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The Effect of the Electric Field on the Kinetics of Dichlorosilane Oxidation in the Absence of Discharge

N. M. Rubtsov, G. I. Tzvetkov, and V. I. Chernysh

Institute of Structural Macrokinetics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

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Abstract—A constant electric field incapable of discharge generation affects the kinetics of the ignition and combustion of dichlorosilane–oxygen mixtures: near the lower self-ignition limit, the induction period decreases and the region of the oscillating combustion regimes is enlarged. These phenomena depend on the material and state of the reactor surface. The lower self-ignition limit P_1 over the $CuSO_4$ and $ZnSO_4$ surfaces abruptly increases with an increase in the voltage of the constant electric field.

INTRODUCTION

Azatyan *et al.* [1] observed chemical ionization in the low-temperature rarefied flame of dichlorosilane (DCS) and found a dramatic decrease in the rate of SiO_2 aerosol formation in the constant electric field, applied before ignition and incapable of generating ionization. This means that the processes involving charged intermediate species affect the kinetics of the formation of solid silicon dioxide, which is the main product of dichlorosilane oxidation. A crucial role of the charged species in the phase formation may be due to the heterogeneous processes with their participation. More recently, we found that the maximum concentration of charged species is attained simultaneously with the maximum rate of the phase formation [2]. Still more recently, the lower limit of flame propagation was found to double in the electric field with a voltage of 250 V/cm (10% of DCS in O_2) [3].

The aim of this work was to elucidate the probability of the effect of the constant electric field on the kinetics of a branched-chain process using dichlorosilane oxidation near the lower self-ignition limit P_1 over different surfaces.

EXPERIMENTAL

The experiments were conducted in a vacuum setup described elsewhere [4]. A reaction vessel a cylinder made of molybdenum glass (diameter, 21 mm; length, 250 mm) was placed into an electric furnace (Fig. 1). The temperature was controlled and measured using a KVA-501 sensor accurate to ±0.5 K. The reactor was equipped with inlets for electrodes and gas supply. An electrode made of molybdenum wire (diameter, 1 mm; length, 500 mm) was positioned along the reactor axis. The outer cylindrical electrode, 300 mm long and made of copper foil, was tight against the outer reactor surface. The direct stabilized voltage $U = +(0–1000)$ V from a B5-24A source was applied to the inner electrode. The electrodes were connected with a capacitor (3 μF) and a resistance (50 kΩ), which were in turn connected in a series. The resistance signal was transmitted to an S9-6 electron-beam memory oscilloscope to control the

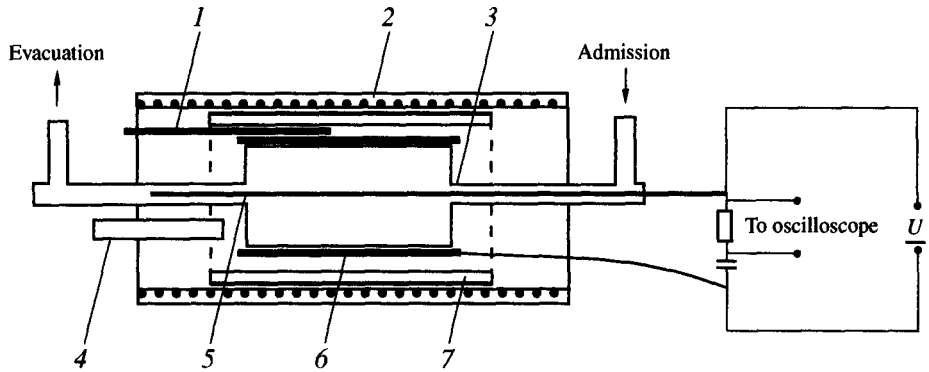

Fig. 1. Setup for studying the effect of the electric field on the kinetics of the self-ignition of the dichlorosilane–oxygen mixtures: (*1*) thermocouple, (*2*) electric furnace, (*3*) reactor, (*4*) light guide, (*5*) inner electrode, (*6*) outer electrode, and (*7*) insulating quartz cylinder.

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breakdown between the electrodes. A fuel mixture prepared beforehand was fed from a bypass volume into the reactor through a vacuum valve made of a single piece of glass. Chemiluminescence upon self-ignition was registered using a light guide (diameter, 2 mm) placed inside a furnace and directed toward the reactor butt-end and an FEU-39 photomultiplier, the signal from which was also transmitted to the S9-6 oscilloscope. Depending on the measurement, the S9-6 oscilloscope starting in a leading-phase mode was synchronized using either the FEU-39 signal or the optoelectronic couple signal corresponding to the time of fuel mixture admission into the reactor. The t_{max} parameter was determined as a period between the times of admission and attainment of the maximum chemiluminescence intensity. The time of attainment of a constant pressure in the reactor upon admission (measured with a 6MDKh4S mechanotron, the signal from which was transmitted to the S9-6 oscilloscope) was shorter than 0.4 s. The t_{max} values in all of the experiments ranged from 0.4 to 6.0 s.

The reactors were evacuated to 10^{-3} torr using 2NVR-5D forevacuum and N-1 oil-diffusion pumps. The residual pressure was measured with a VT-2A-P thermocouple vacuum gauge. The dichlorosilane–oxygen mixture prepared beforehand was admitted into the bypass volume and then into the reaction vessel with the pressure control using a VDG-1 vacuum gauge. The fuel mixture was prepared by dichlorosilane admission into oxygen through a narrow capillary. Either the SiH_4– O_2 or DCS–O_2 mixture was used.

Prior to the runs, the reactor was washed with 10% HF. The reactor surface was treated by washing with H_3PO_4, a TiO_2 suspension, and NaCl, $CuSO_4$, and $ZnSO_4$ solutions. For this purpose, a saturated salt solution (10 ml) was poured into the reactor and evacuated to complete water evaporation.

Oxygen (reagent grade), dichlorosilane (98%) [5], NaCl (analytical grade), TiO_2 (reagent grade), $CuSO_4 \cdot 7H_2O$ (analytical grade), $ZnSO_4$ (reagent grade), and H_3PO_4 (reagent grade) were used. SiH_4 and SF_6 (both of reagent grade) were used in special experiments. The lower self-ignition limit P_1 was determined using the bypass method [4]. The pretreated and preevacuated reactor was first kept at 473 K for 2 h, and then 20–30 self-ignitions were carried out until a constant P_1 value was attained. Simultaneously, the constancy of the P_1 value was controlled by measuring the t_{max} value and the integral chemiluminescence intensity (J).

RESULTS AND DISCUSSION

The reproducibility of the measurement results should be carefully controlled, because the effect of the electric field depends on the material and state of the reactor surface, as was observed experimentally. A series of experiments over each coating were repeated 3–5 times. Then, the coating was removed with a 10% HF solution, and the reactor was recovered with a new substance. We thus checked for each material whether the procedure of the reactor treatment described in the experimental section ensured the reproducible results.

For example, the scatter in the t_{max} values thus obtained over NaCl and TiO_2 and in the J values over $CuSO_4$ and $ZnSO_4$ is lower than ±5% over each surface in each separate series. In this case, the P_1 value remained unchanged within ~±1% at a given composition and temperature. Note that the P_1 values (upon stabilization, see the experimental section) differ for each surface used ranging from 1.06 torr for NaCl (20% DCS, 493 K) to 3.80 torr for TiO_2 (15% DCS, 513 K). This suggests that SiO_2, formed during oxidation in the course of deposition and condensation, produces a nonuniform, island-like coating over the reactor surface because our experimental conditions differ from those of the thin film deposition [2]. In this case, some areas of the initial coating are still available for the active species of the chain reaction.

INFLUENCE OF THE APPLIED FIELD ON t_{max}

Figure 2 illustrates how the voltage between the electrodes affects the t_{max} value for the surfaces of NaCl, TiO_2, H_3PO_4, $CuSO_4$, and glass washed with HF. Figure 2 shows that an increase in the voltage U causes a decrease in the t_{max} values over NaCl, TiO_2, H_3PO_4, and glass washed with a HF solution.

To prevent the influence of the spark breakdown, we performed special experiments to study the conditions of its generation. The flash breakdown (characteristic time, ~50 μs; signal intensity, <20 mV) is observed only during gas admission into the reactor, washed with HF and treated with dichlorosilane ignitions in oxygen after <0.1 s from the admission at $U > 840$ V. To study the effect of the breakdown on the t_{max} value in the reactor placed into the electric field, we first admitted oxygen (1 torr) and then, after the breakdown, fed the fuel mixture until a necessary pressure was attained. This admission procedure did not markedly change the t_{max} value. For example, the breakdown can also be prevented by four or five preliminary treatments of the reactor by self-ignition at $P/P_1 = 1.05$ and $U = 360$ V under the conditions indicated in the caption of Fig. 2. As follows from the comparison of the t_{max} values with and without breakdown, the breakdown affects neither the regularities of self-ignition over the given surface nor the oscillation mode (see below). The lack of the spark breakdown effect is due to the fact that the reaction mixture is outside the self-ignition and flame propagation areas at the instant of spark breakdown [6].

The lower self-ignition limits (P_1) over NaCl, TiO_2, and glass treated with HF and H_3PO_4 are independent of the field applied within the U range studied. The exceptions are the $CuSO_4$ and $ZnSO_4$ surfaces (see below). The rate-limiting reaction of linear branching

involves the fuel molecules [4]. In this case, the following relationship is valid at the lower self-ignition limit P_1:

$$2k_{br}[SiH_2Cl_2] - k_{het} = 0 \quad \text{or}$$
$$\varphi = 1 - k_{het}/2k_{br}[SiH_2Cl_2] = 0, \qquad (1)$$

where k_{br} and k_{het} are the effective rate constants of linear chain branching and heterogeneous chain termination, respectively, and φ is the branching factor.

The facts that the electric field voltage does not affect the P_1 value over the above surfaces and that t_{max} decreases with an increase in the voltage U may be explained as follows:

(a) The k_{br} and k_{het} values increase (because t_{max} decreases in proportion to $1/\varphi$) to the same degree because the P_1 limit is determined by the ratio of these two rate constants;

(b) A certain parameter (e.g., the rate of chain initiation w_0) that is not involved in the self-ignition condition but enters the expression for the t_{max} value (see below) changes.

The NaCl surface is the only one among those studied that exhibits a "memory" effect. If the voltage $U >$ 400 V is applied to the electrodes before self-ignition and removed after it, the t_{max} value of the next self-ignition (without the applied field) will be nearly the same as that obtained when the field is applied. In further self-ignitions in the absence of the electric field, the t_{max} value increases and approaches a value corresponding to the zero field; that is, the surface gradually "forgets" the action of the field. Therefore, the changes in the t_{max} value with the voltage U over NaCl were measured only after a U increase (see the table). Our findings suggest that the NaCl surface accumulates the charge upon self-ignition in the applied field. When the voltage (U) is shut down, the electric field in the reactor is due to this accumulated charge and the charge induced on the central electrode and corresponds, for example, to the field applied (~400 V) under the conditions of run 2 (see the table). On successive ignitions in the absence of the voltage U (runs 3 and 4 in the table), the charge at the inner reactor surface is neutralized and the field in the reactor disappears. Note also that the P_1 value remains unchanged under the above experimental conditions and chain branching should be heterogeneous in case (a). However, this problem requires further studies.

Let us consider some consequences of case (a). Let us relate the t_{max} value to the induction period of the branched-chain reaction τ_i (τ_i corresponds to the maximum curvature of the kinetic curve that illustrates the initial substance consumption [7]). On the other hand, because the characteristic chemiluminescence times are ~2 ms and $t_{max} > 400$ ms under our experimental conditions, we assumed that the times of attainment of both the maximum chemiluminescence and the maximum slope of the kinetic curve of dichlorosilane consumption are nearly the same; that is, $t_{max} \approx \tau_i$.

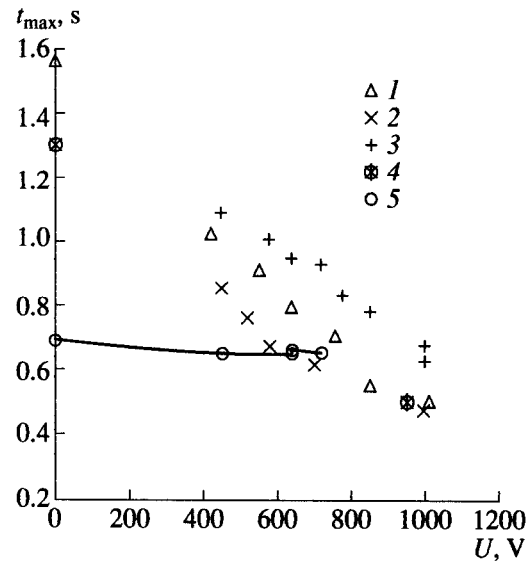

Fig. 2. t_{max} vs. voltage between the electrodes: (*1*) NaCl surface, 220°C, P_1 = 1.06 torr, P = 2.40 torr, and 20% DCS in O_2; (*2*) TiO_2 surface, 240°C, P_1 = 3.80 torr, P = 4.40 torr, and 15% DCS in O_2; (*3*) glass treated with HF, 195°C, oxygen preadmission (1.00 torr) at 1000 V followed by the admission of 11.7% DCS in O_2 to P = 5.10 torr; (*4*) H_3PO_4 surface, 220°C, P_1 = 1.17 torr, P = 1.20 torr, and 20% DCS in O_2; and (*5*) $CuSO_4$ surface, 250°C, P_1 = 3.6 torr, P = 4.20 torr, and 15% DCS in O_2.

Let us consider the hypothetical one-center approximation corresponding to equation (1) and differing from the classical kinetic model [7, 8] in that the material balance equation is fulfilled. At the initial step of a branched-chain process, the equations

$$d[n]/dt = 2k_0[B] + 2k_{br}[B][n] - k_{het}[n],$$
$$d[B]/dt = -k_0[B] - 2k_{br}[B][n] + k_{het}[n]/2 \qquad (2)$$

are true, where k_0 is the rate constant for chain initiation; [n] and [B] are the concentrations of the active species and the molecular reactant involved in linear chain branching; and t is time. The material balance equation is $[B]_0 = [B] + [n]/2$, where $[B]_0$ is the initial concentration of the molecular reactant and 1/2 is the coefficient that takes into account an increase in the number of molecules in the branching step. Using the dimensionless values of $\tau = k_{br}[B]_0 t$, $f = [B]/[B]_0$, $\eta =$

t_{max} vs. number of self-ignitions upon electric field application (1.1 torr, 493 K, and 22% DCS in O_2)

Run no.	t_{max}, s	U, V
1	0.52	590
2	0.99	0
3	1.30	0
4	1.50	0
5	0.49	590

$[n]/[B]_0$, $\omega_0 = k_0/k_{br}[B]_0$, $b = k_{het}/2k_{br}[B]_0$, and $\varphi = 1 - b$, we arrive at

$$f = [B]/[B]_0 = 1 - (\omega_0/2\varphi)(\exp 2\varphi\tau - 1) \quad (3)$$

at $[B] \approx [B]_0$. At the point of the maximum curvature, the following relationship

$$\tau_{ii} = (1/2\varphi)\ln(1/2\omega_0), \quad (4)$$

is valid, where τ_{ii} is the dimensionless τ_i value.

This finding suggests that the dependence of the induction period on the φ value is described by the same equation for different models:

$$\tau_{ii} = (\ln L_0)/\varphi \approx L/\varphi, \quad (5)$$

where $\ln L_0$ is the parameter that slightly changes as compared to the φ value. At the same time, the τ_{ii} vs. ω_0 dependence differs from that obtained in [7]. This means that to study the τ_{ii} vs. ω_0 dependence, one should know the mechanism of the branched-chain process, which has not been studied in detail. Therefore, because it is impossible to correctly consider the influence of the outer electric field in case (b), this case is beyond the scope of the present paper.

Let us consider case (a) when the field affects only the φ value and equation (5) is valid. The branching factor is $\varphi = 1 - P_1/P$ for the kinetics-controlled chain branching and $\varphi = 1 - P_1^2/P^2$ for the diffusion-controlled chain branching, where P is the overall pressure [5]. We found that the P_1 limit takes the lowest value over NaCl and H_3PO_4 (~1.1 torr at 493 K) and one of the highest values over TiO_2 (~3.8 torr at 513 K). Let us use equation (5) assuming that the rate of chain termination is close to the kinetics-controlled one for the NaCl coverage and to the diffusion-controlled one for the TiO_2 coverage.

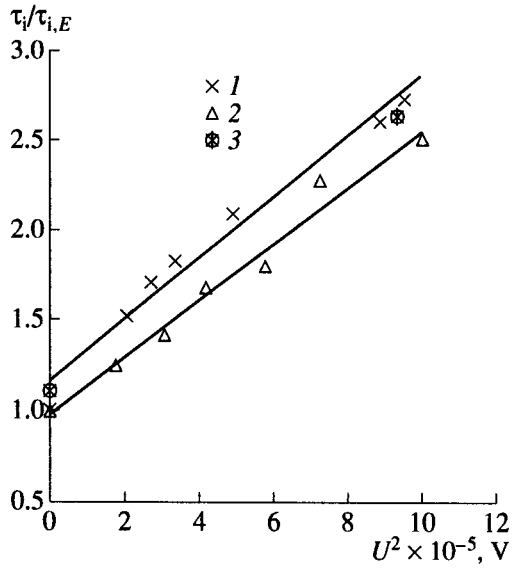

Fig. 3. $\tau_i/\tau_{i,E}$ as a function of the square of the voltage between the electrodes for the surfaces treated with (*1*) NaCl, (*2*) TiO_2, and (*3*) H_3PO_4. The conditions are the same as in Fig. 2.

In the applied electric field, equation (5) takes the form

$$\tau_{ii,E} \approx \text{const}/\varphi_E, \quad (6)$$

where E denotes the parameters that change or can change in the applied field. By dividing equation (5) by equation (6), we obtain $\tau_{ii}/\tau_{ii,E} = \tau_i/\tau_{i,E} \approx \varphi_E/\varphi$. Substituting the above expressions for the φ parameter for the kinetic and diffusion regions and taking into account that the P_1 values are independent of the field over NaCl, H_3PO_4, and TiO_2 (i.e., $P_1 = P_{1,E}$), we arrive at

$$\tau_i/\tau_{i,E} \approx k_{p,E}/k_{br}.$$

Figure 3 illustrates how the $\tau_i/\tau_{i,E}$ value changes with the voltage U for the surfaces treated with NaCl, H_3PO_4, and TiO_2. The experimental data fit the relationship $\tau_i/\tau_{i,E} \approx 1 + \text{const}U^2$. This experimental dependence should be taken into account in further analysis of the reasons for the effect of the electric field on dichlorosilane oxidation.

Note that the P_1 value for the reactor treated with HF corresponds to the intermediate region of chain termination [4], which precludes the application of the above equations for the φ values to describe the τ_i vs. $-U$ dependence over this surface.

The effect of the electric field on the kinetics of the branched-chain process observed for dichlorosilane oxidation directly points to the crucial role of the surface state in such processes. However, the mechanism of the effect of the outer electric field requires further studies.

THE EFFECT OF THE ELECTRIC FIELD ON THE LOWER SELF-IGNITION LIMIT

As noted above, the P_1 value is independent of the electric field voltage over all coverages studied. The exceptions are the $CuSO_4$ and $ZnSO_4$ surfaces dehydrated at 523 K. It is known that copper sulfate chemically binds water molecules to give crystal hydrates. The Cu^{2+} and Zn^{2+} ions can also include hydroxyl groups in their coordination sphere to give cuprates and zincates, respectively [9]. On the other hand, the dichlorosilane molecules react with the surface hydroxyl groups to yield a chemisorbed layer [5, 10]. The surface compounds thus formed are involved in further reactions with gas-phase species [11]. The $CuSO_4$ and $ZnSO_4$ coverages were chosen to change the concentrations of the surface hydroxyl groups and, thus, to affect the above sorption processes. We found that the P_1 values over the $CuSO_4$ surface are high (3.6 torr at 523 K). Figure 4 illustrates how the integral chemiluminescence intensity J varies with the applied field during self-ignition. Figure 4 shows an abrupt inflection on the J curve so that $J = 0$ at $U = 600$–700 V,

other conditions being the same; that is, the P_1 value increases in the electric field. The J value over the $ZnSO_4$ surface becomes equal to zero at 600–800 V. Figure 4 presents the numbers of the experimental points indicating the reproducibility and the lack of hysteresis character in the phenomenon observed. A dramatic change in the J value within a narrow U range in the branched-chain process is a new critical phenomenon that, first of all, points to the principal role of the surface in the branching of the reaction chains during dichlorosilane oxidation. This agrees with the fact that the self-ignition of the dichlorosilane–oxygen mixtures starts at the reactor surface, as was observed earlier using high-speed schlieren cinematography [12]. At the same time, the elucidation of the chemical nature of the sorbed active sites and charged states involved in chain propagation requires further studies.

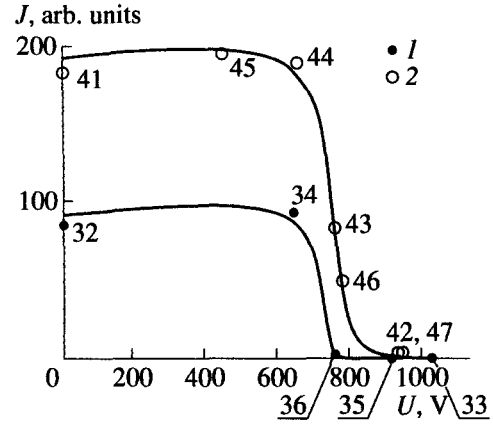

Fig. 4. Integral self-ignition intensity (J) as a function of the voltage between the electrodes at P: (*1*) 3.70 and (*2*) 4.20 torr. $CuSO_4$ surface, 250°C, P_1 = 3.60 torr, and 15% DCS in O_2. The point numbering corresponds to the order number of experiments with 30 preliminary ignitions.

CHEMICAL OSCILLATIONS IN THE ELECTRIC FIELD

We found earlier that, at $P/P_1 > 2$, the self-ignition of dichlorosilane–oxygen mixtures in the closed volume occurs in the oscillation regime [13].

The applied electric field enlarges the range of the oscillation regimes in the closed volume. This is illustrated in Figs. 5a and 5b for the reactor treated with HF. The generation of the flash breakdown has no effect on the period (t_{os}) and intensity (I) of oscillations. At the same time, the oscillation period and intensity are determined by the material of the reactor surface. For example, the oscillation period increases with time over SiO_2 (Fig. 5b) and remains unchanged for each self-ignition in the oscillation mode over NaCl (Fig. 5c). The oscillations over H_3PO_4 are not pronounced even in the applied electric field, and they are accompanied by stationary combustion (Fig. 5d). This indicates that the surface state determines the specific features of chemical oscillations in the closed volume under our operating conditions.

The oscillation modes were also studied under flow conditions. As in [13], we observed chemical oscillations at 0.9–7.0 torr after several ignitions initiated by a Nichrome spiral heated with electric pulses in a glass reactor treated with HF. The application of the electric field during oscillations does not influence their period and intensity. This suggests that the peculiarities of chemical oscillations in the flow reactor (in contrast to the closed one) are determined by the homogeneous reactions of a long-lived intermediate detected in [2, 13]. Thus, the process occurs via two mechanisms resulting in chemical oscillations: (i) homogeneous, involving a long-lived intermediate and dominating during combustion under flow conditions, and (ii) heterogeneous, involving sorbed active species and dominating during combustion in a closed volume.

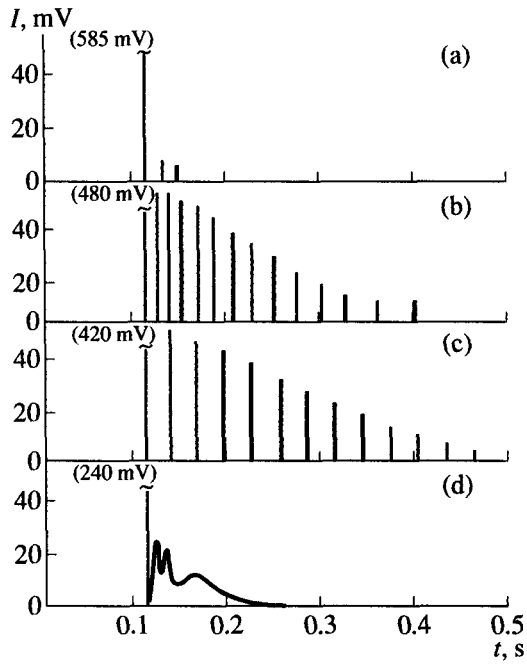

Fig. 5. The effect of the voltage between the electrodes on the chemical oscillation modes (I is the intensity of the oscilloscope signal): (a) SiO_2 surface, 200°C, P = 4.00 torr, U = 380 V, τ_i = 0.45 s, and 11.7% DCS; (b) SiO_2, 200°C, P = 4.00 torr, U = 720 V, τ_i = 0.41 s, and 11.7% DCS; (c) NaCl surface, 210°C, P = 4.20 torr, U = 0, τ_i = 0.68 s, and 22% DCS; (d) H_3PO_4 surface, 220°C, P = 3.00 torr, U = 940 V, τ_i = 0.43 s, and 20% DCS. The numbers in brackets correspond to the I_{max} values.

CONCLUSION

Our main finding is the effect of the constant electric field on the kinetics of dichlorosilane oxidation near the lower self-ignition limit.

The material and state of the reactor surface and the reactions involving the long-lived intermediate deter-

mine the period and number of chemical oscillations, as well as the quantitative effect of this phenomenon on both the lower limit and the induction period of self-ignition. We found a new critical phenomenon that implies a stepwise decrease in the integral chemiluminescence intensity during the self-ignition of dichlorosilane–oxygen mixtures over $CuSO_4$ and $ZnSO_4$ within the narrow range of the electric field voltages.

The mechanism of the effect of the electric field on the lower limits of self-ignition and flame propagation in the dichlorosilane–oxygen mixtures and the nature of the surface memory during self-ignition over NaCl in the applied electric field still remain unclear.

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