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Repetitive Self-ignition in Mixtures of Silane with Oxygen in Closed Vessels

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Kinetic modes of isothermal and non-isothermal repeated self-ignition of mixtures of silane with oxygen and chlorine in enclosed volumes have been observed, and the importance of adsorbed active intermediates in reaction chain propagation and the occurrence of subsequent ignitions by a different mechanism have been established.

Repetitive self-ignition is of special interest for the theory of chemical kinetics in view of its specific peculiarities and the nature of those factors leading to pulsation in the basic kinetic characteristics of a reacting system. The pulsating combustion mode seems also to be of interest for a number of technological processes.

In the great majority of cases, pulsating combustion has been studied in flow systems and is accompanied by considerable self-heating. Under such conditions, the occurrence of multiple explosions is usually governed by the ratio of the gas flow rate to the flame propagation rate, and by the ratio of self-heating to heat losses (see, *e.g.*, refs.1–4). The chemistry is usually in the background. This explains the fact that, in spite of the great number of studies devoted to these processes, sets of elementary reactions capable of giving pulsations in the absence of thermal and gas dynamic factors have been elucidated only for a few rare cases (*e.g.*, the oxidation of CO, decomposition of NCl_3).[2,5–7] The subsequent explosions are generally assumed to occur by the same overall reaction equation. In the present communication, some data are presented on repeated self-ignition in closed vessels of mixtures of silane with oxygen and chlorine which indicate the important part played by the adsorbed intermediate species in the combustion.

The premixed gases were admitted quickly from an auxiliary volume into an evacuated and thermostated reactor (4.0 cm in diameter, 16.5 cm long). In experiments, both chemiluminescence (by photomultipliers FEU-39 and FEU-62 covering the spectral range 160–600 nm) and gas pressure in the reactor were monitored (sensitivity 10^{-1}–10^{-2} Pa). After every experimental run, reactors were evacuated down to 10^{-2} Pa. Before the experiments, the reactor surface was pretreated with the flame of the mixture to be studied until good reproducibility of results was obtained. The experimental procedure is described in detail elsewhere.[5,6] Impurities in the gases did not exceed 0.15%.

Reaction of SiH_4 with O_2 was carried out at 360–700 K in the vicinity of the first self-ignition limit. In typical oscillograms (Fig. 1), the point $t = 0$ corresponds to pressure stabilization just after mixture admission into the reactor. The ranges of different modes of silane oxidation are presented in Fig. 2 by using the reference system pressure–temperature. The limits of these ranges were found to depend on the initial mixture composition, on the chemical nature of the reactor wall and on the state of the adsorption layer.

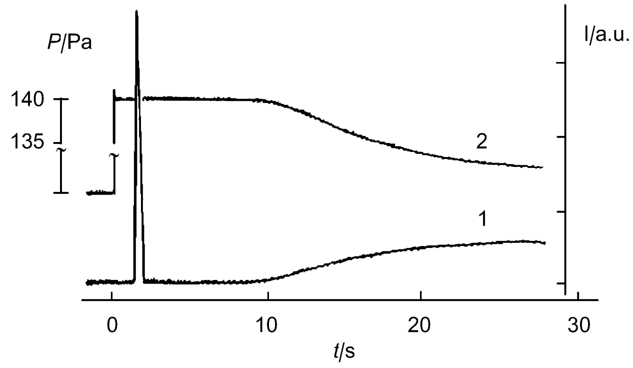

Fig. 1 Oscilloscope traces (in the double combustion pulse mode) of chemiluminescence intensity (1) and pressure (2) of repetitive self-ignition for the mixture 12.2% SiH_4 + 63.6% O_2 + 24.2% He at 211 Pa and 361 K; P_1 = 141 Pa.

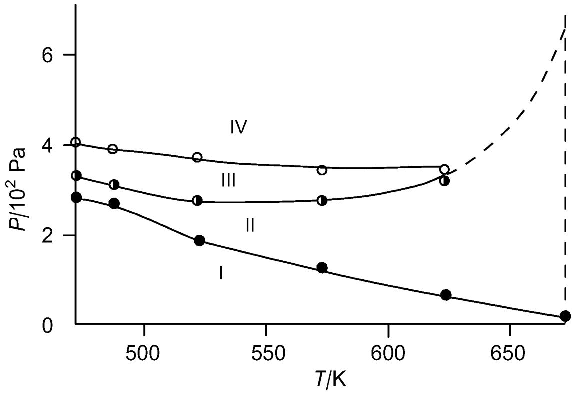

Fig. 2 Different modes of silane oxidation (mixture 3.64% SiH_4 + 85.5% O_2 + 10.86% He): almost complete abscence of reaction, I; self-ignition and chain combustion, II, IV; two-fold self-ignition, III.

As shown in Fig. 1, the pressure remains constant from the very beginning up to completion of the first explosion. This implies that not only temperature, but also the number of gas molecules remains constant in the course of the first explosion. The number of molecules is unchanged in reaction (1):

$$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2 \qquad (1)$$

(note that SiO_2 is in the condensed state). As for the second explosion, the pressure was found to decrease, thus indicating a reduced number of molecules, *i.e.*, water vapour is formed, reaction (2).

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O \qquad (2)$$

Thus, silane oxidation during these two subsequent explosions occurs by different general processes. This is basically different from all known multiple explosions. Upon an increase in initial pressure, the second flash was found to grow to a greater extent than the first one. The time delay between the explosions became progressively smaller until they merged.

The role of heterogeneous reactions is also different in these explosions. The first self-ignition appeared to be localized in the region of the reactor walls. It was also established that the increase in evacuation time of the reactor between experimental runs resulted in a much greater decrease in the intensity of the first flash than that of the second one. Evacuating the reactor evidently removes not only gaseous but also partially adsorbed compounds. Since, upon admission of a new mixture into the reactor the amount of initial reactants both in the gas phase and on the surface is recovered, only the amount of adsorbed components had been decreased to the beginning of the next experimental run under conditions of prolonged evacuation times. The marked decrease in the intensity of the first flash with decreasing amount of adsorbed product species is an indication that some of these species on the surface play an important role in explosions, *i.e.*, participate in chain branching. Heterogeneous propagation of chains differs substantially from heterogeneous initiation both in chemical origin and reaction rate as well as in their role in the chain process as a whole. Some kind of initiation represents the so-called degenerate branching reactions which, just like the conventional initiation, result in the formation of new chains but not branches.[8] The initiation reactions, and particularly degenerate branching, are incapable of initiating explosion.[8,9]

The present data, combined with our previous results[7,10] on heterogeneous chain propagation, show that, contrary to widely accepted belief, chain termination at the surface is far from being the only type of heterogeneous reaction of intermediate species in chain combustion. Mutual interdependence between chain combustion and the composition of the adsorbed layer is also manifested in the data from combined studies on reaction kinetics and IR absorption spectra of the surface in contact with reacting gas. The absorption spectra of the surfaces corresponding to areas 2 and 1′ in Fig. 3 differ in the amount and state of the surface groups Si–OH and Si–H.

Under certain initial conditions at low pressures, there may be more than two self-ignitions in a closed vessel.

Double explosions were also found for mixtures of silane with chlorine. This reaction was carried out in the vicinity of

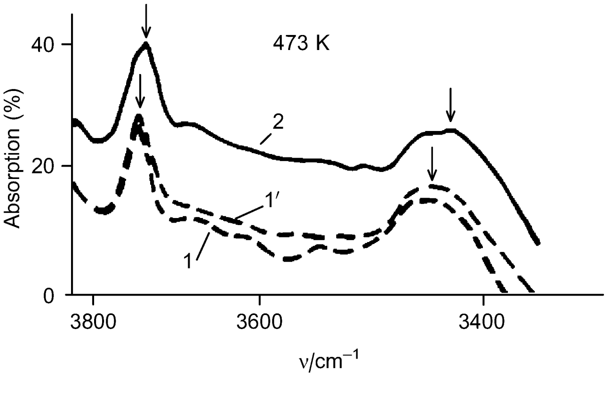

Fig. 3 IR absorption on the surface in contact with the reacting mixture 3.66% SiH_4 + 85.5% O_2 + 10.8% He under 380–680 Pa and at 473 K: (1) after 4 h *in vacuo* at 1023 K and cooling to 473 K; (2) after ignition of the mixture SiH_4 with O_2 at 473 K and *in vacuo*; (1′) after 4 h *in vacuo* at 1023 K.

the first explosion limit, under practically isothermal conditions. Here again, the first and second flashes were found to show different behaviour. In particular, the first flash was greenish in colour, while the second was orange (wavelengths of maximum intensity 510 and 600 nm, respectively).

The discovery and investigation of double explosions in mixtures of SiH_4 with O_2 and Cl_2 provide new indications of a large variety of combustion regularities determined by heterogeneous reactions of chain propagation and chain branching yet to be properly understood.

References

1 D. A. Frank-Kamenetskii, *Diffusiya i teploperedacha v khimicheskoi kinetike (Diffusion and heat transfer in chemical kinetics)*, Nauka, Moscow, 1986, p. 446 (in Russian).

2 P. Gray, *Ber. Bunsen Ges. Physik. Chemie*, 1980, **84**, 309.

3 D. Garrel and O. Garrel, *Oscillations in Chemical Reactions*, Springer-Verlag, Berlin-Heidelberg-New York-Tokyo, 1983.

4 V. K. Ryabinin, PhD Thesis, Chelyabinsk, 1991.

5 V. V. Azatyan and E. N. Aleksandrov, *Gorenie i vzryv (Combustion and explosion)*, Nauka, Moscow, 1972, p. 646 (in Russian).

6 P. Gray and S. K. Scott, in: *Oscillations and Travelling Waves in Chemical Systems*, ed. R. Field, Wiley, New York, 1985, p. 493.

7 V. V. Azatyan, *Usp. Khim.*, 1985, **54**, 33 (*Russ. Chem. Rev.*, 1985, **54**, 21).

8 V. V. Azatyan and R. G. Aivazyan, *Kinet. Katal.*, 1986, **27**, 1086 [*Kinet. Catal. (Engl. Transl.)*, 1987, **27**, 937].

9 N. N. Semenov, *O nekotorykh problemakh khimicheskoi kinetiki i reaktsionnoi sposobnosti (On some problems of chemical kinetics and reactivity)*, Izd. AN SSSR, Moscow, 1958, p. 538 (in Russian).

10 V. V. Azatyan, M. U. Kislyuk, J. J. Tretyakov and A. A. Shavard, *Kinet. Katal.*, 1980, **21**, 538 (in Russian).

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