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Abstract

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ON THE QUESTION OF THE ROLE OF OZONE IN INITIATING OXIDATION REACTIONS OF SATURATED GASEOUS HYDROCARBONS

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Ozone, like many other active admixtures, when added in small amounts to hydrocarbon-oxygen mixtures, considerably lowers the reaction temperature. In the literature there are contradictory reports on the mechanism of the action of ozone. Many investigators believe ($^{1-4}$) that the oxidation of saturated hydrocarbons in the presence of ozone is connected with the direct reaction of the ozone molecule with the fuel. However, in recent years papers have appeared (^{5,6}) in which, using the oxidation of carbon monoxide as an example, it has been established that low-temperature oxidative processes in the presence of ozone are connected with initiation by atomic oxygen formed during the thermal decomposition of ozone. In a recently published paper (^{7}) on the oxidation of methane in the presence of small amounts of ozone, we, on the basis of a number of facts, including the phenomenon observed by us of the coincidence of the temperature of ozone decomposition with the temperature at which a measurable reaction of methane oxidation begins, came to the conclusion that initiation of the oxidation reaction is effected precisely by oxygen atoms.

In the present communication some new data are given on the oxidation of propane and hydrogen which, as it seems to us, confirm the previously expressed idea of the mechanism of ozone action through oxygen atoms. The experiments were carried out at atmospheric pressure in a flow apparatus. The products of propane oxidation—peroxides and aldehydes—were trapped by water and then analyzed by the usual methods: the sum of peroxides was determined iodometrically, and aldehydes by the hydroxylamine method. In experiments on the oxidation of hydrogen, the reacting gases after leaving the reactor were throttled, with the aid of a glass valve, to fractions of a millimeter of mercury column, and the water formed in the reaction was frozen out in a trap cooled with liquid nitrogen. The amount of water formed, after thawing into a calibrated volume, was determined with the aid of a membrane manometer.

Fig. 1. Temperature dependence of the oxidation of hydrogen. Initial mixture:

Fig. 2

Figure 1: Fig. 2

$H_2 = 50\%$, $O_2 = 50\%$; ozone content 0.41%. Total pressure 760 mm Hg, contact time 21 sec.
1—amount of decomposed ozone, 2—amount of water formed.

Experimental data on the oxidation of hydrogen by ozonized oxygen are presented in Fig. 1, from which it is seen that noticeable decomposition of ozone begins at a temperature of 85°. At the same temperature the reaction of hydrogen oxidation begins. With an increase in the contact time from 21 to

40 sec, the temperature at which ozone decomposition begins is lowered by 20–25°. At the same time, the temperature at which the hydrogen oxidation reaction begins is lowered by the same amount.

An analogous picture is observed in the oxidation of propane. In this case, as in the oxidation of methane and hydrogen, the onset of oxidation, as is seen from Fig. 2, coincides with the onset of ozone decomposition.

Fig. 2. Temperature dependence of propane oxidation. Initial mixture: $C_3H_8 = 62\%$, $O_2 = 38\%$; ozone content 2.09%. Contact time 6 sec. 1 —amount of ozone decomposed, 2 —amount of organic peroxides formed, 3 —amount of aldehydes formed

Thus, for the three substances investigated—methane, propane, and hydrogen—the onset of the oxidation reaction coincides with the onset of ozone decomposition. Such a coincidence is evidently associated with the formation of some active particles—atoms or excited oxygen molecules—which initiate chain oxidation.

Further experiments were directed toward elucidating the nature of the initiation. If initiation of the oxidation reaction is brought about by excited oxygen molecules, then additions of an inert gas will increase the rate of deactivation of the excited oxygen molecules and, accordingly, will lower the reaction rate.

For the hydrogen oxidation reaction, experiments were carried out with the reacting mixture remaining in the reaction zone for 16 sec and at a temperature of 206°, ensuring complete decomposition of ozone during the reaction time. In the absence of an inert gas, at a total pressure $P_{\mathrm{H2+O_2+O_3}} = 100$ mm Hg, the reaction rate, found from the amount of water formed, was $2.2 \cdot 10^{-7}$ mol/sec. Upon dilution of the same mixture by a factor of 7.4, when $P_{\mathrm{H2+O_2+O_3+}N_2} = 740$ mm Hg, the rate proved to be $2.5 \cdot 10^{-7}$ mol/sec, i.e., it practically did not change. These data make it possible to consider that excited oxygen molecules do not play a substantial role in the oxidation reaction and, consequently, the initiation of the reaction must be associated with the reaction of atomic oxygen.

In order to verify the correctness of the conclusion reached, we carried out

Fig. 3

Figure 2: Fig. 3

experiments on initiation of the reaction by oxygen atoms produced directly in a mixture of methane with oxygen. For this purpose photochemical initiation was used. The reacting mixture was irradiated at room temperature with ultraviolet light obtained from a hydrogen discharge tube, separated from the reaction zone by a fluorite window. The experiments were carried out in jet and circulation apparatuses at different pressures. The reaction products at the reactor outlet were frozen out in a trap immersed in liquid nitrogen. Special experiments established that methane, under the conditions of our experiments, is completely transparent. In all experiments the oxygen pressure was selected so as to ensure complete absorption of the Schumann region of the spectrum.

Fig. 3. Effect of dilution of a methane-oxygen mixture with nitrogen on the rate of formation of methyl hydroperoxide during photochemical oxidation of methane under the action of the Schumann region of the spectrum. Initial mixture: $CH_4 = 75\%$, $O_2 = 25\%$. Pressure $P_{CH_4} + P_{O_2} = 30$ mm Hg, $t = 20^\circ$

Under circulation conditions for a methane-oxygen mixture (75% CH_4 and 25% O_2) at a pressure of 15 mm Hg, in a 5-hour experiment with freezing out of the reaction products at the temperature of liquid nitrogen, about 9% of the initial methane was oxidized to methyl hydroperoxide and about 7% to formaldehyde. The nearest

consideration of the dependence of these products on the contact time led us to the conclusion that formaldehyde, in all probability, is a secondary product arising upon further photochemical decomposition of the hydroperoxide.

To make certain that in the photochemical reaction, too, initiation is associated specifically with oxygen atoms, and not with excited molecules, whose formation is possible at $\lambda < 2000$ Å, the same method was used of diluting the mixture with an inert gas—nitrogen. The dilution coefficient was varied up to 10. These experiments were carried out using a methane-oxygen mixture as an example. The data from this series of experiments are presented in Fig. 3. The fact that, over a wide interval of dilution of the methane-oxygen mixture with nitrogen, the rate of the methane oxidation reaction remains constant indicates that in these experiments as well, initiation is not associated with excited oxygen molecules. The totality of the data described in the present investigation, as well as in the preceding work, leads us to the conclusion that, in the oxidation of saturated gaseous hydrocarbons by ozonized oxygen, the reaction is initiated by oxygen atoms formed during the thermal decomposition of ozone.

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Note: Figure translations are in progress. See original paper for figures.