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Key Factors of Combustion

From Kinetics to Gas Dynamics

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Contents

1 Nonlinear Phenomena and Kinetic Mechanism of a Gaseous Branching Chain Process by the Example of Thermal Decomposition of Nitrogen Trichloride	1
1.1 Theories of Flame Propagation in Gases (a Brief Review)	2
1.2 Propagation of Non-thermal Flame in the Low-Pressure Thermal Decomposition of Nitrogen Trichloride	10
1.2.1 Experimental	12
1.2.2 Discussion	13
1.3 On the Nature of the Upper Limit of Non-thermal Flame Propagation in the Reaction of Thermal Decomposition of NCl_3	26
1.4 Kinetic Mechanism and Chemical Oscillations in the Branching Chain Decomposition of Nitrogen Trichloride	34
1.5 Promotion of Nitrogen Trichloride Decomposition with the Additives of Molecular Hydrogen in the Vicinity of the Lower Limit of Thermal Ignition	42
1.5.1 Experimental	43
1.5.2 Discussion	44
1.6 Conclusions	52
References	53
2 Nonlinear Effects in Silanes Oxidation and Chlorination in Gaseous Phase: Collecting a Puzzle	57
2.1 The Investigation into Dichlorosilane Chlorination in the Presence of Propylene as Inhibitor and Kr as Deactivator at Low Pressures and 293 K	58
2.2 Non-thermal Flame Propagation in Monosilane and Dichlorosilane Oxidation	66

2.3	A Long-Lived Intermediate in the Oxidation of Monosilane and Dichlorosilane	69
2.4	Experimental.	71
2.5	Discussion	71
2.6	Conclusions	75
	References.	76
3	Electric Phenomena in Silanes Chlorination and Oxidation.	79
3.1	Chemionization in the Chlorination of Dichlorosilane (DCS) at Low Temperatures and Pressures	82
3.1.1	Experimental.	82
3.1.2	Discussion.	83
3.2	Interrelation Between Chemionization and Phase Formation in the Low Temperature Branched Chain Process by the Example of Dichlorosilane Oxidation	85
3.3	Investigation into Thermal Ignition of Dichlorosilane Oxidation by Means of High-Speed Framing Schlieren Cinematography	90
3.3.1	Experimental.	91
3.3.2	Discussion.	92
3.4	Influence of Constant Electric Field in the Absence of Discharge on Kinetic Regularities of Dichlorosilane Oxidation	97
3.4.1	Experimental.	97
3.4.2	Discussion.	99
3.5	Conclusions	105
	References.	106
4	Excited Intermediates in Silanes Combustion	109
4.1	Flame Emission Spectra Over the Region of 400–600 Nm in Low-Pressure Silane and Dichlorosilane Oxidation	109
4.1.1	Experimental.	114
4.1.2	Discussion.	115
4.2	NIR Investigation of Hydro Peroxide Radicals in the Rarefied Flame of Dichlorosilane Oxidation at Low Pressures and 293 K.	120
4.2.1	Experimental.	121
4.3	Conclusions	127
	References.	127
5	Reactions of Hydro Peroxide Radicals in Hydrogen Combustion	131
5.1	Participation of Previously Adsorbed Hydrogen Atoms in the Branching Chain Process of Deuterium Combustion	131
5.1.1	Experimental.	134
5.1.2	Discussion.	135

5.2	Effects of Reactive Admixtures on the Near-IR Emission Spectra of Hydrogen and Deuterium Oxidation Flames	138
5.2.1	Experimental	139
5.2.2	Discussion	141
5.3	Conclusions	149
	References	149
6	Flame Acceleration in Reactive Gas Flows	153
6.1	Reactive Gas Flows: Governing Parameters	154
6.2	Relative Contribution of Gas Dynamics and Chemical Factors into Features of Flame Penetration Through the Small Openings in a Closed Cylindrical Reactor	165
6.2.1	Experimental	166
6.3	Establishment of Gas Dynamics and Kinetic Features of Penetration of Methane-Oxygen Flames Through Complex Obstacles by Means of 3D Spectroscopy and High-Speed Filming	174
6.4	Conclusions	182
	References	183
7	Influence of Hydrocarbon Additives on the Velocity of Detonation Wave and Detonation Limits by the Example of the Reaction of Hydrogen Oxidation	187
7.1	Experimental	192
7.2	Discussion	193
	Appendix	200
	References	204
8	Influence of Metallic Pt on Hydrogen and Methane Combustion	207
8.1	Cellular Combustion and Delay Periods of Ignition of Near Stoichiometric H ₂ —Air Mixtures Over Pt Surface	207
8.2	The Features of Ignition of Hydrogen-Air Mixtures Over Pt at Atmospheric Pressure	215
8.2.1	Experimental	216
8.2.2	Discussion	216
8.3	Experimental Investigation into the Interaction of Chemical Processes on a Pt Wire and Turbulent Flows at Flame Penetration Through Obstacles in the Presence of Iron Nanopowder	222
8.3.1	Experimental	224
8.3.2	Discussion	225
8.4	Conclusions	229
	References	229



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Preface

The huge and growing number of publications every day in various fields of science related to combustion is increasingly contributing to the emergence of rather specialized scientists and often creates certain difficulties for the researcher to appraise the value of his findings. My books are aimed at consideration in general of modern problems of combustion science to allow a reader navigating freely this field of science.

In this book, the issues raised which have not been considered in my previous book “The Modes of Gaseous Combustion”. The book attempts to summarize the main advances in the mechanisms of combustion processes, which in the author’s opinion were not given due attention in contemporary literature. It focuses also on the analysis of kinetic mechanisms of gas combustion processes and experimental investigation into the interrelation of kinetics and gas dynamics in gas combustion based generally on the works of the author and original works of his co-authors. The book may be useful for undergraduate and postgraduate students and researchers in the area of experimental studies of gaseous combustion.

The analysis of experimental regularities of inhibition and promotion of non-thermal flame, as well as of transition of non-thermal mode of flame propagation to a chain-thermal one is carried out. It is performed by the example of thermal decomposition of NCl_3 in He in the presence of inhibitor NOCl , and promoter H_2 . The numerical modeling performed with the use of the detailed kinetic mechanism of NCl_3 decomposition with energy branching taken into account showed a good qualitative agreement with experimental data. It is shown that the occurrence of nonlinear reaction of chain branching in the kinetic mechanism reduces the time required for the development of thermal ignition and respectively increases the flammability of gas mixture.

It was established that both a one-dimensional problem and two-dimensional one on chain-thermal flame propagation in the process with nonlinear chain branching have at least, two solutions: the first corresponds to non-thermal, the second one—to the chain-thermal mode of flame propagation. Even despite the solution of the inverse kinetic problem on the non-thermal flame propagation in diluted mixtures of nitrogen trichloride accounting for the experimental data on the upper limit

of thermal ignition calls for further investigation, one can draw the following major conclusion from the results of the study. The process of thermal decomposition of NCl_3 with the exception for the unidentified reaction of termolecular chain termination can be considered as a model one along with the reaction of hydrogen oxidation. Numerical experiment on modeling of the oscillation modes of thermal ignition of nitrogen trichloride in the closed volume with the use of a one-dimensional system of the ordinary differential equations is performed. It is shown that the mechanism of reaction of NCl_3 decomposition proposed above is in good qualitative agreement with experimental data. It is established that the conditions sufficient to obtain oscillating solutions are the following:

- (a) accounting for adsorption–desorption of NCl_3 on reactor walls,
- (b) accounting for nonlinear chain termination $\text{Cl} + \text{Cl}_2 \text{}^3\Pi_{\text{ou}} \rightarrow \text{Cl} + \text{Cl}_2 \text{}^1\Sigma_{\text{g}}^-$,
- (c) accounting for energy chain branching.

Thus, accounting for the processes of desorption of NCl_3 from the reactor surface during oscillations and the change in a surface state leads to the occurrence of the oscillation modes in calculations, which are in qualitative agreement with experiments.

Promotion of NCl_3 decomposition with molecular hydrogen near the lower limit of thermal ignition P_1 as well as at the developing ignition under non-stationary conditions is revealed; it is shown both in the reduction of delay periods of ignition and in an increase of the rate of NCl_3 consumption with an increase in H_2 concentration. The emission spectrum of the $\text{H}_2 + \text{NCl}_3$ flame contains the intense bands of NCl ($b^1\Sigma^+ - X^3\Sigma^-$), $v = 1 - 0$, $v = 0 - 1$, and $v = 0 - 0$, where v is the vibrational quantum number and the bands of a hydrogen-free compound. The latter bands can be assigned to electronically excited NCl_2 radicals formed in the $\text{H} + \text{NCl}_3$ reaction. The calculations restrict the number of elementary reactions favoring promotion. The promotion effect in the system studied should be due to the side reaction of linear branching. The occurrence of the $\text{H} + \text{NCl}_3$ reaction via two pathways ($\text{NHCl} + 2\text{Cl}$ and $\text{NCl}_2 + \text{HCl}$) ensures the qualitative agreement between the experimental data and calculation.

It has been found that a time delay τ of self-ignition of dichlorosilane–chlorine mixtures occur in the presence of more than 4 % of propylene as inhibitor; the consumption of inhibitor leads to the ignition, in which an absorption spectrum of dichlorosilylene radicals is detected along with the emission of SiHCl ($A^1B_1 - X^1A_1$). The inhibiting effect is due to the fast reactions of propylene with silylenes as chain carriers. In the presence of both inhibitor and of more than 45 % inert additive (sulfur hexafluoride) the dependence of τ on the concentration of deactivator undergoes drastic change. Thus, deactivation processes have marked influence on the flammability. Experimental data are in agreement with calculations based on the generalized kinetic model of the branching chain process, including chain termination via both inhibitor and deactivator.

It is shown that non-thermal flame propagation is inherent both to monosilane and dichlorosilane oxidation. Thus, deactivating properties of an inert additive noticeably influence on the velocities of non-thermal flame propagation in the case of dichlorosilane oxidation. That may be the evidence of participation of excited particles in the nonlinear branching reaction.

An electron-vibration structure of the UV spectrum of a long-lived intermediate is detected during oxidation of SiH_4 and SiH_2Cl_2 . This product is common to both reactions and exhibits the same promoting effect on them. It is shown that the formation of that promoting compound in the course of a branched chain reaction provides non-thermal flame propagation in reacting mixtures outside of the thermal ignition region.

Chemiionization was revealed in the chlorination of dichlorosilane, the lower limit of the concentrations of charged particles was estimated as 10^7 charged units cm^{-3} . The detected relationship between chemiionization and phase formation in a low-temperature heterophaseous BCP, gives grounds to consider the chemical nature of a reaction zone of silanes oxidation over the region of flame propagation as weakly ionized plasma. It is shown that the necessity exists for reassessment of the role of ions in conventional chemical kinetics considering only neutral intermediates in low-temperature combustion. The use of the properties of the plasma in an external electric field has allowed developing an essentially new technique of low-temperature deposition. Evolution of thermal ignition and induced ignition of dichlorosilane–oxygen mixtures over the pressure range from 4 to 500 Torr at initial temperatures from 300 to 400 K was studied by means of framing Schlieren cinematography. It is established that the thermal ignition of dichlorosilane mixtures with oxygen originates at the reactor walls similar to BCP of hydrogen and hydrocarbon oxidation, which testifies to a crucial role of reactions involving adsorbed chain carriers. It is shown that Schlieren photography in parallel beams offers a means of controlling the process of SiO_2 formation in the form of aerosol during chain oxidation of SiH_2Cl_2 . A drastic decrease in the concentration of SiO_2 aerosol can be achieved either by exposing the mixture to a constant electric field or by adding SF_6 in small amounts. SF_6 is shown to inhibit SiH_2Cl_2 thermal ignition in oxygen. SF_6 molecules presumably take part in a competing reaction of chain termination involving also charged species.

The influence of a constant electric field on kinetic regularities of dichlorosilane oxidation near the lower limit of thermal ignition was established. The features of this influence on both the lower limit and the delay period of thermal ignition, as well as on the period and quantity of chemical oscillations are determined with the material and a surface state of the reactor, as well as by the reactions of the long-lived intermediate. The new critical phenomenon is revealed: a sharp decrease of integrated intensity of chemiluminescence at thermal ignition of $\text{DCS} + \text{O}_2$ mixes over CuSO_4 coating within a small interval of electric field strength.

It is shown that the flame emission in the region 400–600 nm in monosilane and dichlorosilane oxidation (initial pressures of 3–20 Torr; $T_0 = 300$ K) is caused by radical luminescence processes on the surface of aerosol ultra-disperse particles of SiO_2 formed during ignition. The generation of energy by the interaction of gas-phase

species with the SiO_2 surface at initial stages of the phase formation depends on the presence of both the intrinsic structural defects $=\text{Si}:$ and defects of Si^+ implanted into SiO_2 . The addition of SF_6 to the initial mixture results in the appearance of the emission bands due to the Si^+ defects in the radical luminescence spectrum. Electronically excited HO_2 radicals ($A^2A'-X^2A''$), OH 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 of 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 the species is reached behind the front of the 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 the developed ignition.

Molecules of H_2O_2 and H_2O are detected in gaseous phase in deuterium–oxygen flame by their near IR emission spectra in the reactor, which surface was previously treated with atomic hydrogen. It was shown that both the formation of these compounds and the observed decrease in the lower limit of spontaneous ignition of $\text{D}_2 + \text{O}_2$ mix under influence of adsorbed hydrogen atoms are caused by heterogeneous elementary reactions providing chain propagation. The initial stage is the reaction of adsorbed atomic hydrogen with O_2 from the gas phase.

The emission spectra of hydrogen–oxygen and hydrogen–air flames at 0.1–1 atm exhibit a system of bands between 852 and 880 nm, which are assigned to the H_2O_2 molecule vibrationally excited into the overtone region. This molecule results from the reaction $\text{HO}_2 + \text{O}_2$. The overtone region also contains bands at 670 and 846 nm, which are assigned to the vibrationally excited HO_2 radical. That radical is the product of the reaction between H and O_2 . The HO_2 radicals resulting from H_2 or D_2 oxidation in the presence of small amounts of propylene are initially in vibrationally excited states.

Combustible mixtures are shown to ignite in a static reactor with a tangential injection of gas at the temperatures, which are significantly lower than those reported in literature for reactors with central injection. This signifies that the temperature at the reactor center exceeds the reactor temperature and, according to the estimates, the difference can attain 150 K and even more. The effect observed is ascribed to the action of centripetal forces that inevitably arise in vortex flows and induce density and temperature stratification in the mixture: the hottest and most quiescent gas with poor heat exchange with surrounding cooler gas layers is concentrated at the reactor center. The pressure rise in the course of gas injection increases the temperature of the gas preheated virtually to the wall temperature by adiabatic compression, so that the central domain becomes hotter than the reactor wall. Convection induced by the centripetal forces hinders heat removal from the reacting mixture volume favoring thereby, its ignition. Therefore, the ignition of the combustible mix in the heated reactor in a swirling flow is unambiguously homogeneous. If the swirling flow is missing in the installation without a rotating gas flow (or another structure of the gas flows occurs) the ignition is heterogeneous,

i.e. the regimes of thermal ignition differ qualitatively. The regimes are not evidently determined with reaction kinetics, which remains the same; those are governed in fact with only gas dynamics. The experimental conditions considered when the certain estimations of the character of the flows in the installation must be performed to exclude the factors, which should hinder obtaining the results required. That estimation cannot be reduced to the comparison of characteristic times of homogeneous chemical and gas dynamic processes; heterogeneous reactions should also be taken into account. It is illustrated by the example of hydrogen oxidation over a Pt wire: in this case the characteristic time of gas dynamic process should be compared with the delay period of ignition, which is markedly larger than the characteristic time of an explosion.

The evidence is obtained for the occurrence of the ignition of diluted stoichiometric methane–oxygen mixes (total pressure up to 200 Torr) behind a single opening at the transition of the laminar flow to the turbulent one rather than after a delay period of ignition. The features of the flame front penetration through rectangular openings in comparison with circular ones with the use of both color speed cinematography and visualization of gas currents by the illumination of fine powder with a laser sheet are experimentally investigated. It is shown that the length of the “flame jump” after the opening in an obstacle is mostly determined by the time of occurrence of the transition from the laminar flow to the turbulent one rather than the time of an ignition delay period. The results are important both for 3D modeling and for the solution of explosion safety problems for volumes with complex geometry. It is experimentally shown that at the penetration of a flame through obstacles gas dynamic factors, for example, flame turbulization can determine the kinetics peculiarities of combustion, for instance a transition of low-temperature hydrocarbon combustion to the high-temperature mode.

The formalism of the one-dimensional detonation theory taking into account both thermal losses and the theory of branched chain processes was applied to hydrogen oxidation in the presence of hydrocarbon additive. It is shown that accounting for both reactions of termination of the active centers of combustion via molecules of hydrocarbon additive, and chain oxidation of hydrocarbon additive allows qualitative interpreting the main features of the process. They are both passing of detonation velocity through a maximum at an increase in the content of the additive in a lean mix and the existence of two detonation limits on the concentration of the additive.

A cellular combustion regime of 40 % H₂–air mixture in the presence of a Pt wire over the interval 270–350 °C was observed for the first time. It is shown that the regime is caused by the catalytic action of Pt containing particles formed by decomposition of volatile platinum oxide in the gas phase.

It is experimentally revealed that the emergence and participation of chemically active surface during gas combustion (by the example of H_2 combustion over the Pt surface) significantly complicates the understanding of the process due to the occurrence of a number of new governing parameters. These include the dependence of chemical activity of the catalyst on its chemical composition, temperature and conditions of mass transfer.

It is shown that under certain conditions Pt catalyst can suppress developing flame propagation of methane–oxygen mixes due to the high efficiency of the Pt surface coated with a Pt oxide layer in the reaction of chain termination. Therefore, kinetic factors could be the determining ones even under conditions of high turbulence.

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Chapter 2

Nonlinear Effects in Silanes Oxidation and Chlorination in Gaseous Phase: Collecting a Puzzle

Abstract It has been found that the time delay τ of thermal ignition of dichlorosilane—chlorine mixtures occur in the presence of more than 4 % of propylene; the consumption of inhibitor leads to ignition, in which absorption spectrum of dichlorosilylene radicals is detected along with the emission of SiHCl ($A^1B_1-X^1A_1$). The inhibiting effect is due to the fast reactions of propylene with silylenes as chain carriers. In the presence of both inhibitor and of more than 45 % inert additive (sulfur hexafluoride) the dependence of τ on the concentration of deactivator undergoes drastic change. Thus, deactivation processes have marked influence on the flammability. Experimental data are in agreement with calculations based on the generalized kinetic model of the branched-chain process including chain termination via both inhibitor and deactivator. It is shown that non-thermal flame propagation is inherent both to monosilane and dichlorosilane oxidation. Deactivating properties of an inert additive influence on the velocities of non-thermal flame propagation in the case of dichlorosilane oxidation. That may be the evidence of participation of excited particles in nonlinear branching reaction. An electron-vibration structure of the UV spectrum of a long-lived intermediate is detected during oxidation of SiH₄ and SiH₂Cl₂. This product is common to both reactions and exhibits the same promoting effect on them. It is shown that the formation of this promoting compound in the course of a branched chain reaction provides non-thermal flame propagation in reacting mixtures outside of the thermal ignition region.

Keywords Ignition delay · Thermal ignition · Monosilane · Dichlorosilane · Chlorine · Oxygen · Deactivation · Energy branching · Long-lived intermediate · Electron-vibration spectra

The application of SiO₂ thin films in integrated circuit processing [1] has evoked an increasing interest to the oxidation of silanes. It is also caused by the fact that the silicon technology of integrated circuit production, at least in the next decade will not have any alternatives. It is due to the fact, that the production of other semiconductor materials (A₄B₄, A₂B₆, A₃B₅ and semiconductor heterostructures) with

higher mobility of electrons has not reached the acceptable price level. The synthesis of nanosized particles based on the branching chain (BC) processes involving inorganic hydrides has also attracted considerable interest [2]. In addition, reacting with F_2 and Cl_2 , silanes form vibrationally excited HF and HCl being of interest for infrared chemical lasers applications [2, 3]. The branched chain nature of monosilane and dichlorosilane (DCS) oxidation has been established [4, 5] but the kinetic mechanisms have not been yet assigned. To control these processes, the kinetics of the oxidation and chlorination of monosilane and its chlorine derivatives by a branched-chain mechanism [6] should be investigated in more detail.

Below the main investigations on the establishment of the mechanism of dichlorosilane chlorination and silanes oxidation are presented. Seemingly, the mechanism of silanes oxidation should be rather similar to hydrocarbon oxidation; however, it is more complicated, because it shows a positive chain interaction along with energy branching (see the following).

Vapor pressure of monosilane SiH_4 is 781 Torr at $-112\text{ }^\circ C$ [7], therefore, silanes are much more flammable than appropriate hydrocarbons; monosilane could be ignited in air at $-120\text{ }^\circ C$, it is very explosive and extremely poisonous; dichlorosilane is a liquid at room temperature; it is less flammable.

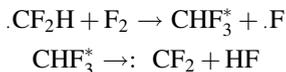
In addition, silanes oxidation is a heterophaseous process exhibiting a marked feedback between the branched chain nature of gas reaction and phase formation [8]; silanes chlorination is a homogeneous process.

The following paragraph is aimed at the establishment of the main features of dichlorosilane chlorination.

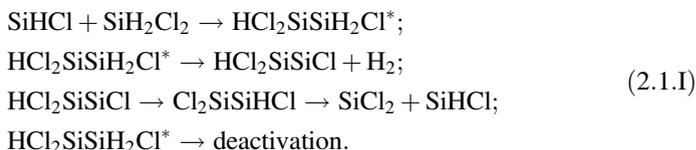
2.1 The Investigation into Dichlorosilane Chlorination in the Presence of Propylene as Inhibitor and Kr as Deactivator at Low Pressures and 293 K

There is a body of compelling evidence that the chlorination of inorganic hydrides: monosilane SiH_4 [9], dichlorosilane (SiH_2Cl_2 , DCS) [10], phosphine PH_3 [11], monogermane GeH_4 [12], some hydrocarbons [13], and thermal decomposition of NCl_3 (see the previous chapter) show special features of branched-chain processes (BCP). The reactions show both the existence of pressure limits of non-thermal flame propagation depending on the state of contacting surface and the sensitivity of kinetics to small additives of promoters and inhibitors. It is evident, that energy branching, namely the participation of excited intermediates in chain branching, plays an important role in chain chlorination, because the material branching like $\cdot H + O_2 \rightarrow \cdot OH + \cdot O$ is evidently ruled out. It is easy to verify that by replacing oxygen with chlorine in the above reaction. However, energy branching in gaseous phase being due to decomposition in atoms or deactivation of electronically excited particles Cl_2 ($^3\Pi_{ou}^+$) formed in chain branching is established experimentally for only NCl_3 decomposition [14]. Energy branching in the reactions of vibrationally

excited particles was detected in fluorination of hydrogen and fluorinated hydrocarbons [15]. Actually, fluorination reactions differ from chlorination ones in that they are more exothermic. In addition, HF has higher first vibrational level than HCl. In fluorination energy branching occurs, if the energy released in one of the elementary steps is enough for monomolecular decomposition of the product of this step, e.g. for $\text{CH}_2\text{F}_2 + \text{F}_2$ reaction the following branching process [15] is suggested:

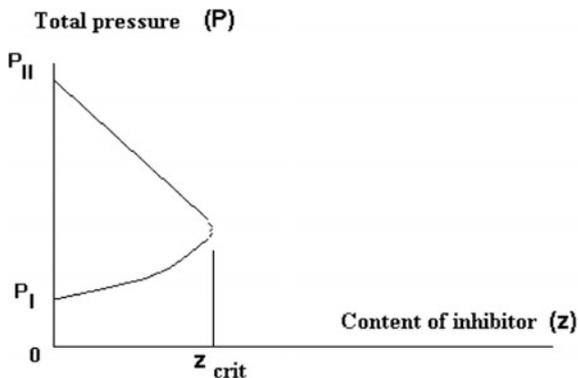


Related sequences of reactions were proposed for 1,1-difluoroethane [13] and monosilane [9] chlorination. In these processes, energy branching occurs involving carbenes and silylenes correspondingly. Ab initio calculations were used to construct a mechanism for the pyrolysis of chlorinated silanes [10]. 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-catalyzed cycle, including energy branching (the energetics of this cycle is shown in Fig. 2.1 in [16]):



It is known that olefins react very rapidly with silylenes [17] (the rate constants vary over a range $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for SiH_2 to $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for SiHCl or SiCl_2). Since SiHCl ($A^1B_1-X^1A_1$) was detected in DCS chlorination [10] the inhibiting action of olefins (e.g. propylene C_3H_6) onto DCS chlorination will indicate that reactions of silylenes as chain carriers are of considerable importance in the BCP. If

Fig. 2.1 The dependence of thermal ignition limits of the combustible mixture on the content of an inhibitor (z)



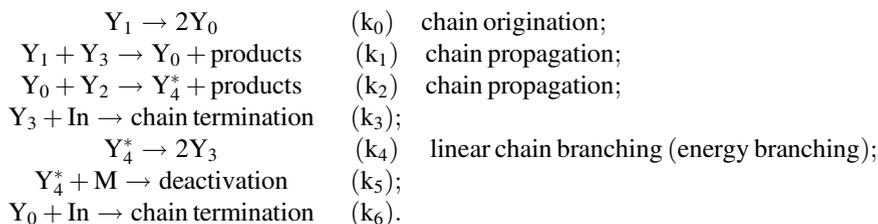
the inhibition takes place, the uniform thermal ignition over the reactor volume can be studied in the presence of C_3H_6 , because thermal ignition of pure DCS and Cl_2 at 293 K occurs immediately after mixing (induction period τ_i makes up less than 300 ms) [10].

This paragraph is aimed to an 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 inhibitor and chemically inert sulfur hexafluoride (SF_6) as deactivator.

In the present paragraph, the method of inhibitor delay was used [18, 19]. The basis for this method is an expansion of thermal ignition region in a time of consumption of an inhibitor. This experimental method is rather simple and requires only a vacuum installation along with a stopwatch. The dependence of thermal ignition limits on the fraction of inhibitor is shown in Fig. 2.1.

As is seen in the Figure, combustible mixture enters the thermal ignition area when the concentration of the inhibitor in it attains a certain critical value z_{crit} . The time τ_C the mixture takes to enter the thermal ignition area and then to ignite is combined from the time τ required to reach the boundary of the thermal ignition area (inhibitor delay) and ignition delay τ_i that is $\tau_C = \tau + \tau_i$. Calculations performed in this paragraph hold for $\tau \gg \tau_i$, or $\tau_C \cong \tau$. In case of participation of excited intermediates in chain branching, the addition of effective deactivator will provide an additional pathway of chain termination and have a certain effect on τ .

Let us demonstrate that the dependence of τ on initial conditions in the presence of both inhibitor and deactivator differs markedly from that in the presence of a single inhibitor. The mechanism of DCS chlorination is unknown; therefore, the generalized kinetic model of BCP with energy branching in the presence of both inhibitor (In) and deactivator (M) is qualitatively considered. Obviously, the model of BCP must include chain origination, propagation, and (energy) branching and termination steps.



Here Y_1 and Y_2 are initial reagents, for instance fuel and oxidizer, Y_0 and Y_3 —active centers, Y_4^* —excited particles that cause branching via monomolecular decomposition. Since the lower limit of the DCS + Cl_2 reaction is markedly low [10] the heterogeneous chain termination is not taken into account [18]. To simplify the following treatment and make it more illustrative, the probable occurrence of material branching along with energy branching is ignored. The amounts of initial reagents consumed as well as intermediates formed during inhibitor delay may be

considered as negligibly small [18, 19]. 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 above we obtain for stationary concentrations of Y_0, Y_3, Y_4 :

$$2k_0/(k_1[B]) + x - k_2yA/k_1 - k_6yz/k_1 = 0 \quad (2.1.1)$$

$$-x + 2k_4u/(k_1[B]) - k_3xz/k_1 = 0 \quad (2.1.2)$$

$$k_2y[A]/k_1 - k_4u/(k_1[B]) - k_5up/k_1 = 0 \quad (2.1.3)$$

Equation (2.1.3) can be solved for u . Substituting this value in Eq. (2.1.2) and inserting $h = k_4/(k_4 + k_5 p[B])$ we obtain:

$$2k_0/(k_1[B]) - x + 2k_2hy[A]/k_1 - k_3xz/k_1 = 0 \quad (2.1.4)$$

It is evident that parameter h changes from 1 to 0 with an increase in dimensionless amount of deactivator p . As is seen from Eq. (2.1.4), if in certain experiment p amounts up to the partial pressure such that h takes the value 0.5, chain branching is completely terminated, therefore at $h > 0.5$ inhibitor delays are not liable to exist. Solving Eqs. (2.1.1) and (2.1.4) for x and y we derive:

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

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

If the denominator of these latter equations equals to 0, then x and y increase infinitely, i.e. thermal ignition occurs. Therefore z_{crit} is determined by the equation: $z_{crit} = k_1(50h k_2 + 25k_2 + 2k_6)/(k_3(25k_2 + 2k_6))$. We divide the equation $d[In]/dt = -k_6Y_0 [In] - k_3Y_3 [In]$ that determines the rate of consumption of inhibitor by $[B]$ [10]:

$$dz/dt = -[B](k_6yz + k_3xz), \quad (2.1.5)$$

Let us substitute x and y into Eq. (2.1.5) and integrate Eq. (2.1.5) numerically with respect to z between the limits z and z_{crit} and with respect to t between 0 and τ for the purpose of obtaining the dependence of τ on z and h . The results of numerical calculation are shown in Fig. 2.2a. The values of the rate constants are chosen to be close to those for silylenes [17] being considered as chain carriers in the process.

As is seen, the linear dependence of τ on a ratio of inhibitor to initial reagent can be expected, the shape of this dependence is significantly determined by the value of k_0 . It is seen also that at $h < 0.5$ inhibitor delays are missing (see curve 1 Fig. 2.2a). The result obtained was tested by numerical solution of non-stationary system of the corresponding equations for the kinetic mechanism above using forth

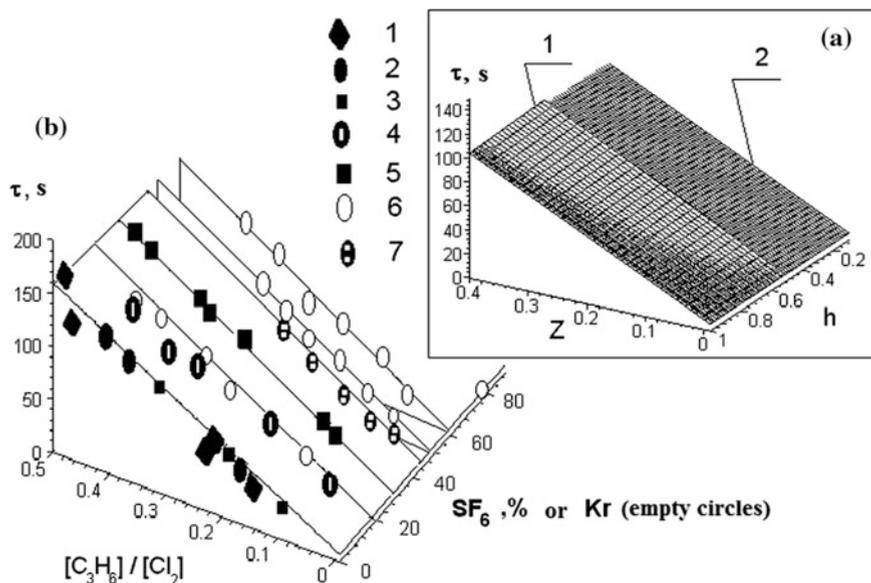


Fig. 2.2 a The calculated dependence of the value of inhibitor delay τ on the content of inhibitor z and deactivator h . The values of parameters are the following: $B = 5 \cdot 10^{16} \text{ cm}^{-3}$, $k_0 = 2 \cdot 10^{-3} \text{ s}^{-1}$, $k_1 = 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $k_2 = 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, $k_3 = 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $k_6 = 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Curve 1 energy branching occurs, curve 2 $h = 1$: energy branching does not occur; **b** experimental dependencies of inhibitor delay τ on the ratio between inhibitor and Cl_2 and concentration of SF_6 (full circles) and Kr (empty circles) Reactor I. 1 1.5 Torr Cl_2 + mixture of DCS + 8 % C_3H_6 ; 2 2.1 Torr Cl_2 + mixture of DCS + 8 % C_3H_6 ; 3 0.9 Torr Cl_2 + mixture of DCS + 8 % C_3H_6 ; 4 1.5 Torr Cl_2 + mixture of DCS + 6.4 % C_3H_6 + 20 % SF_6 ; 5 1.5 Torr Cl_2 + mixture of DCS + 5.4 % C_3H_6 + 32 % SF_6 ; 6 1.5 Torr Cl_2 + mixture of DCS + 8 % C_3H_6 + 20 %, 50 %, 60 % Kr; 7 1.5 Torr Cl_2 + mixture of DCS + 80 % Kr; 7 1.5 Torr Cl_2 + mixture of DCS + 4.5 % C_3H_6 + 45 % SF_6

order Runge-Kutta method (for $Y_1 = 1$ and $Y_2 = 0.5$). It was shown that at $h < 0.5$ inhibitor delays are also missing: the system does not tend to ignite at all. Therefore, calculations based on the qualitative analysis of the generalized model of BCP predict a drastic change in the dependence of τ in BCP in the presence of both inhibitor and deactivator on an amount of deactivator.

The experiments were carried out under static conditions at 293 K and total pressures in the range of 2–15 Torr. Two quartz cylindrical reactors 15 cm long, 3 cm and 12 cm in diameter (denoted as the reactor I and reactor II correspondingly) had inlets for gas evacuation as well as optical windows. Chlorine was initially allowed to bleed into the reactor up to necessary pressure (0.5–3 Torr). Then the mixture containing DCS + C_3H_6 + SF_6 or Kr (if necessary) was admitted up to total pressure over the interval 3–15 Torr. 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 SF₆. The mixtures of DCS + 3–8 % C₃H₆ + 20–80 % SF₆ or 20–80 % Kr as well as the same mixtures without C₃H₆ were prepared prior to the experiment. The concentration of Cl₂ was recorded by absorption at 300 nm by means of a monochromator VM-25 (Germany), a photomultiplier sensitive over the range of 200–600 nm and Hg–He lamp (as a light source with the continual spectra) using synchronous detection. In these measurements, the Hg–He lamp was equipped with 3.3 kHz chopper. The output signal was recorded by means of either memory oscilloscope or X–Y recorder Endim 620.02. Emission and absorption spectra of thermal ignition were recorded either with the photomultiplier or with an optical spectrum analyzer OSA-500 (Germany) with the resolution 0.2 nm per channel. The required number of scans (1 scan = 500 channels per 32 ms) was stored in computer memory. The change in total pressure P during thermal ignition in reactor II was measured by a mechanotron. The output signal was recorded by means of a memory oscilloscope.

It was shown, that thermal ignition occurs immediately after mixing of pure DCS and Cl₂ in accordance with [10]. However, additives of C₃H₆ > 4 % cause inhibitor delays more than 5 s pointing to the fact that C₃H₆ acts as an inhibitor, i.e. in the present work $\tau \gg \tau_i$. By this means, the reagents may be considered as well mixed. Therefore, in this work the uniform thermal ignition of DCS and Cl₂ in the presence of C₃H₆ over the reactor volume was studied. Moreover, the inhibiting action of C₃H₆ suggests that linear chain branching gives rise to short τ_i rather than chain initiation. The only known very rapid step silylene + C₃H₆ → chain termination (10^{-10} – 10^{-11} cm³ s⁻¹, see above) is responsible for this inhibiting action.

An example of simultaneous recording of chemiluminescence at 470 nm and absorption at 300 nm is shown in Fig. 2.3. As is seen from the absorption curve, two intermediates form in thermal ignition. The long-lived one has a non-structured spectrum over an interval 270–480 nm; it is observed only at $[\text{DCS}]/[\text{Cl}_2] \leq 1$. No evidence in the literature has been found of the assignment of this spectrum. The spectrum of the short-lived one is shown in Fig. 2.3 as well as the spectrum of emission. As is shown in Fig. 2.3, the emission bands observed are due to SiHCl ($A^1B_1-X^1A_1$) [20], the absorption ones—to SiCl₂ [21]. The silylenes detected are chain carriers of the BCP because C₃H₆, which reacts rapidly with silylenes, has marked inhibiting effect on this BCP.

It was shown that τ values increase with an increase in the amount of DCS + C₃H₆ added at constant [Cl₂] i.e. τ increases directly with an increase in the ratio $[\text{C}_3\text{H}_6]/[\text{DCS}]$, therewith τ does not depend on total pressure but only on the ratio $([\text{DCS}] + [\text{C}_3\text{H}_6])/[\text{Cl}_2]$. This dependence is almost linear. Since in each set of experiments $[\text{DCS}]/[\text{C}_3\text{H}_6] = \text{const}$ (the mixtures were prepared prior to experiment, see above) then τ depends only on the ratio between inhibitor and Cl₂ (Fig. 2.2b). The data shown in Fig. 2.2b was obtained from the dependencies of [Cl₂] on time in the system Cl₂ + DCS + C₃H₆ + SF₆ (or Kr). Typical experimental ones are shown in Fig. 2.4.

However, it is seen in Fig. 2.4, that τ in the presence of 8 % C₃H₆ and 50 % SF₆ τ makes up >30 min, whereas τ in the presence of 8 % C₃H₆ and 50 % Kr does not exceed 110 s. As one would expect, deactivating action of Kr, if any, is markedly

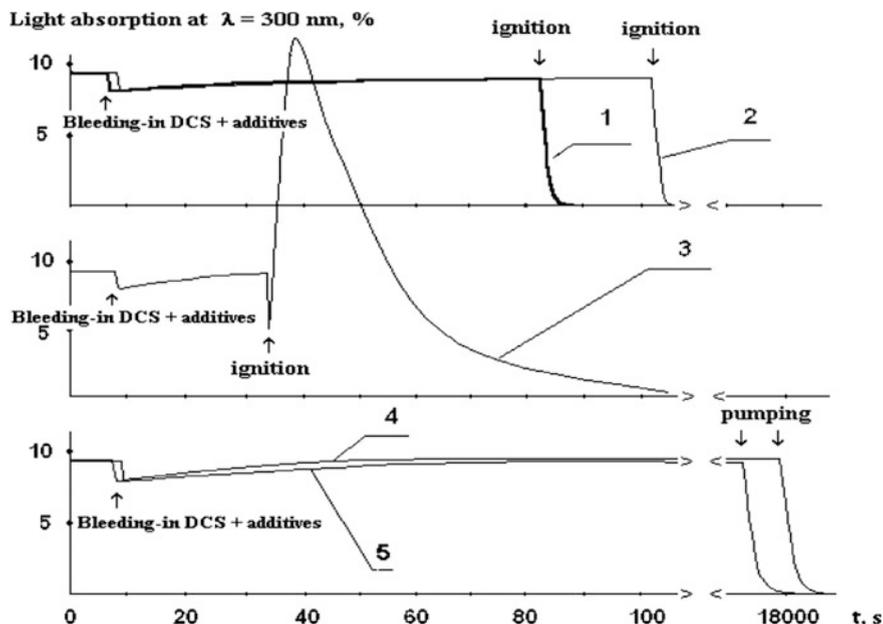


Fig. 2.4 Experimental dependencies of Cl_2 concentration on time: 1 1.5 Torr Cl_2 + 4.2 Torr (DCS + 8 % C_3H_6); 2 1 Torr H_2 + 1.5 Torr Cl_2 + 4.2 Torr (DCS + 8 % C_3H_6); 3 1.5 Torr Cl_2 + 1.5 Torr (DCS + 8 % C_3H_6 + 50 % Kr); 4 1.5 Torr Cl_2 + 1.5 Torr (DCS + 8 % C_3H_6 + 5 % SF_6); 5 1.5 Torr Cl_2 + 1.35 Torr (DCS + 80 % SF_6)

may be indirect evidence that SiH_2 radicals occur in DCS chlorination. Then heat emission can take place in the fast reactions (rate constant of the reaction $\text{SiH}_2 + \text{Cl}_2$ is $1.4 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [17]):



Note that the energy released in (2.1.II) is enough to obtain excited SiHCl (A^1B_1). SiH_2 can result from the steps much as considered in [16]: $\text{SiCl}_2 + \text{SiH}_2\text{Cl}_2 \rightarrow \text{Cl}_3\text{SiSiH}_2\text{Cl}^* \rightarrow \text{SiH}_2 + \text{SiCl}_4$.

The set of given reactions (2.1.I–2.1.III) represents a certain of possible steps of DCS chlorination including silylenes as chain carriers and formation of electronically excited SiHCl as well as energy branching. This suggestion is still to be refined by an establishment of the chemical composition of reaction products; especially of interest is the detection of H_2 formation.

The brief summary is the following. It has been found that time delay τ of thermal ignition of dichlorosilane—chlorine mixtures occur in the presence of more than 4 % of propylene as inhibitor; the consumption of inhibitor leads to ignition in which absorption spectrum of dichlorosilylene radicals is detected along with the

emission of SiHCl ($A^1B_1-X^1A_1$). The inhibiting effect is due to the fast reactions of propylene with silylenes as chain carriers. In the presence of both inhibitor and >45 % inert additive (sulfur hexafluoride) the dependence of τ on the concentration of deactivator undergoes drastic change. Thus, deactivation processes have marked influence on the flammability. Experimental data is in agreement with calculations based on the generalized kinetic model of the branching-chain process, including chain termination via both inhibitor and deactivator.

2.2 Non-thermal Flame Propagation in Monosilane and Dichlorosilane Oxidation

We remind the reader that non-thermal flame propagation considered in Chap. 1 is one of the most interesting phenomena in chemical kinetics and combustion. This kind of flame propagation was predicted by Zeldovich together with Frank-Kamenetskii [24] and shortly after it was observed experimentally by Voronkov and Semenov in the reacting system of carbon disulfide (CS_2) and air [25]. The phenomenon is the following. In certain conditions, even if the combustible gas is outside the region of thermal ignition, a stationary and almost isothermal flame front runs through the reaction mixture after initiation with an external source. The temperature in the front of the flame remains lower than that of ignition under a given pressure, so that this flame propagation is not caused by heat release and heat transfer. For a long time the oxidation of CS_2 was the only known system that exhibited such a kind of flame propagation. So this combustion mode was regarded as a quite exotic one, although it was considered as a very interesting phenomenon. However, a number of other combustible gas mixtures are known at the present, in which this kind of flame propagation occurs [6, 26]. The phenomenon is used for elucidation of reaction mechanisms [e.g. 26–29] and production of dielectric and protective layers as a version of chemical vapor deposition (CVD) [30]. The non-thermal mode of flame propagation is observed in combustion processes occurring by branching chain mechanism and is caused by a special kind of chain branching reaction.

The data illustrating the lower and upper limits of non-thermal propagation of the flame of silane (SiH_4) and oxygen is presented in Fig. 2.5 [27]. It is seen that these limits form a peninsula like that of thermal ignition (Fig. 2.6). As is suggested in [31] there are enough evidence to claim that the following nonlinear reaction occurs [27, 32, 33]:



which competes with the reaction $\text{HO}_2 \rightarrow$ chain termination on the wall. Though the number of free valences does not increase immediately in the step (2.2.1), however, the less active radical HO_2 leading mainly to chain termination is

Fig. 2.5 Dependence of the velocities of flame propagation in the mixture 1.1 % SiH₄ + 13.4 % O₂ + 85.5 % He on the initial pressure at temperatures, K: (1) 330, (2) 338, (3) 345, (4) 359, (5) 374, (6) 397 [27]

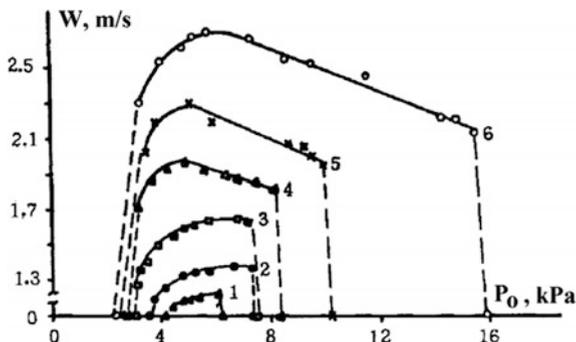
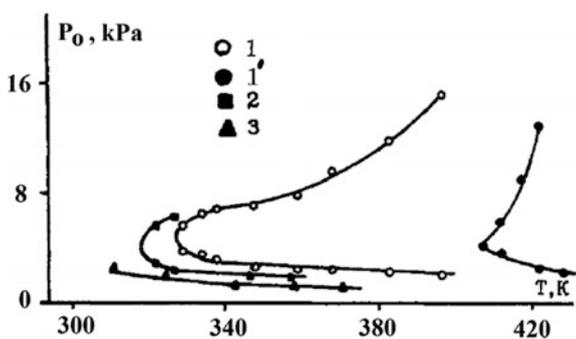


Fig. 2.6 Temperature dependence of the lower and upper limits of flame propagation (1, 2, 3) and thermal ignition (1') for the mixtures: (1 and 1') 1.1 % SiH₄ + 13.4 % O₂ + 85.5 % He; (2) 1.6 % SiH₄ + 16.5 % O₂ + 81.9 % He; and (3) 2.1 % SiH₄ + 17.0 % O₂ + 80.9 % He [27]



substituted because [9] of fast reaction (2.2.2) by very active OH radical, which actively enters into the reaction of chain propagation:



SiH₃ radicals easily react with molecular oxygen and lead to chain branching. Thus, the nonlinear step (2.2.1) finally provides chain branching. As is suggested in [31], high flammability of monosilane in the air is caused in a great extent by the nonlinear branching, occurring together with the linear one. As is seen from Fig. 2.6, the peninsula of non-thermal flame propagation is wider than that of thermal ignition in agreement with the theory [25, 29].

As is known, there is experimental evidence for the fact that the excited particles take part in the reactions of branching in the course of monosilane oxidation. An indirect argument for it is the increase of the lower limit of thermal ignition of monosilane in the presence of chemically inert additives N₂ or CO₂ [34]. As the specified gases have the absorption frequencies close to the first oscillatory quantum of SiH (2250 cm⁻¹ [35]), it is possible to expect the transfer of vibrational excitation from hypothetical particles containing Si-H bonds to molecules of inert additives at the expense of a quasi-resonant V-V energy exchange and respectively the reduction of the rate of chain branching.

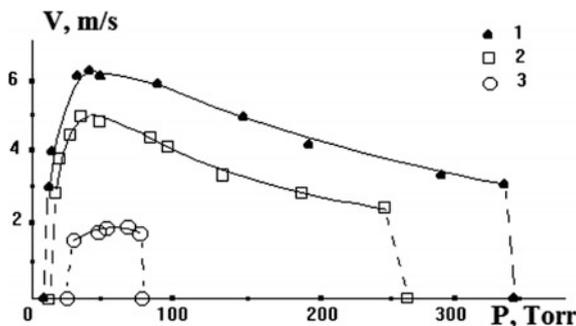
In connection with above mentioned, it is of interest to establish the features of influence of inert additives on the regularities of non-thermal flame propagation in dichlorosilane oxidation reaction. The influence of inert gas on the lower limit of the flame propagation will serve as unambiguous proof of participation of excited particles in non-linear branching; the influence on the upper limit will be the proof that the specified additive is either a deactivator or a rather effective third particle in the reaction of termolecular termination.

The experiments were performed in static conditions. Flame propagation was studied in a temperature-controlled quartz tube 40 mm in diameter and 1000 mm length. The heating of the pipe was carried out by means of a bifilar furnace; the temperature was determined by the compensating sensor. The tube was supplied with vacuum inputs for bleeding-in previously prepared gaseous mix and electric contacts for a thermocouple. Initiation of flame propagation in gas mixture was carried out by fast heating of a small additional furnace placed on the butt-end of the reactor.

Flame propagation in the gas mixture was detected by use of a multichannel light guide and a photomultiplier through optical windows located at a 20 cm distance from each other. The signal from the photomultiplier was transmitted to a memory of an oscilloscope. Pressure limits of flame propagation were determined similarly to the procedure described in Chap. 1 as the mean of two pressures at one of which flame propagates over the whole reactor; at another pressure only ignition in an initiation zone is observed.

By measurement of temperature by means of the thin 30 μm thermocouple placed in the reactor, it was shown that the warming up over the pressure interval does not exceed 15° , therefore, flame propagation has non-thermal character. Along with the lower pressure limit, we detected also the upper limit P_{II} of the flame propagation (Fig. 2.7). The similar experimental dependence of the flame velocity V on total pressure P is measured also in [36] (2.7 % of SiH_2Cl_2 in O_2) however, on the V - P dependence as pressure rises up to 450 Torr P_{II} is not detected; although, relying on the data from [36] it is impossible to judge the absence of P_{II} definitely. The occurrence of P_{II} as is known [22] is not an unambiguous indicator of non-thermal character of the flame propagation. In this regard it should be noted that the area of flame propagation in DCS- O_2 mixtures corresponds to lower

Fig. 2.7 Dependencies of the velocity of the flame propagation on total pressure in lean mixes of dichlorosilane with oxygen. filled circles $\text{SiH}_2\text{Cl}_2 = 2\%$; $T = 140^\circ\text{C}$; 98 % O_2 squares — $\text{SiH}_2\text{Cl}_2 = 3\%$; $T = 100^\circ\text{C}$; 97 % O_2 empty circles — $\text{SiH}_2\text{Cl}_2 = 3\%$; $T = 100^\circ\text{C}$; 48.5 % $\text{O}_2 + 48.5\%$ N_2



pressures and temperatures, than the area of thermal ignition for the same concentration of SiH_2Cl_2 in O_2 [37].

In the following series of experiments, the influence of N_2 inert additives on velocities and limits of flame propagation was studied. To do this, the mixes were prepared in such a way that (at $[\text{SiH}_2\text{Cl}_2] = \text{const}$) the 50 % fraction of oxygen was replaced by nitrogen. The velocity of flame propagation was measured at $T = \text{const}$ over the pressure interval of the occurrence of non-thermal flame. We will note that near the lower limit of flame propagation, the termination of active centers has heterogeneous character and a contribution of termolecular termination step is small as one can easily estimate.

As is seen in Fig. 2.7 the nature of the inert additive strongly influences both on flame velocity at pressure values over 30 Torr and on P_{II} , and noticeably influences on the lower limit P_{I} of the flame propagation. The fact of the influence of N_2 on the lower limit of non-thermal flame propagation means that deactivating N_2 properties at the lower limit of flame propagation are significant. In so doing, the influence of the nature of an additive on the non-thermal flame velocity in the range of 30 Torr— P_{II} indicates that N_2 and O_2 have various efficiency in the reaction of termolecular termination. Thus, O_2 as the third body shows significantly lower efficiency in reaction of termolecular termination, than N_2 . We will note that at thermal flame propagation P_{II} is missing.

Summarizing briefly, we conclude that non-thermal flame propagation is inherent both to monosilane and dichlorosilane oxidation. As this takes place, deactivating properties of an inert additive markedly influence on the values of the velocities of non-thermal flame propagation in the case of dichlorosilane oxidation. That may be the evidence of participation of excited particles in the nonlinear branching reaction.

As it was shown in Chap. 1 (Sect. 1.1), the intermediate providing a positive chain interaction in a quadratic reaction of branching should be a long-lifetime species. The following paragraph is aimed at the attempt of the detection of the long-lived intermediate in the BCP of monosilane and dichlorosilane oxidation in the reaction of non-linear branching.

2.3 A Long-Lived Intermediate in the Oxidation of Monosilane and Dichlorosilane

The kinetic features of the oxidation of SiH_2Cl_2 and SiH_4 revealed earlier are indicative of the formation of long-lived (with a lifetime of ~ 300 s) intermediate species promoting the thermal ignition of mixtures of these hydrides with oxygen [10, 38]. The results obtained suggest that these regularities can be used to obtain oscillating regimes of combustion. These regularities were observed in experiments on thermal ignition under the conditions of two-step admission of the combustible mixture (~ 10 % fuel in oxygen, 373 K) into the reactor [38].

Experiments were carried out as follows. First, the combustible mixture was admitted into the reactor at desired pressure and the process of thermal ignition was observed (under these conditions, the fuel completely burned out). Then, after a selected time interval (10–300 s), the second portion of the combustible mixture was introduced into the reactor and the thermal ignition limit for each time interval between the injections was measured. As the time delay between the first and second injections was shortened, the thermal ignition limit upon the second injection sharply decreased. When the first portion of the combustible mixture was replaced by an inert gas, this effect was not observed. Attempts to initiate the reaction with a glow discharge between the first and second injections also failed. Thermal ignition after the second injection was observed only after the ignition, which was previously initiated by a glow discharge at room temperature. These observations are indicative of the formation of a long-lived compound promoting combustion and expanding the thermal ignition limits for these combustible mixtures [39].

The expansion of the thermal ignition limits of the above reactions under the influence of a promoter suggests the existence of a nonlinear chain-branching process in the overall reaction mechanism [29]. This process is responsible for the propagation of non-thermal flames through the diffusion of active species in the initial mixture. Indeed, the propagation of non-thermal flame during the oxidation of monosilane is a well-known experimental fact [6]. Experimental data on the propagation of non-thermal flames during dichlorosilane oxidation was presented in the previous paragraph.

Until now, the lifetimes of active species participating in the reactions of non-linear chain branching were assumed commensurate with those of free atoms and radicals [e.g. 29, 40]. Indeed, active intermediate species were identified in some reactions: atoms and radicals NCl_2 , CS , O with short lifetimes. However, the experimental data described above, suggest that, in the oxidation of silanes, the lifetimes of intermediate species responsible for the observed features are much longer than the ignition times; the lifetimes are several orders of magnitude longer than those for atoms and radicals in combustion processes. Therefore, we believe that the ignition of mixtures of SiH_4 and SiH_2Cl_2 with oxygen involves a rather stable intermediate species whose reactions with free atoms and radicals lead to chain branching. Then, it is reasonable to expect the expansion of ignition limits and the effect of non-thermal flame propagation with participation of that intermediate species.

It has been found that the UV absorption spectrum of the intermediate species formed in the course of silane oxidation is localized within 190–300 nm with a maximum at 260 nm [38]. The main goal of this paragraph is to record the vibrational structure of the UV absorption spectrum of that species during the oxidation of SiH_4 and SiH_2Cl_2 . These results will be useful in clarifying whether the intermediate species is the same for the oxidation reactions under study and whether it is possible to observe a non-thermal regime of flame propagation for mixtures that contain a long-lived promoter but whose composition is outside of the thermal ignition region.

2.4 Experimental

A vacuum installation described in [10] was used. The UV absorption of intermediate reaction products was studied in a quartz vessel (170 cm long and with an inner diameter of 0.9 cm). The vessel was equipped with quartz windows on the butt-ends, electrical contacts, and gas valves. The ignition of the mixture was initiated by heating a nichrome spiral ($t \sim 0.3$ s) placed near one of the butt-ends. The emission of a mercury-hydrogen lamp with a continuous spectrum in the UV region passed through a collimator and the reactor and was focused by a condenser on the inlet slit of an OSA-500 optical spectrum analyzer (Germany). The resolution of the optical system was ~ 0.4 nm for each channel. The spectrum analyzer permits signal accumulation, with one accumulation run corresponding to 500 spectrum intervals recorded during 32 ms. The spectra were stored in separate files. It was shown earlier [41, 42] that, in the presence of sulfur hexafluoride (10–40 % of the fuel content), the amount of SiO_2 aerosol formed during ignition of the mixtures of monosilane and dichlorosilane with oxygen significantly decreases. We performed the oxidation reaction in the presence of SF_6 additives to avoid light scattering on aerosol particles and relevant undesirable effects.

The reactor was evacuated to a pressure of 10^{-3} Torr with a fore pump and a diffusion pump. The residual pressure was measured with a thermocouple vacuum gauge. The dichlorosilane-oxygen mixture was admitted into a buffer vessel and then into the reactor. The pressure was controlled by a gas-discharge pressure gauge. The combustible mixture was prepared by the admission of dichlorosilane to oxygen through a narrow capillary. Before the experiments, the reactor was washed with a 10 % HF solution. Chemically pure oxygen, silane, SF_6 , and 98 % pure dichlorosilane were used [10].

2.5 Discussion

UV absorption spectra of the long-lived intermediate product recorded during the ignition of mixtures of DCS and SiH_4 with O_2 and SF_6 additives using the above procedure are presented in Fig. 2.8. The spectra show a well-resolved structure, indicating that the absorbance in the UV range is not associated with light scattering by aerosol. As is seen, the spectra for the oxidation of SiH_4 and DCS are identical. This fact suggests that the intermediate product is common to both oxidation reactions. The characteristic lifetime of this compound ($t_{\text{pr}} \sim 90$ s) was estimated by processing kinetic curves during thermal ignition, assuming first-order kinetics for the time interval covered in [10] (see below) (Fig. 2.9, curves 1 and 2). This characteristic time is much longer than that of aerosol consumption (Fig. 2.9, curve 4). We did not manage to identify the spectrum observed with any literature data. We believe that this product is a long-lived compound capable of polymerization, such as HO-SiH=O , $\text{H}_2\text{Si=O}$, or a peroxide, containing silyl or siloxane fragments.

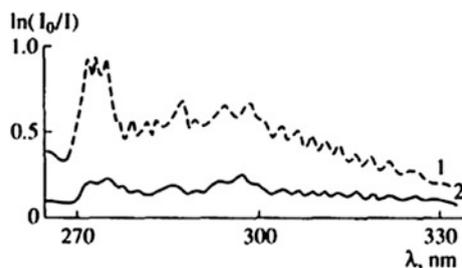


Fig. 2.8 UV absorption spectrum of the long-lived intermediate compound during the ignition of (1) 10 % SiH_4 in O_2 in the presence of 10 % SF_6 and (2) 20 % DCS in O_2 in the presence of 20 % SF_6 . The spectra were recorded in 15 s after ignition: five accumulations. $P = 5$ Torr, $T = 293$ K

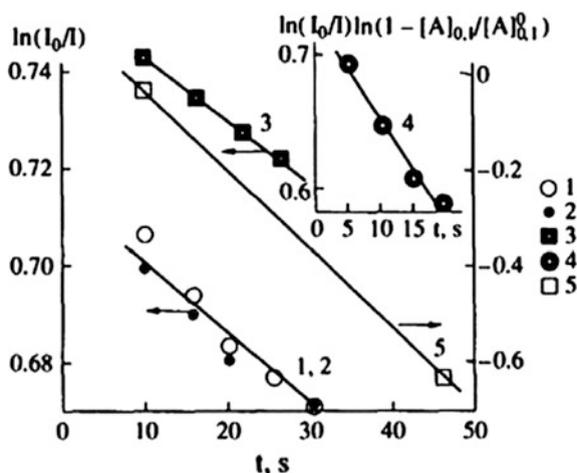
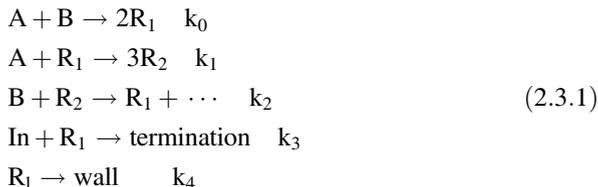


Fig. 2.9 Concentration profiles of the intermediate product (straight lines 1–3, and 5) and aerosol (4) in the reactor measured at (1) 272, (2) 292, (3) 312, and (4) 235 nm [38] and (5) calculated according to Eq. (2.3.5). Experimental conditions are $P_0 = 3.3$ Torr, $T = 296$ K, mixture 15 % $\text{SiH}_4 + 23$ % $\text{SF}_6 + \text{O}_2$ (for lines 1–4); the sensitivity of detection for curve 4 was increased by a factor of 10. The conditions for straight line 5 are presented in the table. The actual dependencies 1–5 are shifted along the axes to present these dependencies on a single plot

At the same time, this compound is not hydrogen peroxide found in the products of SiH_4 oxidation [43]; the spectral absorbance of hydrogen peroxide has neither maxima nor the line structure in this spectral range [44].

Let us consider a tentative mechanism responsible for non-thermal flame propagation. Theoretical analysis of non-thermal flame propagation in a mixture containing inhibitor [45] shows that the ignition with an external source of the combustible mixture near a butt-end of a long tube initiates non-thermal flame propagation caused by consumption of inhibitor added in advance to initial mixture.

In case of effective inhibition, the velocity of the front is close to a stationary one. In the considered kinetic scheme, which does not formally include any nonlinear branching reactions, the reaction $\text{In} + \text{R}_2$ acts as a nonlinear term leading to a reduction of the rate of chain termination at inhibitor (In) consumption. We will write this scheme as follows:



where A and B—initial substances ($[\text{A}]_0 \ll [\text{B}]_0$). Determining dimensionless variables $\tau = k_1[\text{A}]_0 t$, $f = [\text{A}]/[\text{A}]_0$; $\varphi = [\text{R}_1]/[\text{A}]_0$; $\psi = [\text{In}]/[\text{A}]_0$; $\omega_0 = k_0[\text{B}]_0/(k_1[\text{A}]_0)$; $k = k_3/k_1$, $2\gamma = k_4[\text{B}]_0/(k_1[\text{A}]_0)$, we obtain the following set of equations under condition of stationarity of $[\text{R}_2]$:

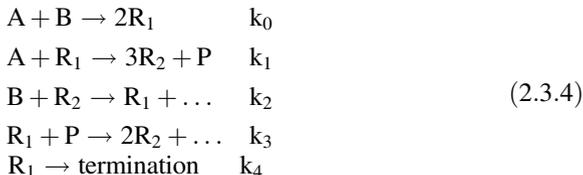
$$\begin{aligned}
 d\varphi/d\tau &= 2\omega_0 f + (2f - k\psi - 2\gamma)\varphi, \\
 df/d\tau &= -(\omega_0 + \varphi)/f \\
 d\psi/d\tau &= -k\psi\varphi
 \end{aligned}
 \tag{2.3.2}$$

It is shown in [45], that replacing the left part of operators of differentiation $[d/dt]$ with $[-Dd^2/d\tau^2 + Vd/d\tau]$ in the system (2.3.2) (D—dimensionless diffusivity, V—dimensionless velocity of flame front propagation) leads to non-thermal flame propagation out of area of thermal ignition under the following conditions. They are $2f - k\psi - 2\gamma < 0$ (out of region of thermal ignition), $\omega_0 = 0$ and boundary conditions are $f = 1$, $\varphi = 0$, $\psi = \psi_0 \ll 1$ (low percentage of inhibitor).

We will show that the problem can lead to similar results if one considers accumulation of promoter instead of consumption of inhibitor. It means that the stationary front of non-thermal flame can arise after ignition with an external source owing to formation of the promoter in the initial mix, which is out of the area of thermal ignition. Really, in the system (2.3.2) the inhibitor consumption φ can be considered formally as the actual emergence of the promoter ϕ . We will assume in (2.3.2) $\psi_0 - \psi = \phi_0 + \phi$ (index 0 means initial concentration) and, respectively, $\psi = \phi_0 - \psi_0 - \phi = C - \phi$. We obtain:

$$\begin{aligned}
 d\varphi/d\tau &= 2\omega_0 f + [2f - k\phi - (2\gamma + kC)]\varphi \\
 df/d\tau &= (\omega_0 + \varphi)f \\
 d\phi/d\tau &= kC\varphi - k\phi\varphi
 \end{aligned}
 \tag{2.3.3}$$

On the other hand, the kinetic model including promoter (P) instead inhibitor is of the form:



after transformations similar to those made at derivation of (2.3.2) ($\varphi = [P]/[A]_0$), leads to the system of the following equations:

$$\begin{aligned}
 d\varphi/d\tau &= 2\omega_0 f + [2f - k\phi - 2\gamma]\varphi \\
 df/d\tau &= -(\omega_0 + \varphi)f \\
 d\phi/dt &= f\varphi - k\phi\varphi
 \end{aligned}
 \tag{2.3.5}$$

As is seen from the set (2.3.5), at the slow formation of the effective promoter (i.e. at slowly changing parameter f) the systems (2.3.3) and (2.3.5), including boundary conditions, are identical up to a constant. Thus, the system of the Eq. (2.3.5) describes the occurrence of the front of chemical reaction out of the region of thermal ignition, i.e. the expansion of the combustion region. It means that it is possible to consider the scheme (2.3.3) with a system of the Eq. (2.3.4) as the model of action of the detected long-lived intermediate, which does not contradict to experimental data [10, 38].

Now it is possible to show that the data presented in Fig. 2.9 are in agreement with the experimental results given in [38]. The spontaneous ignition condition from (2.3.3) and (2.3.4) has a form:

$$2f - k\phi - 2\gamma = 0.$$

In a dimensional form, taking into account the fact that the lower limit of thermal ignition without promoter is determined by a ratio $2f - 2\gamma = 0$, we get after simple transformations:

$$[A]_{0,I}/[A]_{0,I}^0 = 1 - k_3[P]/\left(k_1[A]_{0,I}^0\right) \tag{2.3.6}$$

where $[A]_{0,I}$ —concentration of fuel on the lower limit of ignition in the presence of the promoter with concentration $[P]$, $[A]_{0,I}^0$ —concentration of fuel on the lower limit without promoter. In Fig. 2.9 (straight lines 1–3) the dependencies of change of an intensity (I) of the absorption spectrum of an intermediate of SiH_4 oxidation (Fig. 2.8) on time t are presented in coordinates $\ln(I_0/I)$ — t for three different wavelengths (272, 292, 312 nm respectively). As is seen, the characteristic time of reduction of intensity is approximately identical for the specified wavelengths. It is evidence in support of the proposal that the area of absorption belongs to the same substance, in so doing, the aerosol absorption (235 nm, dependence 4 in Fig. 2.9)

Table 2.1 The conditions of the first flash: 5 Torr of 10 % SiH₄ + O₂, 100 °C

Time between gas admissions, s	Minimum quantity of 10 % of SiH ₄ for thermal ignition at the second gas admission, Torr	Total pressure after two ignitions at a limit of the second ignition, Torr	Concentration limit of the second thermal ignition, [SiH ₄], %
300	2.2	7.2	3.0
45	1.0	6.0	1.7
10	0.1	5.1	0.2

falls off much faster. We will put, according to Fig. 2.2 (straight lines 1–3) that $[P] = [P]_0 \exp(-k_{pr}t)$ where $[P]_0$ —concentration of the promoter directly after spontaneous ignition, t —time. Then (2.3.6) takes a form:

$$\ln\left(1 - [A]_{0,I}/[A]_{0,I}^0\right) = \ln\left(k_3[P]/\left(k_1[A]_{0,I}^0\right)\right) - k_{pr}t \quad (2.3.7)$$

Experimental data on double bleeding-in from [38] for dependencies of concentration limits of thermal ignition of 10 % SiH₄ + O₂ on time between the first and second bleeding-in are presented in Table 2.1 (the conditions of the first flash: 5 Torr of 10 % SiH₄ + O₂, 100 °C).

As at $t = 300$ s a promoting effect is missing [38], the first line in the fourth column corresponds to $[A]_{0,I}^0$, the second and third lines—to $[A]_{0,I}$ for $t = 45$ and 10 s respectively. We will substitute these data into (2.3.7) for the purpose of an independent estimation of k_{pr} and comparison with the slopes of dependencies 1–3 in Fig. 2.9 The straight line 5 in Fig. 2.9 represents the dependence satisfying ((2.3.7). As is seen, the slopes of all four straight lines are close to each other, i.e. the promoter disappears out of the volume with the same rate that the detected UV-spectrum.

Thus, experimentally detected non-thermal flames in oxidation of monosilane and dichlorosilane are most likely caused by nonlinear reactions of the long-lived intermediate with the active centers of combustion. In reactions of oxidation of SiH₄ and SiH₂Cl₂ the vibronic UV-spectrum of long-lived intermediate, similar for both reactions is revealed. It is shown that the formation of the promoting substance during branched chain process can cause non-thermal flame propagation in gas mixture which is out of the region of thermal ignition.

2.6 Conclusions

It has been found that the time delay τ of thermal ignition of dichlorosilane—chlorine mixtures occurs in the presence of more than 4 % of propylene; the consumption of inhibitor leads to ignition, in which absorption spectrum of dichlorosilylene radicals is detected along with the emission of SiHCl ($A^1B_1-X^1A_1$).

The inhibiting effect is due to the fast reactions of propylene with silylenes as chain carriers. In the presence of both inhibitor and >45 % inert additive (sulfur hexafluoride) the dependence of τ on the concentration of deactivator undergoes drastic change. Thus, deactivation processes have marked influence on the flammability. Experimental data are in agreement with the calculations based on the generalized kinetic model of the branched-chain process, including chain termination via both inhibitor and deactivator.

It is shown that non-thermal flame propagation is inherent both to monosilane and dichlorosilane oxidation. As this takes place, deactivating properties of an inert additive noticeably influence on the values of the velocities of non-thermal flame propagation in the case of dichlorosilane oxidation. That may be the evidence of participation of excited particles in the nonlinear branching reaction.

An electron-vibration structure of the UV spectrum of a long-lived intermediate is detected during oxidation of SiH_4 and SiH_2Cl_2 . This product is common to both reactions and exhibits the same promoting effect on them. It is shown that the formation of this promoting compound in the course of a branched chain reaction provides non-thermal flame propagation in reacting mixtures outside of the thermal ignition region.

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