INVESTIGATION OF THE REACTION OF LOW-TEMPERATURE OXIDATION OF METHANE INITIATED BY OXYGEN ATOMS FORMED DURING THE THERMAL DECOMPOSITION OF OZONE

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INVESTIGATION OF THE REACTION OF LOW-TEMPERATURE OXIDATION OF METHANE INITIATED BY OXYGEN ATOMS FORMED DURING THE THERMAL DECOMPOSITION OF OZONE

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In previous works (1) it was shown that, in the oxidation of methane by ozonized oxygen, the reaction is initiated by oxygen atoms arising as a result of the thermal decomposition of ozone. Under these conditions the principal reaction products are methyl hydroperoxide and formaldehyde. It seemed important to study the dependence of the yield of these products on various parameters: the composition of the mixture, the ozone concentration, the contact time, etc., and to compare the regularities obtained with the results for the mercury-sensitized oxidation of methane and its higher homologues, where the initial active centers initiating chain oxidation are alkyl radicals.

Experiments on oxidation with ozonized oxygen were carried out at atmospheric pressure in a jet apparatus, with contact times from 6 to 32 sec. Aeration methane was used in the work, carefully purified from carbon dioxide and traces of unsaturated hydrocarbons. The oxygen was taken from a cylinder and thoroughly dried by passage through sulfuric acid. Ozone was obtained by passing part of the oxygen supplied to the reactor through three ozonizers connected in series. Analysis for ozone and methyl hydroperoxide was carried out by the iodometric method. Formaldehyde was determined by the polarographic or hydroxylamine method.

Results of the Experiments and Their Discussion

Figure 1 presents kinetic curves for the formation of methyl hydroperoxide, obtained for three mixture compositions at $T = 150°$. The experiments were carried out under conditions of constant ozone concentration in the initial mixture and under conditions in which the exit gases contained a certain amount of undecomposed ozone. As can be seen, in the investigated range of residence times the peroxide yield increases according to a linear law.

Figure 2 shows the relation between the yield of peroxide and formaldehyde and

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

the ozone concentration for an equimolecular mixture of methane with oxygen at a contact time of 21 sec and temperatures of 150 and 180°. It is evident from the figure that the amounts of peroxide and formaldehyde formed are proportional to the concentration of the initial ozone in the mixture. It should be noted that the linear dependence is retained as long as the exit gases contain ozone. At high temperatures (200° and above), when the gas entering the reactor

ozone decomposes before reaching its end, and the proportional dependence is disturbed.

To clarify the influence of methane on the yield of methyl hydroperoxide, a special series of experiments was carried out. These experiments were conducted at $T = 150^{\circ}$, a constant contact time ($t = 21$ sec), and an ozone content in the initial mixture equal to 1.08%. In all experiments the oxygen concentration was kept constant, while the methane concentration was varied by replacing part of it with nitrogen. From the data obtained it followed that the amount of peroxide formed increases with increasing methane concentration according to a linear law. Analysis of the exit gases showed that in these experiments the amount of decomposed ozone remains constant. A similar dependence was obtained at $T = 180^{\circ}$.

If the oxygen concentration is not kept constant during the experiments, and the composition of the mixture is changed by replacing oxygen with methane, then in this case, as is seen from Fig. 3 (curve 1), the linear dependence between the amount of peroxide formed and the methane concentration is disturbed. Detailed consideration shows that the deviation from linearity is connected with the fact that, as the methane concentration increases, the amount of decomposed ozone increases, owing to which the amount of peroxide formed also increases.

Fig. 1. Dependence of the yield of methyl hydroperoxide on contact time for three compositions of the mixture. $T = 150^{\circ}$. Ozone concentration in the initial mixture 0.32 vol. %.
1—10% CH_4 + 90% O_2, 2—50% CH_4 + 50% O_2, 3—90% CH_4 + 10% O_2.

Fig. 2. Dependence of the yield of methyl hydroperoxide (1, 2) and formaldehyde (3, 4) on the ozone concentration in the initial mixture at two temperatures. 1, 3 at 150°, 2, 4 at 181°. Contact time 21 sec. Mixture composition: 50% CH_4 + 50% O_2.

Fig. 3. Dependence of the yield of methyl hydroperoxide (1) and the decomposition of ozone (2) on the composition of the methane-oxygen mixture. 3—

Fig. 3

Figure 3: Fig. 3

Fig. 4. Dependence of the yield of methyl hydroperoxide (1) and ozone decomposition (2) on oxygen concentration at a constant methane concentration of 10% and ozone of 0.3 vol. %. $T = 150°$. Contact time 21 sec.

Figure 4: Fig. 4. Dependence of the yield of methyl hydroperoxide (1) and ozone decomposition (2) on oxygen concentration at a constant methane concentration of 10% and ozone of 0.3 vol. %. $T = 150°$. Contact time 21 sec.

the yield of methyl hydroperoxide recalculated to a constant amount of decomposed ozone. $T = 150°$. Contact time 21 sec. Ozone concentration in the initial mixture 0.28 vol. %.

Curve 2 in Fig. 3 shows how the amount of decomposed ozone increases with increasing methane concentration. If the experimental data are now recalculated to the same amount of decomposed ozone, taking

the amount of decomposed ozone, where the reacting mixture contains 90% methane, as unity, we still obtain a rectilinear dependence between the amount of peroxide formed and the methane concentration (Fig. 3, 3). It follows from these experiments that the decomposition of ozone increases when part of the oxygen is replaced by methane. Such a phenomenon was not observed when part of the methane was replaced by nitrogen. This means that methane and nitrogen act on ozone decomposition in approximately the same way. Oxygen affects ozone decomposition considerably more weakly than methane and nitrogen. This is in agreement with the conclusions of other investigators (^{2}), who studied the rate of ozone decomposition as a function of additions of various gases.

Figure 4 shows the dependence of the peroxide yield on oxygen. In this series of experiments the methane concentration in the initial mixture was kept constant, while part of the oxygen was replaced by nitrogen. It is seen from Fig. 4 that the peroxide yield (curve 1) decreases with increasing oxygen content in the mixture. However, here too closer examination showed that, although

Fig. 4. Dependence of the yield of methyl hydroperoxide (1) and ozone decomposition (2) on oxygen concentration at a constant methane concentration of 10% and ozone of 0.3 vol. %. $T = 150°$. Contact time 21 sec.

the ozone concentration in the initial mixture was kept constant, the amount of decomposed ozone is different at different points (Fig. 4, 2). As the oxygen concentration increases, i.e., as the amount of nitrogen decreases, the amount of decomposed ozone decreases. Recalculating the experimental results obtained to the same amount of decomposed ozone, taking the amount of decomposed ozone at the point corresponding to 90% oxygen as unity, we obtain straight line 3, parallel to the abscissa axis. This means that, in the investigated range of oxygen concentration variation (from 30 to 90%), the amount of peroxide formed does not depend on the oxygen concentration.

In the course of the work it became clear that the ratio between the reaction products—peroxide and formaldehyde—depends strongly on the ratio S/V. As S/V decreases, the ratio of methyl hydroperoxide to formaldehyde increases. At small values of S/V, the amount of peroxide may become noticeably greater than that of formaldehyde. From these data one may conclude that peroxide radicals apparently perish on the walls of the vessel with formation of formaldehyde. In addition, part of the formaldehyde arises from peroxide, which under certain conditions may partially decompose into formaldehyde and water.

Comparing the principal results obtained by us (proportionality of the reaction rate to the methane concentration, its independence of the oxygen content in the mixture, proportionality to the concentration of oxygen atoms, etc.) with the results obtained in the photochemical oxidation of methane, ethane, and propane (^{3}–^{7}), in which, in the same temperature range, identical reaction products were obtained and analogous dependences established, one may assert that, despite the difference in initiation (in the first case oxygen atoms, in the second alkyl radicals), the oxidation mechanism is the same in both cases. In both cases the reaction proceeds through the same stages. Evidently, under the action of oxygen atoms

oxygen on methane, methyl radicals are also formed (according to the scheme: $\dot{O} + CH_4 \to \dot{C}H_3 + \dot{O}H$), which also carry the main chain. Further development of the chains proceeds according to the scheme:

low temperatures	$CH_3 + O_2 \to CH_3OO$, $CH_3OO + CH_4 \to CH_3OOH + CH_3$;
intermediate temperatures	$CH_3OO + CH_4 \to CH_3OOH + CH_3$, $CH_3OO \to CH_2O + OH$;
high temperatures	$CH_3OO \to CH_2O + OH$.

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REFERENCES

1. N. A. Kleimenov, I. N. Antonova, A. M. Markevich, A. B. Nalbandyan, *ZhFKh*, **30**, 794 (1956); *J. Chim. Phys.*, **54**, 321 (1957); N. A. Kleimenov, A. B. Nalbandyan, *DAN*, **122**, No. 1 (1958).

2. E. H. Riesenfeld, E. Wasmuth, *Zs. phys. Chem.*, **143 A**, 397 (1929); V. Beretta, H. J. Schumacher, *Zs. phys. Chem.*, **17 B**, 417 (1932); W. D. Grath, R. G. W. Norrish, *Proc. Roy. Soc.*, **242**, 265 (1957).

3. A. B. Nalbandyan, *ZhFKh*, **22**, 1443 (1948).
4. A. B. Nalbandyan, *DAN*, **66**, 413 (1949).
5. N. F. Fok, V. V. Bereslavskii, A. B. Nalbandyan, V. Ya. Shtern, *DAN*, **67**, 499 (1949).
6. N. F. Fok, A. B. Nalbandyan, *DAN*, **85**, 1093 (1952); **86**, 589 (1952); **89**, 125 (1953).
7. N. F. Fok, A. B. Nalbandyan, in *Questions of Chemical Kinetics, Catalysis, and Reactivity*, Publishing House of the Academy of Sciences of the USSR, 1955.

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