

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 $\text{Cl} + \text{Cl}_2 \rightarrow \text{Cl} + \text{Cl}_2$ $^3\Pi_{\text{ou}} \rightarrow \text{Cl} + \text{Cl}_2$ $^1\Sigma_{\text{g}}^-$,
- (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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