Mendeleev Commun., 2002, 12(1), 37–39

Dichlorosilane chlorination in the presence of propylene as an inhibitor at low pressures and 293 K

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10.1070/MC2002v012n01ABEH001537

The strong inhibiting effect of C_3H_6 on the self-ignition of dichlorosilane–chlorine mixtures points to silylenes as chain carriers of the reaction. A critical concentration of chemically inert SF_6 (> 45%) drastically improves the inhibiting action of C_3H_6 indicating the occurrence of energy branching.

The chlorination of inorganic hydrides [monosilane,[1] dichlorosilane (DCS),[2] phosphine,[3] germane[4]] and hydrocarbons,[5] the reaction of monosilane with nitrogen trichloride[6] and the thermal decomposition of NCl_3[7] show special features of branched-chain processes (BCP). These are the existence of self-ignition isothermal limits and their dependence on the state of contacting surfaces, as well as the sensitivity of the kinetics to small additives of promoters and inhibitors.[8,9] The energy branching (EB, the participation of excited intermediates in chain branching) plays an important role in chain chlorination because the material branching, *e.g.*, $\cdot H + O_2 \rightarrow \cdot OH + \cdot O\cdot$, is evidently ruled out. EB in the reactions of electronically excited particles was established for NCl_3 decomposition.[7] EB in the reactions of vibrationally excited particles was detected in the fluorination of H_2 and fluorinated hydrocarbons.[11] In fact, fluorination reactions differ from those of chlorination in that they are more exothermic. Moreover, HF has a higher first vibrational level than that of HCl. In fluorination, EB occurs if the energy released in a certain step is enough for unimolecular decomposition of the product of this step, *e.g.*, for the $CH_2F_2 + F_2$ reaction the following branching process is suggested: $CF_2H + F_2 \rightarrow CHF_3^* + \cdot F$; $CHF_3^* \rightarrow :CF_2 + HF$.[11] Related reactions were proposed for 1,1-difluoroethane[5] and SiH_4[1] chlorination. In these mechanisms, carbenes and silylenes, respectively, participate in the EB process. *Ab initio* calculations were used to construct a mechanism for the pyrolysis of chlorinated silanes.[12] The insertion reactions of chlorinated silylenes into chlorinated silanes, which yield chlorinated disilanes, were examined. It was assumed that DCS decomposition could be accelerated by a chlorosilylene-catalysed cycle including EB [its energetics is shown in Figure 1 (ref. 12)]:

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

It is known that olefins react very rapidly with silylenes.[13] The rate constants vary from 10^{-10} (for SiH_2) to 10^{-11} cm^3 s^{-1} (for SiHCl and $SiCl_2$). Since SiHCl (A^1B_1–X^1A_1) was detected in DCS chlorination,[2] the inhibiting action of olefins (*e.g.*, propylene) will indicate that the reactions of silylenes as chain carriers are of considerable importance in the BCP. If inhibition takes place, the uniform self-ignition over the reactor volume can be studied because the self-ignition of pure DCS and Cl_2 at 293 K occurs immediately after mixing (induction period τ_i is < 300 ms).[2]

This work is aimed at the establishment of the important role of silylenes as chain carriers, as well as energy factors, in the chain branching in BCP of DCS chlorination in the presence of propylene as an inhibitor and chemically inert sulfur hexafluoride (SF_6) as a deactivator.

The method of ignition delay was used.[14,15] The basis for this method is an expansion of self-ignition area in the time of consumption of an inhibitor. The dependence of self-ignition limits on the fraction of an inhibitor is shown in Figure 1.[16] As is seen, a combustible mixture enters the self-ignition area when the inhibitor concentration attains a certain critical value z_{crit}. The time τ_C it takes for the mixture to enter the self-ignition area and then to ignite is combined from the time τ required to reach the boundary of the self-ignition area (ignition delay) and induction period τ_i, that is, $\tau_C = \tau + \tau_i$. Subsequent calculations hold for $\tau >> \tau_i$, or $\tau_C \cong \tau$. In case of the participation of excited intermediates in chain branching, the addition of an effective deactivator will provide an additional pathway of chain termination and affect τ.

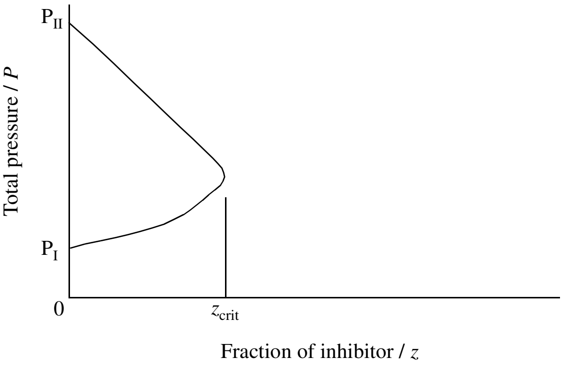

Figure 1 The dependence of self-ignition limits of a combustible mixture on the concentration of an inhibitor (γ).[16]

Let us demonstrate that the dependence of τ on the concentrations of initial reactants in the presence of both an inhibitor and a deactivator differs markedly from that in the presence of a single inhibitor by an example of the generalized kinetic model of BCP with EB. The mechanism of DCS chlorination is unknown; therefore, the qualitative model of BCP must include chain origination, propagation, EB and termination *via* both an inhibitor (In) and a deactivator (M).

$$\begin{array}{rcll}
Y_1 & \longrightarrow & 2Y_0 & (k_0)\ \text{chain origination;}\\
Y_1 + Y_3 & \longrightarrow & Y_0 + \text{products} & (k_1)\ \text{chain propagation;}\\
Y_0 + Y_2 & \longrightarrow & Y_4^* + \text{products} & (k_2)\ \text{chain propagation;}\\
Y_3 + \text{In} & \longrightarrow & \text{chain termination} & (k_3);\\
Y_4^* & \longrightarrow & 2Y_3 & (k_4)\ \text{linear chain branching (EB);}\\
Y_4^* + M & \longrightarrow & \text{deactivation} & (k_5);\\
Y_0 + \text{In} & \longrightarrow & \text{chain termination} & (k_6).
\end{array} \qquad (II)$$

Here, Y_1 and Y_2 are the initial reactants, for instance fuel and an oxidizer; Y_0 and Y_3 are active centres, Y_4^* is the excited species that causes branching *via* unimolecular decomposition. Since the lower limit of the DCS + Cl_2 reaction is low,[2] the heterogeneous chain termination is not taken into account.[14] The amounts of initial reactants consumed and intermediates formed during ignition delay may be considered as negligibly small.[14,15] Therefore, dY_i/dt (i = 0,3,4) may be put equal to zero and $[Y_1]_0 = [B]$ and $[Y_2]_0 = [A]$. Then, by entering new variables $y = Y_0/[B]$, $x = Y_3/[B]$, $u = Y_4/[B]$, $A = Y_2/[B]$, $z = [In]/[B]$, $p = [M]/[B]$ into the corresponding equations for the kinetic mechanism (II), for the stationary concentrations of Y_0, Y_3 and

Y_4 we obtain:

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

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

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

Equation (3) can be solved with respect to u. Substituting this value in equation (2) and inserting $h = k_4/(k_4 + k_5p[\mathrm{B}])$ we obtain:

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

It is no doubt that parameter h changes from 1 to 0 with an increase in the dimensionless amount of deactivator p. Equation (4) suggests that if in certain experiment p amounts up to the partial pressure enough for h to take the value 0.5 chain branching is completely terminated. Therefore, at $h > 0.5$, ignition delays are not liable to exist. Let us consider that the initial mixture always contains 8% In with respect to A. Then, $[\mathrm{A}] = z/0.08$. Solving equation (1) and equation (4) for x and y, we derive

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

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

If the denominator of these latter equations is equal to 0, x and y increase infinitely, *i.e.*, self-ignition occurs. Therefore, z_{crit} is determined by the equality

$$z_{\mathrm{crit}} = k_1(50hk_2 + 25k_2 + 2k_6)/[k_3(25k_2 + 2k_6)].$$

We divide the equation $\mathrm{d}[\mathrm{In}]/\mathrm{d}t = -k_6Y_0[\mathrm{In}] - k_3Y_3[\mathrm{In}]$, which determines the rate of inhibitor consumption, by $[\mathrm{B}]^2$:

$$\mathrm{d}z/\mathrm{d}t = -[\mathrm{B}](k_6yz + k_3xz). \qquad (5)$$

Let us substitute x and y into equation (5) and integrate equation (5) numerically with respect to z between the limits z and z_{crit} and with respect to t between 0 and τ for obtaining the dependence of τ on z and h. The results of numerical calculation are shown in Figure 2(*a*). The chosen values of the rate constants are close to those of silylenes[13] being considered as chain carriers in the process. It can be seen that the linear dependence of τ on [In]/[B] is expected, the shape of this dependence is determined significantly by the value of k_0. It can be seen in Figure 2(*a*) (curve *1*) that at $h < 0.5$ there are no ignition delays in the presence of the deactivator in the wide range of the ratios [In]/[B], whereas for $h = 1$ (no deactivation), *i.e.*, in the absence of EB [Figure 2(*a*), curve *2*] this effect is missing. To simplify the treatment, the possible occurrence of material branching along with EB was ignored. However, there are also no ignition delays at $h < 0.25$ if material branching, *e.g.*, $Y_0 + Y_3 \rightarrow 3Y_1$ ($k_{\mathrm{m}} \sim k_2$), is included, *i.e.*, the critical character of the dependence of τ on h also occurs. The result was tested by the numerical solution of a nonstationary system of kinetic equations for mechanism (II) using the forth-order Runge–Kutta method. It was shown that there are no ignition delays at $h < 0.5$: the system does not tend to self-ignite at all. Therefore, the qualitative calculations predict a drastic change in the dependence of τ on the amount of a deactivator in the presence of both an inhibitor and the deactivator.

The experiments were carried out under static conditions at 293 K and total pressures of 0.27–2 kPa. Two cylindrical quartz reactors (15 cm long, 3 cm in diameter, reactor I and 15 cm long, 12 cm in diameter, reactor II) had inlets for gas evacuation and optical windows. Chlorine was initially allowed to bleed into a reactor up to a necessary pressure (0.07–0.4 kPa). Then, the mixture containing DCS + C_3H_6 + SF_6 or Kr (if necessary) was admitted up to a total pressure of 0.4–2 kPa; τ was taken as an interval from this moment up to that of a severe decrease in Cl_2 concentration. Mixtures containing SF_6 were investigated in parallel with mixtures containing the same amount of Kr instead 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 experiments. The concentration of Cl_2 was measured by the absorption at 300 nm using a VM-25 monochromator (Germany), a FEY-39 photomultiplier and a Hg–He lamp. The emission and absorption spectra of self-ignition were recorded with an OSA-500 optical spectra analyser (Germany) with a resolution of 0.2 nm per channel. The required number of scans (1 scan = 500 channels per 32 ms) was stored in a computer. The change in total pressure P during self-ignition in reactor II was measured by a mechanotrone.

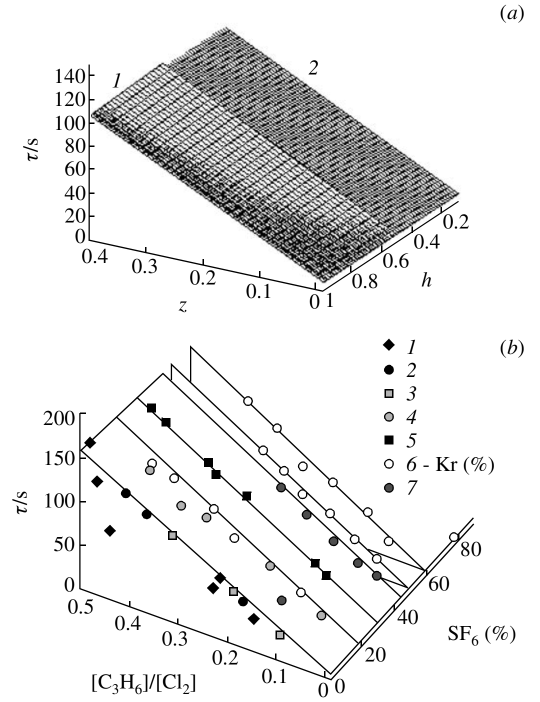

Figure 2 (*a*) Calculated dependence of ignition delays τ on the concentration of inhibitor z and deactivator h. $B = 5\times10^{16}$ cm^{-3}, $k_0 = 2\times10^{-3}$ s^{-1}, $k_1 = 10^{-12}$ cm^3 s^{-1}, $k_2 = 10^{-14}$ cm^3 s^{-1}, $k_3 = 10^{-12}$ cm^3 s^{-1}, $k_6 = 10^{-11}$ cm^3 s^{-1}. (*1*) generalized model (II), EB occurs; (*2*) generalized model (II), EB does not occur, $h = 1$ (no deactivation); (*b*) experimental dependences of ignition delays τ on the ratio between an inhibitor and Cl_2 and concentration of SF_6 (closed circles) and Kr (open circles) Reactor I. (*1*) 0.20 kPa Cl_2 + mixture of DCS + 8% C_3H_6; (*2*) 0.28 kPa Cl_2 + mixture of DCS + 8% C_3H_6; (*3*) 0.12 kPa Cl_2 + mixture of DCS + 8% C_3H_6; (*4*) 0.20 kPa Cl_2 + mixture of DCS + 6.4% C_3H_6 + 20% SF_6; (*5*) 0.20 kPa Cl_2 + mixture of DCS + 5.4% C_3H_6 + 32% SF_6; (*6*) 0.20 kPa Cl_2 + mixture of DCS + 8% C_3H_6 + 20%, 50%, 60% Kr; 0.20 kPa Cl_2 + mixture of DCS +80% Kr; (*7*) 0.20 kPa Cl_2 + mixture of DCS + 4.5% C_3H_6 + 45% SF_6.

It was shown that self-ignition occurs immediately after the mixing of pure DCS and Cl_2 (see ref. 2). However, the addition of > 4% C_3H_6 caused ignition delays more than 5 s pointing to the fact that C_3H_6 acts as an inhibitor, *i.e.*, $\tau \gg \tau_{\mathrm{i}}$. By this means that the reactants may be considered mixed well; therefore, the uniform self-ignition over the reactor volume occurs in the presence of C_3H_6. Moreover, the strong inhibiting action of C_3H_6 suggests that linear chain branching gives rise to short τ_{i} rather than chain initiation. The only known very rapid step silylene + C_3H_6 → chain termination (10^{-10}–10^{-11} cm^3 s^{-1}) is responsible for this inhibiting action.

An example of the simultaneous recording of chemiluminescence (470 nm) and absorption (300 nm) is shown in Figure 3. As can be seen from the absorption curve, two intermediates form in self-ignition. The long-lived species has a structureless spectrum at 270–480 nm; it is observed only at $[\mathrm{DCS}]/[Cl_2] \leq 1$. There is no evidence for the assignment of this spectrum in the literature. The spectra of the short-lived intermediate are shown in Figure 3. The emission bands are due to SiHCl (A^1B_1–X^1A_1)[17] and the absorption bands, due to $SiCl_2$.[18] The silylenes detected are chain carriers of the BCP because C_3H_6, which reacts rapidly with silylenes, has a marked inhibiting effect on this BCP.

It was shown that τ increases linearly with an increase in $[C_3H_6]/[\mathrm{DCS}]$ at constant $[Cl_2]$. It was also shown that τ does not depend on the total pressure, but it depends on the ratio $([\mathrm{DCS}] + [C_3H_6])/[Cl_2]$. This dependence is almost linear. Since in each set of experiments $[\mathrm{DCS}]/[C_3H_6]$ = const, τ depends only on the ratio between an inhibitor and Cl_2 [Figure 2(*b*)]. The data

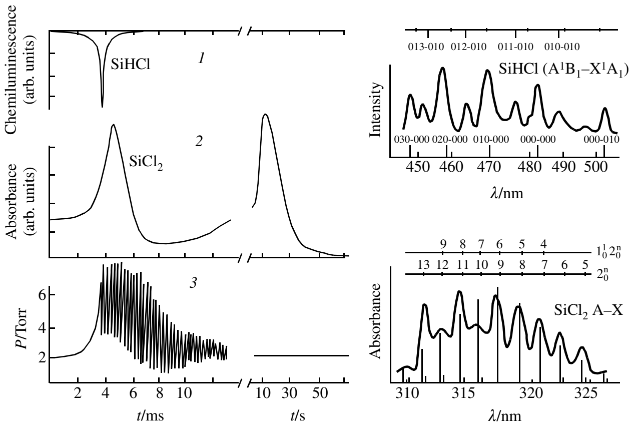

Figure 3 The time dependences of (*1*) chemiluminescence at 400 nm, (*2*) absorption at 300 nm and (*3*) total pressure in the self-ignition of 0.13 kPa Cl_2 + 0.13 kPa (DCS + 8% C_3H_6) and experimental spectra of SiHCl (A^1B_1–X^1A_1) and $SiCl_2$ [10 scans, 10 accumulations, 0.20 kPa Cl_2 + 0.20 kPa (DCS + 8% C_3H_6)]. Reactor II. Curve *3* demonstrates the inherent vibrations of a mechanothrone (300 Hz) under the impact of an expanding gas.

shown in Figure 2(*b*) were obtained from the time dependence of [Cl_2] in the Cl_2 + DCS + C_3H_6 + SF_6 (or Kr) system. Typical data are shown in Figure 4. In the presence of 8% C_3H_6 and 50% SF_6, $\tau > 30$ min whereas τ in the presence of 8% C_3H_6 and 50% Kr is no longer than 110 s. As is expected, the deactivating action of Kr, if any, is markedly weaker than that of SF_6. Actually, as can be seen in Figure 2(*b*), ignition delays are observed at 80% Kr (open circles), *i.e.*, in the context of our qualitative consideration, h_{Kr} is close to 1. However [Figure 2(*b*), closed circles], the critical amount (~45%) of SF_6 exists such as the dependence of τ on [SF_6] undergoes a drastic change. A comparison of Figures 2(*a*) and 2(*b*) shows that the result can be qualitatively rationalised on the basis of the generalized model of BCP with EB; in this case, in the context of kinetic mechanism (II), $h_{SF6} \approx 0.5$.

The self-ignition in reactor II at [Cl_2] > 0.03 kPa and $P >$ > 0.20 kPa is always followed by a sharp sound. The time dependence of the total pressure during self-ignition is shown in Figure 3. As can be seen, an almost three-fold increase in P during the self-ignition is observed. It means that the BCP at low surface to volume ratios occurs in a chain-thermal explosion regime,[19] and the warming-up makes up $\Delta T = 293.\Delta P/P \approx$ $\approx 1000°$. Therefore, the set of reactions (I) of a chlorosilylene-catalysed cycle may occur.

In a series of experiments, H_2 was added into a reactor before Cl_2 (Figure 4). It was shown that τ in the presence of H_2 slightly increases (Figure 4, curve *2*). Note that τ does not depend on the total pressure in our conditions. SiHCl and $SiCl_2$ do not react with H_2,[13] the reaction $Cl + H_2 \rightarrow H + Cl_2$ is chain propagation, and it cannot cause an increase in τ. However, the rapid chain termination $SiH_2 + H_2 \rightarrow SiH_4$ (10^{-13} cm³ s⁻¹, ref. 13) can give rise to an increase in τ. It may serve as indirect evidence for SiH_2 formation in DCS chlorination. Then, a heat emission can take place in the fast reactions (rate constant of the reaction $SiH_2 + Cl_2$ is 1.4×10^{-10} cm³ s⁻¹, ref. 13):

$$SiH_2 + Cl_2 \longrightarrow SiHCl + HCl + 363\ \text{kJ mol}^{-1}\ \text{(ref. 20)} \qquad \text{(III)}$$

$$SiH_2 + Cl_2 \longrightarrow SiH_2Cl + Cl + 221\ \text{kJ mol}^{-1}\ \text{(ref. 20)} \qquad \text{(IV)}$$

Note that the energy released in (III) is enough to obtain excited SiHCl (A^1B_1). SiH_2 can result from the steps[12] $SiCl_2 + SiH_2Cl_2 \rightarrow$ $\rightarrow Cl_3SiSiH_2Cl^* \rightarrow SiH_2 + SiCl_4$. The set of reactions (I), (III) and (IV) represents possible steps of DCS chlorination including silylenes as chain carriers and formation of SiHCl (A^1B_1) and EB. This presumption is still to be refined by the establishment of the composition of reaction products, especially, detection of H_2.

We are grateful to Professor V. V. Azatyan for many useful discussions. This work was supported by the Russian Foundation for Basic Research (grant no. 00-03-32979a).

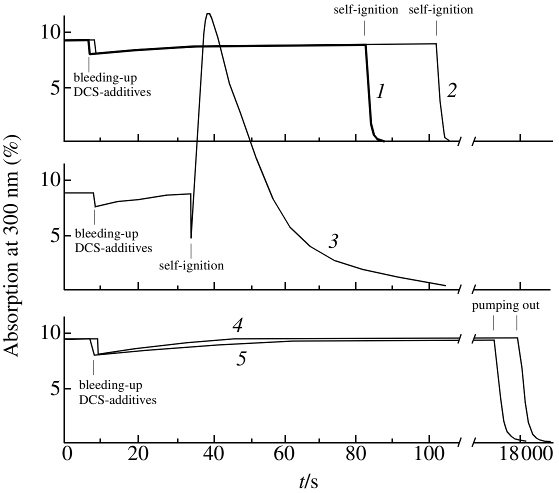

Figure 4 The experimental time dependences of Cl_2 concentration: (*1*) 0.20 kPa Cl_2 + 0.56 kPa (DCS + 8% C_3H_6); (*2*) 0.13 kPa H_2 + 0.20 kPa Cl_2 + 0.56 kPa (DCS + 8% C_3H_6); (*3*) 0.20 kPa Cl_2 + 0.20 kPa (DCS + 8% C_3H_6 + 50% Kr); (*4*) 0.20 kPa Cl_2 + 0.20 kPa (DCS + 8% C_3H_6 + 50% SF_6); (*5*) 0.20 kPa Cl_2 + 0.18 kPa (DCS + 80% SF_6).

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Received: 5th December 2001; Com. 01/1863