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Decomposition of chlorine and (or) fluorine-bearing substances in a gas mixture ignited by a slipping surface discharge

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Abstract

Experimental investigation of decomposition of chlorofluorocarbons (CF_2Cl_2 , CF_4), as well as SiCl_4 and SiF_4 contained in an oxygen-hydrogen gaseous mixture, combustion of which is initiated by a high-current pulse slipping surface discharge, has been carried out.

It was found that a ternary gaseous mixture of oxygen+hydrogen+chlorine- and (or) fluorine-bearing gas, even with a large amount of the third component, maintains the explosion combustion property inherent in a binary hydrogen–oxygen mixture, based on the branched chain processes.

High-efficient (near complete) destruction of chlorine–fluorine-containing substances has been demonstrated.

Combustion dynamics was investigated. It was shown that initiation by slipping surface discharge combustion propagation behaviour has some peculiarities that are beyond the ordinary combustion wave or detonation wave mechanisms.

Peculiarities of the observed phenomena may be attributed to the strong UV irradiated by a high-current slipping surface discharge.

1. Introduction

In recent years, the problem of decomposing chlorine- and (or) fluorine-bearing substances has assumed special importance in connection with the role that these chemical compounds play in the progressively deteriorating ecological situation throughout the world. First of all we should mention Freons destroying the ozone layer (CF_2Cl_2 , CFCl_3 , etc), compounds with a high greenhouse potential (CF_4 , etc), gaseous-phase poisoning substances stockpiled in a number of countries, etc.

At present, recovery of the above-mentioned compounds is generally carried out in high-temperature furnaces. However, recently a number of rather successful attempts have been made to involve thermo-nonequilibrium plasmachemistry to solve this problem. For example, in [1] the results of Freon decomposition in pulse discharges excited by the beams of high-power microwave radiation is discussed. Reference [2] contains evidence of plasmachemical destruction of Freons by

a slipping surface discharge or a spark excited in a gas medium by a pulse CO_2 laser.

The experiments were carried out in nitrogen, argon or air, to which various chlorine- and fluorine-bearing substances were added. The reasonably high efficiency of plasmachemical decomposition has been shown, wherein the only consumed energy is the electrical energy. The energy cost of the decomposition is:

$$W = P(t/M) \cong 1 \text{ kW h kg}^{-1} \quad (1)$$

where P is the average power of consumed electrical energy, t is the time of treatment, and M is the mass of a treated substance. From equation (1) it follows that at $P \cong 1 \text{ kW}$, the output of a plasmachemical reactor makes up a magnitude of the order of $\eta \cong 1 \text{ kg h}^{-1}$.

The present work discusses the results of experimental studies on the decomposition of chlorine- and fluorine-bearing substances in a reactor where combustion in a

hydrogen+oxygen+Freon mixture is initiated by an electrical discharge. The purpose of such research is to find ways to reduce essentially the energy cost of destruction, as well as to increase the reactor output through including a source of chemical power (i.e. energy released in combustion of a mixture).

Electrical discharge is one of the most widely used techniques for initiating combustion in gaseous combustible mixtures. It has been comprehensively discussed in a series of monographs (see, for example, [3, 4]). As a rule it represents a relatively low-power spark excited between two electrodes immersed in a combustible gas medium (analogous to a spark in internal combustion engines). In the present work, a high-current pulse slipping surface discharge was used instead of a spark.

2. Scheme of the experiment

The scheme of the reactor based on electro-discharge initiation of combustion is shown in figure 1. The chamber of the reactor (1) represents a cylindrical quartz pipe (or, in a series of experiments, a metal pipe) of diameter, $\Phi_c \approx 50$ mm and length $L_c \approx 100$ –200 mm. The chamber is evacuated up to a pressure of $p_o < 10^{-2}$ Torr and filled with a gaseous mixture of $H_2 + O_2 + \text{Freon}$ at pressures in the range $100 \leq p \leq 500$ Torr. It is in this three-component gas mixture that combustion is initiated with the help of a discharger (2). The restriction on the applied pressure by 500 Torr is associated with the safety of a quartz or glass chamber with respect to the high value of pulse excess pressure.

The discharger represents a multielectrode system fixed in a particular way (see [5–8]) on a dielectric (quartz, Teflon, ceramic) tube of diameter $\Phi_d \approx 6$ mm. The length of the metal–dielectric cylindrical discharge system is $L_d \approx 40$ mm. The discharger is located close to one of the end flanges of the reactor chamber. When a high-voltage pulse is applied to the discharger, it gives rise to the formation of a high-current ($I \leq 1$ –10 kA), low-threshold ‘slipping’ discharge along the discharger and an extended plasma layer at its surface. Such discharge systems have been widely applied at the General Physics Institute of the Russian Academy of Sciences for generating the dense hot collisionless plasma [5], as sources of the metal plasma [6], for excitation of converging toroidal shock waves in a gas medium [7, 8], etc. The present work is the first attempt to use discharges on a slipping surface discharge for initiating combustion in a gas mixture.

One advantage of the multielectrode metal–dielectric dischargers applied in [5–8] is that they permit the creation of sufficiently dense plasma layers, which represent sources of intense UV radiation, in virtually all kinds of gases and gas mixtures in an extremely broad interval of pressures: $10^{-4} \leq p \leq 760$ Torr.

In the present work two generators of high-voltage pulses were used as power supplies of dischargers (3), with the following parameters:

- (a) Generator G1 with low pulse energy: pulse amplitude $U \cong 40$ kV, pulse duration $\tau \cong 40$ ns, and energy in a pulse $E \leq 0.1$ J.
- (b) Generator G2 with high pulse energy: $U \cong 20$ kV, $\tau \cong 20$ μ s; $E \leq 30$ J.

The content of Freon, as well as the contents of a number of products of its decomposition, were determined by the absorption spectroscopy method with the use of a spectrophotometer IKS-29 in selected samples of a gas mixture (before initiation of the combustion and after excitation of the combustion in the investigated gas mixtures).

Dynamics of the reactor glow was investigated with the use of a photoelectric recorder (streak camera) FER-7 (4). Time characteristics of the glow, integrated on the volume of the chamber and on the spectrum, were determined with the help of a photomultiplier FEU-106 (5). Viewing windows were made of quartz or of KRS-6.

Molecular chlorine produced in the reactor was recorded by radiation absorption at a wavelength of $\lambda = 3274$ Å. Radiation was generated by a deuterium lamp (8) and separated out of the spectrum with the help of a monochromator MDR23 (6) and a photomultiplier (5).

3. Results

Excitation of a surface slipping discharge in a hydrogen + oxygen + Freon mixture gives rise to combustion of the gas mixture throughout the chamber volume and leads to changes in its chemical structure. The efficiency of the Freon component plasmachemical decomposition in the course of one realization may be inferred by the characteristic results represented in table 1. The table shows data on the degree of decomposition of two types of Freon: Freon-12 (CF_2Cl_2) and Freon-14 (CF_4) at different ratios of the mixture, different values of the initial pressure of the mixture and two different values of energy in a pulse igniting a slipping surface discharge. As shown from the results, in every case of exciting a surface discharge, the gas mixture combustion is accompanied by essential (and, in the majority of experiments, virtually complete) Freon decomposition. This effect of the Freon destruction was recorded in the sufficiently broad range of pressures of the mixture and ratios between hydrogen, oxygen and Freon components.

We have also performed a series of experiments in which SiF_4 and $SiCl_4$ were used as a third component of the mixture. It was shown that, as in the case of the mixtures containing Freon-12 and Freon-14, initiation of combustion by a discharge was accompanied by virtually complete destruction of the initial fluorine- and (or) chlorine-bearing component¹.

When analysing the products of Freon-12 decomposition using an IR-spectrophotometer in a gaseous phase, we revealed extremely weak areas of absorption, which can be identified as lines (bands) corresponding to CF_3Cl , CF_4 , $CFCl_3$, COF_2 , HCl , HF . When experiments were carried out in a quartz chamber or in a metal chamber with quartz windows, strong absorption lines corresponding to SiF_4 were detected. According to the test data, between 20 and 50% of the initial Freon-12 is transformed into SiF_4 in one act of the mixture combustion. If the chamber is metal and the windows are made of KRS-6 ($TlBr-TlCl$), the absorption band of SiF_4 is missing, but an absorption band corresponding to HF molecules is observed.

¹ It is worth noting that deep decomposition of an initial Freon additive is also achieved in the cases when combustion is initiated by a plasmaless technique, namely, with the help of a tungsten filament heated up to a high temperature.

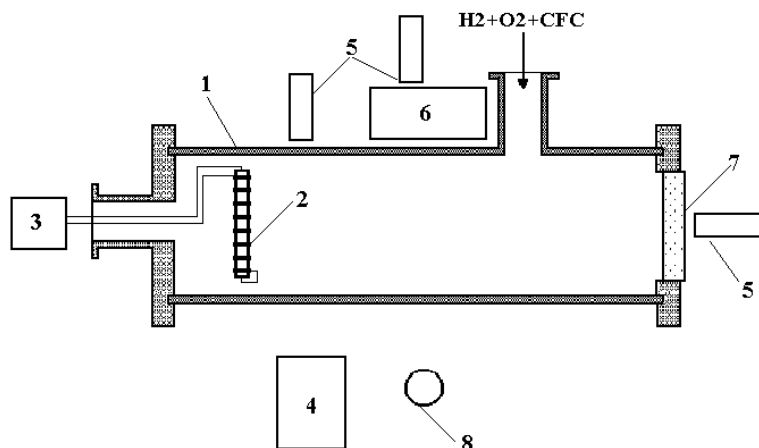


Figure 1. Scheme of experiment: (1) metallic or quartz chamber; (2) discharger initiating combustion; (3) high-voltage power supply; (4) streak camera FER-7; (5) photomultipliers; (6) monochromator MDR-23; (7) quartz or KRS-6 window; (8) UV lamp.

Table 1. Results of Freon decomposition.

Mixture contents	Components ratio	Overall pressure (Torr)	Igniting pulse energy (J)	Degree of Freon component decomposition (%)
$H_2 + O_2 + CF_2Cl_2$	1:1:1	182	10	98.7 ± 0.4
	1:1:1	182	0.1	98.5 ± 0.5
$H_2 + O_2 + CF_4$	1:1:0.5	170	10	89
	2:1:1	243	10	94
	1:1:0.5	152	0.1	40
	2:1:0.5	213	0.1	94
	2:1:1	243	0.1	91

For a mixture of hydrogen+oxygen+Freon-12, the characteristic absorption spectrum in the IR range of the gas medium after initiation of combustion is shown in figure 2. The initial mixture had the ratio $H_2:O_2:CF_2Cl_2 = 1:1:1$ at an overall pressure $p = 180$ Torr. The final pressure of Freon makes up ~ 0.9 Torr, which means that about 98% of the Freon has been destroyed.

We have also performed measurements of molecular chlorine production in initiating combustion using a high-voltage pulse of high energy and low energy. Molecular chlorine was recorded at a wavelength of $\lambda = 3274 \text{ \AA}$ by the absorption of radiation generated by the deuterium lamp ((8) in figure 1) and separated out from the spectrum with the help of the monochromator MDR-23 ((6), in figure 1) and the photomultiplier ((5) in figure 1). The final content of the produced chlorine, that of the initial Freon, and the content of products of its transformation, only slightly depend on the energy contributed to an electrical discharge initiating combustion.

The characteristic time relations of the mixture combustion are exhibited in a signal from the photomultiplier, which records from the end face of the chamber the glow from the reactor integrated over the spectrum and the volume. Figures 3(a) and 3(b) show oscillograms of a signal from the photomultiplier in initiating combustion by a slipping discharge excited by the generator G1 with a low pulse energy (figure 3(a)) and the generator G2 with a high pulse energy (figure 3(b)). At the origin of the beam sweep a short splash of the glow is observed, the source of which is a breakdown

of the metal–dielectric discharger. Then, after some delay, which is much longer than the lifetime of a plasma formation, a ‘long-lived’ glow from the reacting volume of the gas mixture appears. This glow builds up rather slowly, reaches its peak and then slowly decreases. Apparently, it is precisely this glow, which is characterized by the lifetime $\Delta\tau$ determined by the half-height of the ‘long-lived’ part of a pulse, which accounts for the process of the gas mixture combustion. The characteristic lifetimes of the post-discharge glow $\Delta\tau$ depend on the properties of the discharge initiating the combustion, decreasing with the increase in the energy in a pulse igniting a slipping surface discharge. Thus, when initiating by the ‘low-energy’ generator G1, $\Delta\tau \cong 40\text{--}90$ ms. At the same time, when working with the ‘high-energy’ generator G2, $\Delta\tau \cong 5\text{--}10$ ms.

We have also studied the axial distribution of the glow in the quartz reactor with the use of the photomultiplier. For this purpose three light fibres connected to the input window of the photomultiplier were placed along the axis at $\Delta Z \cong 3\text{--}5$ cm intervals. Figures 3(c) and 3(d) show the signal from the photomultiplier obtained when applying ‘low-energy’ or ‘high-energy’ pulses to the discharger igniting the mixture $CF_2Cl_2:H_2:O_2 = 60:60:60$ Torr. There are no characteristic peaks on the oscillogram shown in figure 3(d) (‘high-energy’ pulse) separated in time and pointing to the axial distribution of the combustion as a wave. In any case, the velocity of this wave, if such exists, exceeds $v_z \geq 10^5 \text{ cm s}^{-1}$. Attention should also be paid to the characteristic fluctuations of the glow with a frequency of about $f \geq 1 \text{ kHz}$. The glowing duration

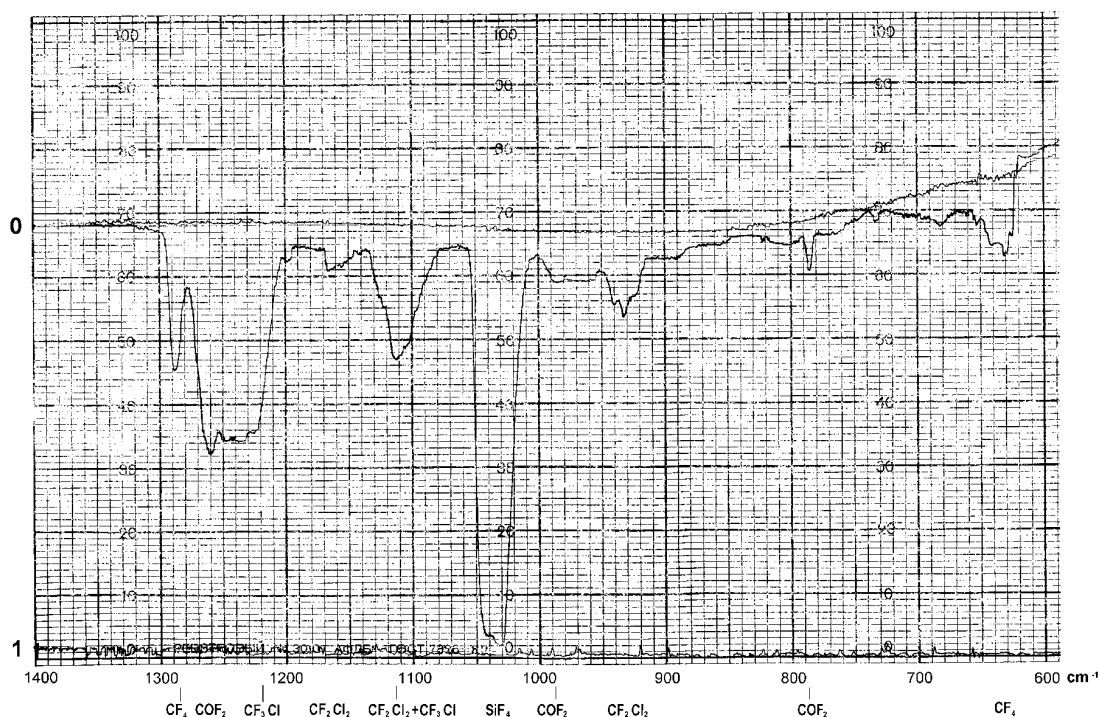


Figure 2. Absorption spectrum in the IR range ($1400\text{--}600\text{ cm}^{-1}$) of a ternary gaseous mixture hydrogen+oxygen+ CF_2Cl_2 after combustion initiated by slipping surface discharge. Initial composition of gaseous mixture: $\text{H}_2:\text{O}_2:\text{CF}_2\text{Cl}_2 = 60:60:60$ Torr. On the vertical axis '0' refers to the total transmission and '1' to the total absorption of IR radiation.

identified with the combustion process is much longer under initiation by the 'low-energy' pulse than in the case of 'high-energy' pulse lighting.

The oscillograms shown in figure 3 have been received at different oscillographic amplifications and different photomultiplier voltages and demonstrate only a temporal behaviour of visible light irradiated by the reactor. At the same time, a correlation between the signals in their amplitudes testifies that the radiation in the discharge stage using generator G2 is much higher than that with generator G1. As to the integral over the post-discharge glow associated with the combustion of a gas mixture it has a weak dependence on the energy of the igniting pulse.

The dynamics of the glow from the working gas mixture exposed to an electrical discharge, which was localized at the end flange, was investigated with the help of the photoelectric recorded FER-7. The slot of the recorder was placed along the axis of the chamber, thus isolating for viewing an area of length $\Delta Z \cong 90\text{ mm}$ and width $\Delta Y \cong 5\text{--}6\text{ mm}$. Characteristic photographs are shown in figures 4 and 5. The recorded light signal displacement along the horizontal axis represents the time displacement, while that along the vertical axis depicts the axial displacement. The full duration of the time sweep in a frame makes up $\Delta\tau_p \cong 3\text{ ms}$.

The FER-7 is selected to start recording in order to catch the time of excitation and the existence of an electrical discharge, which initiates the combustion in the reactor. A vertical glowing band, seen on the left of the photographs, corresponds to the lifetimes of a discharge on the initiating discharger. The streak camera FER-7 is adjusted in such a way as to record the glow of one of the discharge gaps of the multielectrode devices on the electro-discharge initiator.

It is precisely the bright glow in the centre of the band that represents the interelectrode space glow at the surface of the initiator.

Figures 4 and 5 were obtained at different energy values, which contribute to the slipping surface discharge on the initiator ($\sim 0.1\text{ J}$ in figure 4 and $\sim 30\text{ J}$ in figure 5). Figure 4(a) shows a photograph for the hydrogen-oxygen mixture $\text{H}_2:\text{O}_2 = 60:60$ Torr (without the addition of Freon), while figures 4(b) and 4(c) depict the same mixture with the addition of 30 and 75 Torr of Freon-12, respectively. In figures 4(a) and 4(b) the streak camera started recording at the same time as a high-voltage pulse was applied to the electro-discharge initiator. In figure 4(c) the FER-7 was started 3 ms after starting the electro-discharge initiator, demonstrating the uniformity of the luminosity well into the post-discharge time. Figures 5(a) and 5(b) differ by the content of Freon-12 in the mixture (60 and 75 Torr, respectively). The streak camera started recording at the same time as a high-voltage pulse was applied to the electro-discharge initiator.

Following on from the above photographs, a glow wave breaks away into the surrounding gas from the discharge, appearing near the discharger surface. This wave looks like a luminous strip (with axial dimension $\Delta Z_w \cong 6\text{--}7\text{ mm}$) moving along the Z-axis. The velocity of the glow wave remains almost constant over a period of time (τ_1) then the wave slows down and stops at some distance, ΔZ_1 , from the discharger. Shortly after stopping (at the instant τ_2), increasing fluctuations of the wave front are observed. Simultaneously, the appearance of a relatively weak and uniform glow occupying almost the whole length of the chamber is observed. Glow waves moving to meet the initial wave (namely, toward the initiator) are silhouetted against the background uniform luminescence.

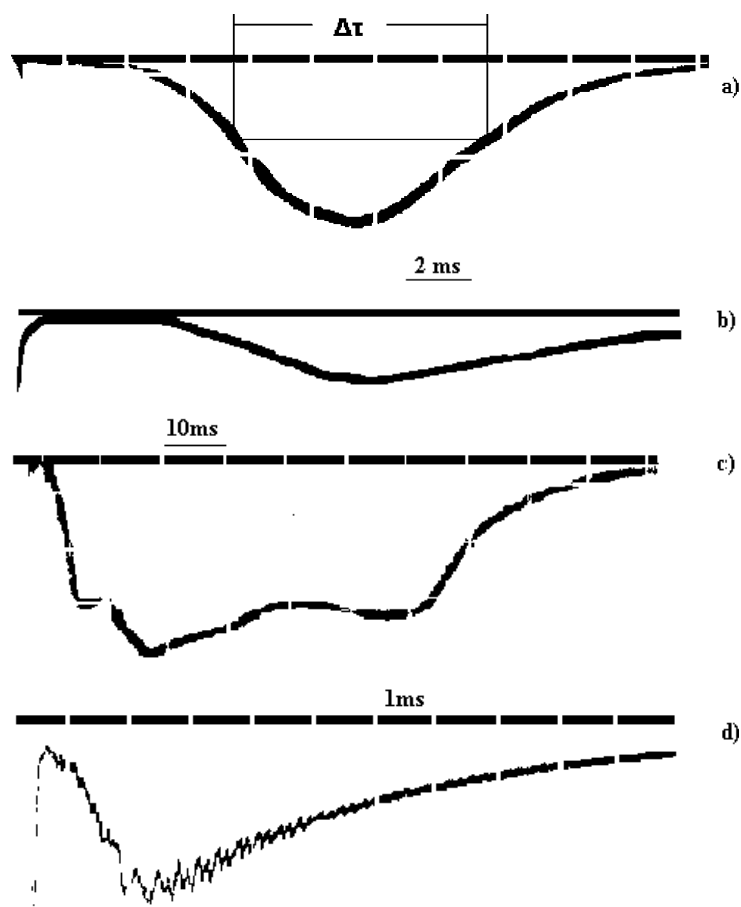


Figure 3. Oscillograms from the photomultiplier under the detection of light emission through the end of the metallic chamber (a, b) and along the axis of the quartz chamber (c, d). (a, c) 'low-energy' pulses initiating combustion; (b, d) 'high-energy' pulses initiating combustion. Initial composition of gaseous mixture: $\text{H}_2:\text{O}_2:\text{CF}_2\text{Cl}_2 = 60:60:96$ Torr (a, b); and $\text{H}_2:\text{O}_2:\text{CF}_2\text{Cl}_2 = 60:60:60$ Torr (c, d).

4. Discussion

A comparison with previously published data allows us to point out in the performed research, based on using a new high-power electro-discharge device, results which are of obvious interest from a physics (physicochemistry) point of view, as well as some actual applications.

The fast combustion of a three-component gas mixture is very interesting *per se*. Two-component mixtures (oxygen-hydrogen), such as the combustible gas, have been studied quite extensively (see, for example, [4, 9–11]). The basis for ignition (with a fast, explosive energy release) of an oxygen-hydrogen mixture is formed by chain branching processes described by the well known and thoroughly developed reactionary scheme.

The addition of a third component (Freon, SiF_4 , SiCl_4) with a partial pressure comparable with that of the oxygen and hydrogen components, renders the realization of the chain process basically questionable, as the availability of a significant number of chlorine- or fluorine-bearing molecules may interrupt the chain of interactions between the elements of a two-component mixture. However, experiments have shown that the addition of a Freon (chlorine- or fluorine-bearing) component maintains the process of chain ignition. Thus, the existence of fast combustion in a three-component, oxygen-hydrogen-Freon mixture may be regarded as a novel approach.

The dynamics of combustion initiated by a pulse surface slipping discharge is of unconditional interest for the physics of observable phenomena. As follows from the results of high-speed photography, a discharge on the initiator gives rise to a glow wave emanating from the discharger and going into the surrounding gas medium. At the beginning of the process the wave is propagated in a direction orthogonal to the initiator, with a virtually constant velocity. However, at some distance, ΔZ_1 , from the discharger the wave slows down and halts. Then, after a certain time interval, fluctuations of the 'halted' front and a glow flash along the whole length of the reactor chamber are observed.

Such is the scenario of the gas medium response to a pulse discharge, which takes place at the initial stage preceding the basic process of the gas mixture combustion in the volume of the reactor. The time intervals spanned by the initial stage do not exceed 3 ms and are comparable to the time delay of the initiation of the glow recorded by the photomultiplier and attributed to the volume combustion of a mixture. The time of the combustion itself significantly exceeds the lifetime of the initial glow wave and, depending on the energy contribution to the discharge initiating the combustion, makes up 10–90 ms.

The observable glow wave propagates along the Z -axis of the reactor, with the velocity increasing with a rise in the energy release. So, in the case of a 'high-energy' initiating discharge in a mixture of $\text{CF}_2\text{Cl}_2:\text{H}_2:\text{O}_2$

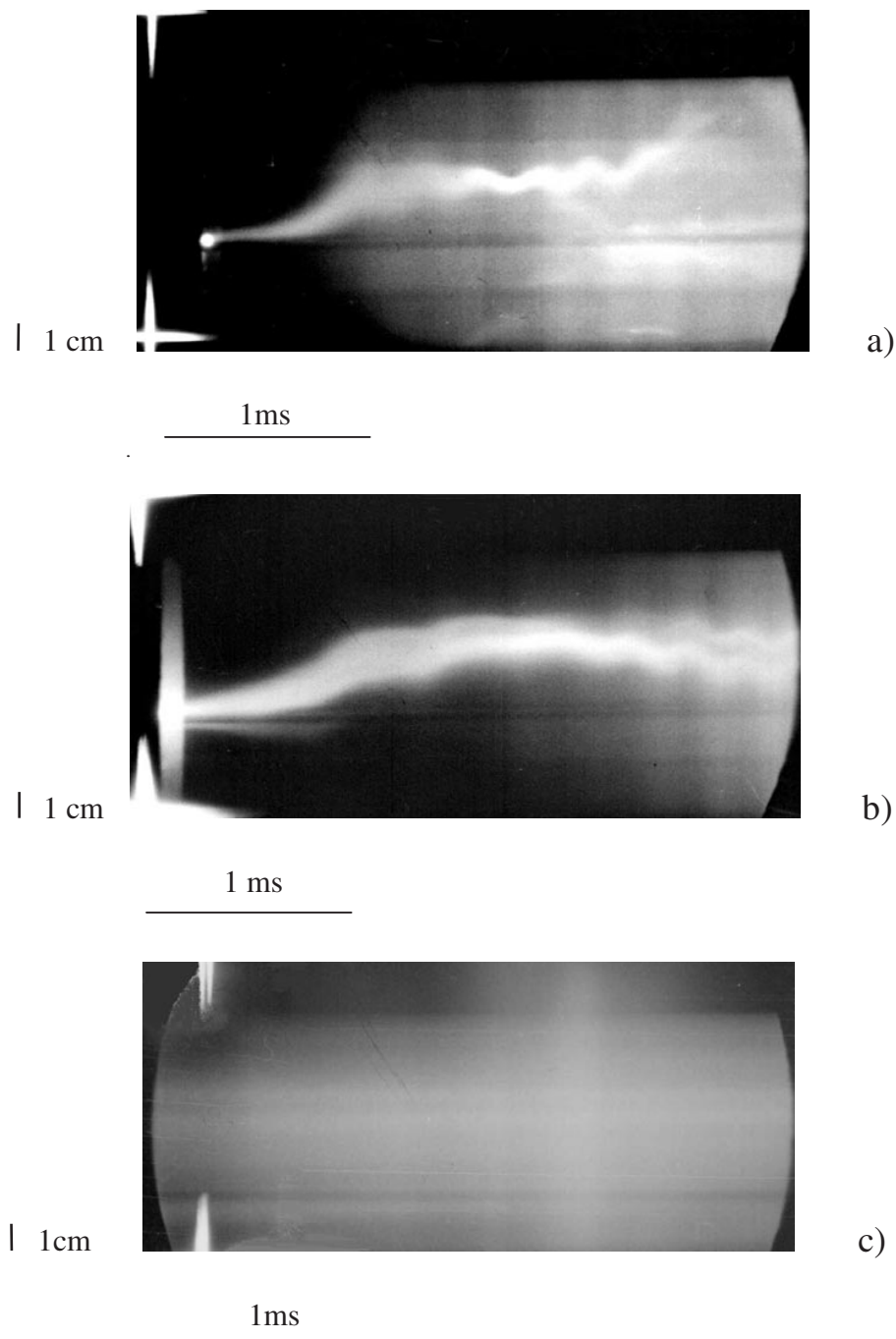


Figure 4. Characteristic photographs taken by the streak camera under the combustion initiation with ‘low-energy’ pulses. (a) $\text{H}_2:\text{O}_2 = 60:60$ Torr; (b) $\text{H}_2:\text{O}_2:\text{CF}_2\text{Cl}_2 = 60:60:30$ Torr; (c) $\text{H}_2:\text{O}_2:\text{CF}_2\text{Cl}_2 = 60:60:75$ Torr.

$= 60:60:60$ Torr, the axial velocity of the initial glow wave amounts to $v_z \cong 3 \times 10^4 \text{ cm s}^{-1}$. For the ‘low-energy’ initiation in a mixture of $\text{CF}_2\text{Cl}_2:\text{H}_2:\text{O}_2 = 30:60:60$ Torr, $v_z \cong 2 \times 10^3 \text{ cm s}^{-1}$, while in a mixture of $\text{CF}_2\text{Cl}_2:\text{H}_2:\text{O}_2 = 60:60:60$ Torr, $v_z \cong 8 \times 10^2 \text{ cm s}^{-1}$. The observable glow wave cannot be identified with a detonation wave, as the measured propagation velocity is much less than the detonation velocity in a hydrogen–oxygen mixture (which amounts to, according to [12, 13], some 10^5 cm s^{-1}). The wave (first of all, in the case of the ‘high-energy’ initiation) can hardly be attributed to the combustion waves described in the literature,

since velocities of such waves at standard ignition are lower than those recorded in the present experiment (see, for example, [9]).

The final part of the process is even more unusual, as once the initial glow has halted, a flash along the whole length of the chamber is observed, followed by the more or less homogeneous combustion of the mixture as a whole.

Thus, application of the high-current initiator on a slipping surface discharge changes significantly the process of ignition of the gaseous volume remote from the initiator (as compared with standard low-power two-electrode spark

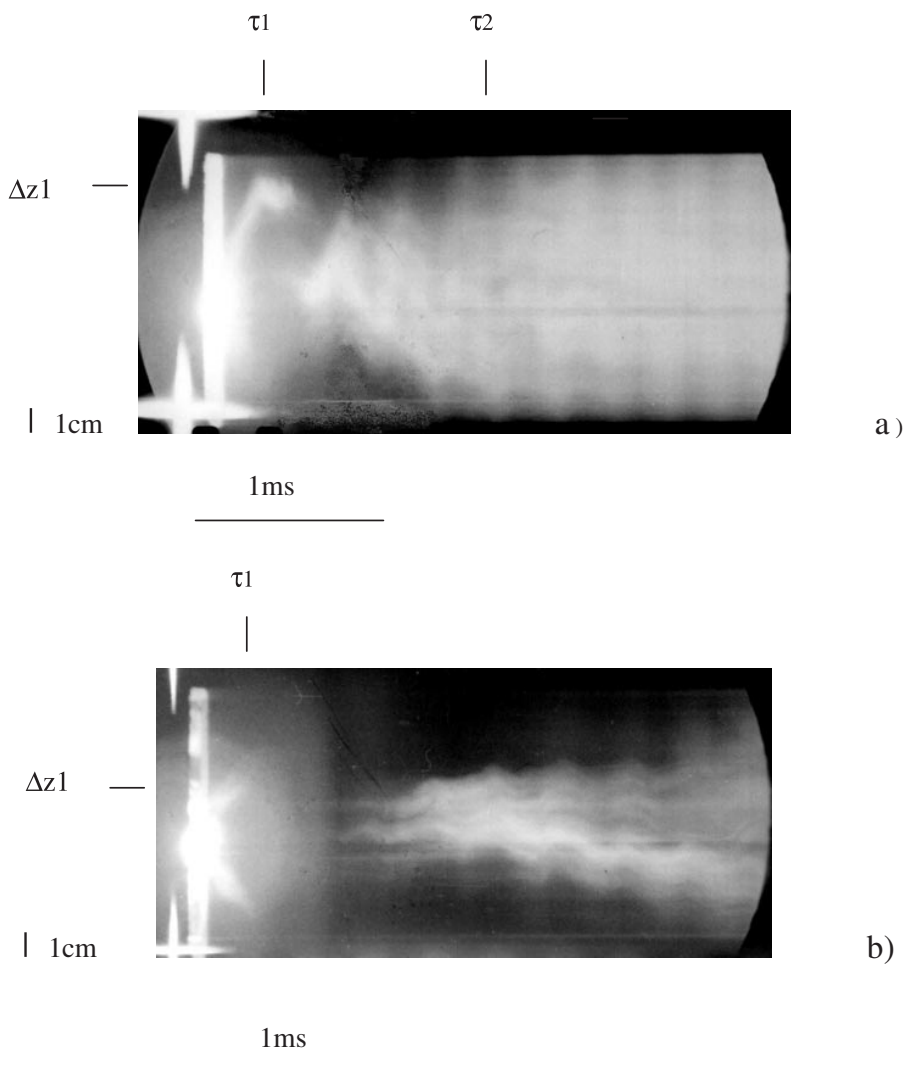


Figure 5. Characteristic photographs taken by the streak camera under the combustion initiation with ‘high-energy’ pulses. (a) $\text{H}_2:\text{O}_2:\text{CF}_2\text{Cl}_2 = 60:60:60$ Torr; (b) $\text{H}_2:\text{O}_2:\text{CF}_2\text{Cl}_2 = 60:60:75$ Torr.

ignition or ignition with a heated up metal filament). The standard dynamics of combustion, described by thermal or detonation waves propagated from a point of local heating (or a breakdown) of gas medium, is replaced—on initiating by a high-current slipping discharge—by a complicated sequence of phenomena. Such a sequence consists of exciting a wave that lifts off the initiator and halts in the vicinity of the initiator with subsequent homogeneous combustion throughout the whole volume of the reactor. In this case the glow wave cannot be identified with a combustion wave or with a detonation wave.

The ‘combustion’ time of a gas mixture depends significantly on the energy released at initiation, decreasing with an increase in that energy (40–90 ms for a ‘low-energy’ generator and 5–10 ms for a ‘high-energy’ generator). This property of combustion initiated by a high-current surface slipping discharge is also of interest from the viewpoint of fundamental physics. At the same time the detected phenomenon opens up fresh opportunities for applications, permitting one to influence the combustion rate of an oxygen–hydrogen mixture through the parameters of an initiator.

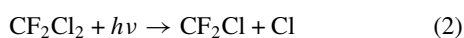
Analysing the results, we may assume that the radiation of a high-current surface discharge plays a decisive role in the observable pattern. The intensity of this radiation and its spectrum should essentially differ from the intensity and spectrum of a spark commonly used as an initiator of combustion in gas mixtures.

The specificity of a high-current ($I \cong 10^2\text{--}5 \times 10^3$ A) slipping discharge as an emanating object has been previously highlighted in a series of publications. In particular, in [14] a high fraction of a relatively rigid UV component was observed in the slipping discharge spectrum. This component leads to the formation of an anomalously long-lived photoionized plasma in the gas medium surrounding the discharge. In [15], the highly effective decomposition of Freon in the volume of a gas mixture filling the reactor (argon+Freon, air+Freon) was also explained by the singularities of the slipping discharge radiation leading to photo-ionization, photoexcitation and photodissociation of the gas remote from the energy release area.

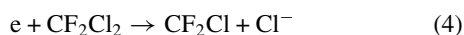
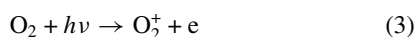
The ability of a high-current surface discharge to significantly affect the properties of a gas medium in a volume

which considerably exceeds the volume occupied by a plasma formation may be regarded as one of the peculiarities of this type of gas discharge.

As for the experiments with the hydrogen+oxygen+Freon mixture, it also seems probable that during its short lifetime (from a few tens of nanoseconds up to several microseconds) a high-current discharge pressed to the surface of the discharger leads not only to the initiation of plasmachemical phenomena in its immediate vicinity, but also—through an UV radiation component—to the modification of the gas medium characteristics virtually in the whole volume of the reactor. The flash of UV radiation transforms the initial mixture of molecules H_2 , O_2 , CF_2Cl_2 (or any other Freon) into a new mixture containing, among the initial components, new components that are extremely active chemically. Thus, for example, a series of processes may give rise to atomic chlorine (or negative ions of chlorine). Among these processes the reaction of direct photodissociation should be mentioned:

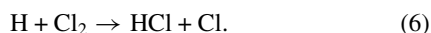


as well as a series of indirect processes related to photoionization, such as:

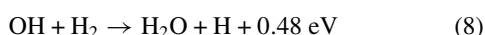


UV radiation may also lead to the photodissociation of molecular oxygen and the production of electron-excited metastable atoms or molecules of oxygen (for example, oxygen singlets). There is also a possibility of direct or indirect dissociation of hydrogen molecules.

All the above-mentioned processes may increase the probability of ignition—up to the point of spontaneous ignition—of the investigated three-component mixture. Thus, the production of atomic chlorine may give rise to a new chain cycle, which is complementary to that of oxygen–hydrogen, namely [4]:



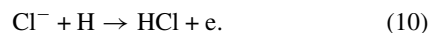
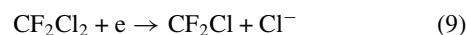
According to [8, 11], the production of atomic hydrogen and atomic oxygen may initiate a thermal explosion in the hydrogen–oxygen mixture. So, in [4] it was stressed that the role of primary centres of ignition may play hydrogen atoms emerging as a result of photochemical processes and participating in a catalytic cycle characterized by a significant energy release:



Thus, in the whole volume of the reactor, available for penetration of UV radiation generated by a high-current slipping surface discharge, ‘combustibility’ of the mixture is increased up to the point of its spontaneous ignition.

Photoexcitation of molecular oxygen and its de-excitation during the propagation of hydrodynamic perturbation from the discharger surface may also be related to a glow wave observed in the initial phase of the process preceding the combustion.

When analysing chemical and discharge kinetics of the investigated reactor, one has to bear in mind the possibility of a catalytic process involving an electronic component, the role of which in fast and deep decomposition of Freons was highlighted in [16]. For example, the following cycle of reactions:



The chemical influence of UV radiation on the water formation reaction was revealed by Andreev as early as in 1911 [17]. References [8, 11] describe the series of experiments in which a hydrogen–oxygen mixture was exposed to UV lamp radiation, and it was demonstrated that the growth of the rate of the hydrogen oxidation reaction occurred due to the dissociation of the oxygen molecules. A series of experiments on the dissociation of hydrogen molecules (through the mechanism of sensitization) was also performed, and it was shown that it led to the significant acceleration of combustion of the $H_2 + O_2$ mixture.

Quite recently it was shown that a spark excited by a CO_2 laser in a propane–air mixture initiated explosive combustion [18]. The authors of this work attribute the observable phenomenon to the essential modification of the initial combustible mixture structure under the action of a spark.

It is not improbable that the processes leading to the acceleration of combustion by a laser spark are closely related to the processes developed in our experiment, where for the first time an open high-power surface discharge (without quartz walls as in a UV lamp) has been used as an irradiation source for a combustible medium. It is precisely this type of discharge that determines the specificity of the observable phenomena.

The above general considerations should be strengthened with detailed theoretical analysis based on a kinetic scheme of the processes, thus on a gas-dynamic model describing conditions specific to the given experiment. However, it should be noted that the above-described experiments are of independent applied value, pointing toward the possibility of creating a high-performance reactor for utilizing both ozone-depleting Freons and Freons with a high greenhouse potential.

Based on the results obtained, it is easy to evaluate the efficiency of a reactor representing a discharger of a described type placed in a cylindrical chamber of cross section S and length L . For this purpose we may use the simple relationship:

$$\eta \approx 2 \times 10^{-7} p_p M S L / \tau_c \quad (\text{kg h}^{-1}) \quad (11)$$

where p_p is partial pressure of the decomposed Freon (CF_2Cl_2) in Torr; M is the molecular weight of the decomposed Freon ($M \cong 120$); and τ_c is the burn-up time of the mixture (s). For $p_p = 100$ Torr, $S = 20 \text{ cm}^2$; $L = 50 \text{ cm}$ and $\tau_c = 10^{-2} \text{ s}$, $\eta \approx 200 \text{ kg h}^{-1}$. In this case the consumed electrical power will not exceed 50 W, which means that the energy cost of decomposition (i.e. expenditure on electrical energy) will be $W \approx 2 \times 10^{-4} \text{ kW h kg}^{-1}$, which is many orders of magnitude lower than in the case of plasmachemical decomposition of a combustible gas mixture (see [1, 2] and equation (1)).

For ensuring high efficiency of the reactor, the gas flow velocity through its chamber should be:

$$v \approx L / \tau_c \approx 5 \times 10^3 \text{ cm s}^{-1} \quad (12)$$

which is, apparently, quite simple to realize. It is evident that such a reactor is reasonable to use through the utilization of ozone-depleting Freons as well as greenhouse gases containing Cl and F.

Performance studies similar to those described in this article using various gaseous-phase combustible mixtures, including a methane-air mixture, will doubtless be of interest. The possibility of 'explosive' utilization of chlorofluorocarbons in mixtures of this type will make the plasmachemical reactor essentially cheaper.

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