INVESTIGATION OF THE REGION OF INHIBITION OF THE FLAMES OF H₂-O₂-N₂ MIXTURES BY HALOGENATED HYDROCARBONS

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In this paper we present the results of a series of experiments concerning the effect of tetrafluorodibromomethane and ethyl bromide on the development of the explosion in a constant-volume bomb and the normal burning velocity of hydrogen-air mixtures.

The inhibiting effect of alkyl halides on flames is known to depend on a complex of physicochemical processes. The numerous previous investigations in this area have generally involved the estimation of the effect of such additives on the ignition region and burning velocity [1].

It is worthwhile tracing the effect of inhibitors on the development of explosion. This is a universal method, since it permits the determination of the effect of the additives on explosion pressure, burning velocity, and the degree of reaction, as well as an analysis of the reaction products. The investigations were carried out with the apparatus shown schematically in Fig. 1. An H₂-O₂-N₂ mixture of given composition was prepared in chamber 5, carefully mixed and ignited by a spark obtained by discharging a 0.25-μF capacitor at a plate voltage of 4 kV. The explosion pressure was measured with transducers and the results recorded on a loop oscillograph. From the p = f(t) diagrams we calculated the normal burning velocity:

\[ \frac{\mu_n}{d} = \frac{1}{\tau_p} \sqrt{\frac{3(p - p_0)}{4\varepsilon(t - 1)}}, \]

where \( p \) is the explosion pressure in kg/cm²; \( p_0 \) is the initial chamber pressure (atmospheric) in kg/cm²; \( v \) the chamber volume in cm³; \( \tau_p \) the time required for the chamber pressure to rise to the value \( p = 0.05 \) gauge atm, in sec; and \( \varepsilon \) the expansion coefficient, which takes into account the change in the molarity and temperature of the gas mixture in the process of combustion.

Fig. 1. Experimental apparatus, schematic: 1) gas meter with mixture, 2) nitrogen cylinder, 3) absorption bottles, 4) drying columns, 5) vacuum gauge, 6) igniter, 7) fan, 8) 20-liter explosion vessel, 9) amplifier, 10) loop oscillograph, 11) synchronization unit, 12) high-voltage source (T₁ and T₂ pressure transducers).

Strictly speaking, \( \varepsilon \) is not a constant; however, during the initial period of development of the explosion, corresponding to the combustion of about 3% of the starting volume, the variation of \( \varepsilon \) can be neglected [2].
The extent of hydrogen combustion was estimated from the change in mixture volume during combustion and by analyzing the reaction products in a "Tsvet" chromatograph. The samples for analysis were obtained with an aspirator filled with alkali solution. After neutralization of the acid reaction products (pH) and drying in a calcium chloride column, the samples were separated chromatographically on 5-Å molecular sieves. The analysis was directed primarily toward determining the residual oxygen content.

In addition, we determined the normal burning velocity of a hydrogen-air mixture containing tetrafluoro-dibromoethane and ethyl bromide by the bunsen-burner method. The burning velocity was obtained from schlieren photographs of the flame cone [2] in accordance with the formula

$$u_n = \frac{w \cdot \sin \frac{\alpha}{2}}{V \cdot \tau_m},$$

where $w$ is the mean velocity of the gas mixture in cm/sec and $\alpha$ is the angle of the cone tip.

At the same time, by photographing the flame cone we directly determined the thickness of the luminous zone, which was measured on an MF-4 microphotometer with ten-fold magnification of the flame image obtained on the film. From these data we were able to estimate the change in the mean molecular weight of the active chain carriers, in accordance with the Van Tiggelen theory [3], from the equation

$$\frac{u_n}{V \cdot \tau_m} = \frac{\text{const}}{V \cdot M_R} \cdot \frac{1}{S},$$

where $u_n$ is the normal burning velocity referred to the unignited gas, in cm/sec; $M_R$ is the mean molecular weight of the active chain carriers; $S$ is the thickness of the flame front, in cm; and $T_m$ is the mean flame temperature (°K), which in accordance with [4], was taken as $T_m = T_0 + 0.74(T_f - T_0)$ ($T_f$ is the theoretical flame temperature, $T_0$ the initial temperature of the mixture).

The effect of additives on the development of the explosion of a hydrogen-air mixture is illustrated in Fig. 2. As the investigated alkyl halides are introduced, the rate of pressure increase is markedly reduced. This reduction is particularly effective when the first small amounts of inhibitor are introduced. Mixtures rich in the fuel component are inhibited much more easily than lean mixtures. When only about 0.85% C$_2$F$_4$Br$_2$ is added to a mixture containing 60% hydrogen, the mixture becomes nonexplosive. In the case of lean mixtures the flame is propagated even after the inhibitor is introduced in amounts exceeding 5%.

It is interesting to note that adding inhibitors reduces the resultant explosion pressure, which is obviously attributable to the dilution of the mixture and the reduced temperature of the combustion products. In rich mixtures, however, a constant value of the resultant explosion pressure is preserved up to the cessation of combustion, which indicates the absence of a significant reduction in combustion temperature. These facts suggest that when C$_2$F$_4$Br$_2$ and C$_2$H$_5$Br are introduced into lean mixtures the reduction in burning velocity is achieved both by chemical inhibition and by dilution of the fuel mixture, while in the case of rich mixtures combustion is chiefly suppressed by the first factor (Fig. 3).

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As the C$_2$F$_4$Br$_2$ content increases, $u_n$ begins to fall (for example, for a mixture with 10% H$_2$) according to a