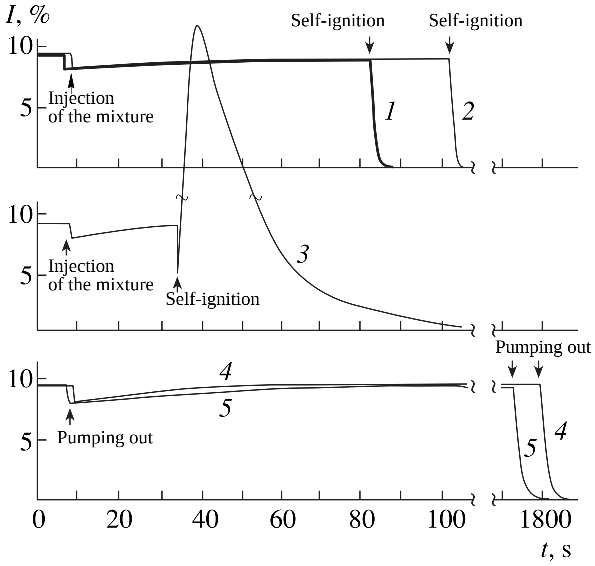

Fig. 5. Experimental time dependence of the concentration of Cl_2 (absorption intensity (*I*) at λ = 300 nm) in the self-ignition: (*1*) Cl_2 (0.20 kPa) + (DCS + 8% C_3H_6) (0.56 kPa); (*2*) H_2 (0.13 kPa) + Cl_2 (0.20 kPa) + (DCS + 8% C_3H_6) (0.56 kPa); (*3*) Cl_2 (0.20 kPa) + (DCS + 8% C_3H_6 + 50% Kr) (0.20 kPa); (*4*) Cl_2 (0.20 kPa) + (DCS + 8% C_3H_6 + 50% SF_6) (0.20 kPa); and (*5*) Cl_2 (0.20 kPa) + (DCS + 80% SF_6) (0.18 kPa).

obtained from the kinetic curves of molecular chlorine consumption in Cl_2 + DCS + C_3H_6 + SF_6 (or Kr) mixtures as described in Experimental. Figure 5 shows typical kinetic curves. As can be seen in Fig. 5, the value of τ is greater than 1800 s in the presence of 8% C_3H_6 and 50% SF_6 (curve *4*); however, the value of τ is no greater than 110 s in the presence of 8% C_3H_6 and 50% Kr (curve *3*). This criticality was predicted above. The detection of this criticality indicates that processes with the participation of excited species play a considerable role in the chlorination of silanes. Thus, the deactivating properties of Kr with respect to the BCP of DCS chlorination are much less pronounced than those of SF_6. Indeed, as can be seen in Fig. 1b, self-ignition delays were observed at 80% Kr (point *6*). That is, in accordance with the above qualitative consideration, the value of h_{Kr} is close to unity. At the same time, a critical concentration of SF_6 (~45%) exists (Fig. 1b, points *7*) at which the dependence of τ on the concentration of SF_6 is critically changed: self-ignition delays and ignition were not detected at $[SF_6] > 45\%$. Comparing Figs. 1a and 1b, we concluded that the results could be qualitatively interpreted with the use of the generalized kinetic model of BCPs with EB. In this case, in the context of kinetic mechanism (II), $h_{SF_6} \approx 0.5$.

Available experimental data are insufficient for detailing the kinetic model of DCS chlorination. Experimental results that provide additional information on the kinetics of DCS chlorination are given below. We found that self-ignition in reactor II at $[Cl_2] > 0.03$ kPa and a total pressure above 0.20 kPa was accompanied by a characteristic click. Figure 2 (curve *4*) demonstrates a typical oscillogram of the change in the total pressure during self-ignition. As can be seen, the pressure increased by a factor of ~3 during the self-ignition. As indicated above, the reaction occurs without changes in the number of moles. Consequently, at surface-to-volume ratios lower than that in reactor I, self-ignition occurs in the regime of a chain-thermal explosion [23]; in this case, the self-heating was $\Delta T = 293\Delta P/P \approx 1000°C$, where ΔP is the change in the total pressure upon self-ignition, and P is the total pressure of the mixture before self-ignition. At this temperature, the set of reactions (I), which was proposed by Swihart and Carr [12] for the description of the pyrolysis of chlorine-substituted silanes, can occur.

In a number of experiments, H_2 (5–8%) was added to reactor I before bleeding molecular chlorine. We found that self-ignition delays in the presence of H_2 noticeably increased (Fig. 5, curve *2*). Note that self-ignition delays were independent of the total pressure under the conditions of our experiments. It is also well known [13] that the :SiHCl and $:SiCl_2$ radicals almost do not react with molecular hydrogen. The reaction $Cl + H_2 \longrightarrow H + HCl$ is a chain propagation reaction, and it cannot be responsible for an increase in τ. The only known reaction capable of increasing τ is the fast chain-termination reaction $:SiH_2 + H_2 \longrightarrow SiH_4$ (10^{-13} cm^3/s [13]). This can be considered as indirect evidence for the participation of $:SiH_2$ radicals in the chlorination of DCS. In the case of $:SiH_2$ radical formation in BCPs, heat can be released in the following fast reactions (according to [13], the rate constant of the reaction $:SiH_2 + Cl_2 \longrightarrow$ products is 1.4×10^{-10} cm^3/s):

$$:SiH_2 + Cl_2 \longrightarrow :SiHCl + HCl + 363\ \text{kJ/mol [24]}, \qquad \text{(III)}$$

$$:SiH_2 + Cl_2 \longrightarrow {}^{\bullet}SiH_2Cl + Cl + 221\text{kJ/mol [24]}. \qquad \text{(IV)}$$

The energy released in reaction (III) is sufficient for the excitation of :SiHCl to the state A^1B_1. Chlorine atoms formed in reaction (IV) can result in the production of $:SiCl_2$ in the course of the sequential abstraction of hydrogen atoms from the DCS molecule (chain propagation). In turn, $:SiH_2$ radicals can be formed in a reaction sequence analogous to (I), which was also discussed in [12]:

$$:SiCl_2 + SiH_2Cl_2 \longrightarrow Cl_3SiSiH_2Cl^* \longrightarrow :SiH_2 + SiCl_4\ (\text{end product}). \qquad \text{(V)}$$

It is easy to verify that the set of reactions (I) and (III)–(V) results in chain branching; the reactions of silylenes with C_3H_6, along with the deactivation of excited disilanes on SF_6 molecules, are the reactions of homogeneous chain termination. At the same time, the assumption concerning the participation of silylenes in chain propagation reactions should be further checked experimentally.

Let us summarize the main results of this study.

In the BCP of DCS chlorination at low pressures and 293 K, the chlorine-substituted silylene radicals :SiHCl (A^1B_1–X^1A_1) and :$SiCl_2$ in the electronic ground state were detected directly on self-ignition. The inhibiting effect of propylene additives (>4 vol %) on the self-ignition of DCS mixtures with molecular chlorine was found, which resulted in self-ignition delays. It was found that the inhibiting effect dramatically increased in the presence of a chemically inert additive of SF_6 (>45%). It was demonstrated that in the BCP of DCS chlorination, as distinct from the BCP of DCS oxidation, hydrogen atoms as chain carriers do not play a considerable role. A modified method of self-ignition delays was proposed, which includes the use of deactivating additives along with inhibitors. An important role of excited species in branching was found with the use of this method in the study of the BCP. Only a chain-thermal regime of flame propagation was observed in the BCP of DCS chlorination; in this case, the apparent flame velocities were higher than 15 m/s. The absence of a isothermal regime of flame propagation suggests that at 293 K chain branching occurs in a reaction that is linear with respect to the concentration of active centers. Based on the assumption that inhibition is due to fast reactions of identified silylenes with C_3H_6 molecules, a number of conceivable elementary reactions ((I) and (III)–(V)), which occur in the chlorination of DCS are proposed. These reactions with silylenes as chain carriers include the formation of electronically excited :SiHCl radicals and the participation of excited species in chain branching.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 00-03-32979a and 02-03-32993).

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