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Abstract

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STUDY OF THE REACTION OF OXYGEN ATOMS WITH METHYL ALCOHOL

Earlier (^{1,2}) we showed that, by measuring the lower limits of self-ignition of mixtures of carbon monoxide and oxygen containing small additions of hydrogen-containing substances, it is possible to determine the rate constants of elementary reactions of oxygen atoms with the additive molecules. The present work is devoted to the study of the reaction of oxygen atoms with methyl alcohol. Using methyl alcohol as an example, the possibility is also considered of determining the site of attack in the reaction of oxygen atoms with molecules containing hydrogen atoms by studying, by the EPR method, the rarefied flame of mixtures of CO and O_2 in the presence of small additions of the hydrogen-containing substance under investigation.

The data available in the literature concerning the reaction of O atoms with methanol are ambiguous. In papers ($^{3-5}$), in the luminescence spectrum of the reaction of methanol in the gas phase with O atoms obtained in a discharge in molecular oxygen, lines of the free hydroxyl radical were detected, which indicates an appreciable rate of the reaction involving abstraction of hydrogen atoms from the alcohol molecule with formation of OH radicals. However, these papers do not consider the possibility of competition with this reaction by other reactions between oxygen atoms and methanol.

Avramenko, Kolesnikova, and Kuznetsova (^{6}), who also studied the reaction of oxygen atoms with methanol, come to the conclusion that the reaction involving abstraction of an H atom at 347—506°K is much slower than the reaction

$$\mathrm{O} + \mathrm{CH_3OH} = \mathrm{H_2O} + \mathrm{CH_2O}, \tag{A}$$

which proceeds in a single act or, more probably, through the stage of insertion of the O atom into the alcohol molecule. The authors substantiate this conclusion by the fact that in the reaction products the content of hydrogen peroxide proved to be 10 times less than the content of formaldehyde, whereas in the case of the reaction of hydrogen atoms with methanol (^{7}), when other reaction paths except abstraction of an H atom from the alcohol molecule are excluded, upon subsequent introduction of the alcohol radical into the reaction with O_2 the content of H_2O_2 proved to be three times less than the content of CH_2O.

It should be noted, however, that the smaller relative content of H_2O_2 in the case of the reaction of O atoms with methanol may be due, in particular, to the reaction of atomic oxygen with HO_2 and H_2O_2, formed in the course of the reaction during interaction of the alcohol radical with O_2.

It was to be expected that, as in the case of the reaction with hydrocarbons ([2,8–10]), the principal reaction of oxygen atoms with methanol is abstraction of H atoms with formation of hydroxyl radicals.

In addition to studying the flame of mixtures of CO and O_2 with various additions of methanol by the EPR method, we also studied the dependence of the lower ignition limit of these mixtures on the magnitude of the additive. The method for determining the lower ignition limits was described earlier ([2]).

It is seen from Fig. 1 that, as in the case of additions of other hydrogen-containing substances (2,8,9), in the region of small additions the ignition limit decreases as the alcohol content increases.

The experiments on studying the reaction by the EPR method were carried out in a vacuum-flow apparatus. The quartz reaction vessel passed through the resonator of the spectrometer. Previously purified and dried carbon monoxide was bubbled through methyl alcohol at 6°, after which it passed through a coil immersed in a thermostat at 0°. The carbon monoxide thus saturated with alcohol vapor at a pressure corresponding to 0° was mixed, through a regulating valve, with a jet of a mixture of carbon monoxide and oxygen, also carefully purified and dried. The alcohol content in the jet was changed by changing the amount of CO supplied that had been saturated with its vapor. The experimental procedure in other respects was described earlier (2).

The gas pressure in the jet in the various experiments was varied from 3 to 7.4 mm Hg, the temperature from 685 to 755°C, and the initial methanol content in the jet from 0.86 to 1.7%. The volumetric flow rate of the jet in various experiments was $18 \div 25$ cm^3/min at NTP. The ratio (CO)/(O_2) was maintained close to stoichiometric.

In these conditions, in the presence of a flame, we recorded EPR spectra of atomic hydrogen and oxygen. The concentrations of these particles, close to 10^{14} particles/cm^3, depend on the experimental conditions and, in particular, on the content of alcohol vapor in the mixture.

For the detection of hydroxyl radicals, a cylindrical tube widening in the resonator was used as the reaction vessel, similar to the tube used in works (11,12). By raising the temperature to 755°, it was possible to reduce the gas pressure in the flame to 4.2 mm Hg (at a mixture flow rate of 25 cm^3/min and 1.7% alcohol) and under these conditions to record the EPR spectrum of the hydroxyl radical (11).

Fig. 1

Figure 1: Fig. 1

Fig. 1. Dependence of the lower ignition limits of mixtures $2CO+O_2+mCH_3OH$ on the magnitude of the methanol addition at temperatures 670 (1) and 690° (2)

The lowering of the first ignition limit of mixtures of CO and O_2 with increasing alcohol-vapor content, shown in Fig. 1, indicates that the effective rate of chain branching is limited by the reaction of the active chain carrier with methanol, which subsequently leads to branching. Such a reaction is the reaction of oxygen atoms with methanol with abstraction of a hydrogen atom. The lowering of the first limit with increasing addition of alcohol vapor to the mixture also means that this reaction is the principal reaction between O atoms and alcohol molecules. The hydroxyl radicals formed in this reaction, entering into reaction with CO, form CO_2 and H atoms.

Thus, the mechanism of CO combustion in the presence of methanol is basically analogous to the mechanism of its combustion in the presence of other hydrogen-containing substances and, under the conditions of our experiments, may be represented as the set of the following principal elementary reactions:

$$\mathrm{OH + CO = CO_2 + H} \tag{1}$$

$$\mathrm{H + O_2 = OH + O} \tag{2}$$

$$\mathrm{O + CH_3OH = OH + CH_2OH} \quad \text{or}$$

$$\mathrm{O + CH_3OH = OH + CH_3O} \tag{3}$$

$$\mathrm{H + wall \rightarrow termination} \tag{4}$$

$$\mathrm{O + wall \rightarrow termination} \tag{5}$$

$$\mathrm{H + CH_3OH = H_2 + CH_2OH} \tag{6}$$

The detection of H atoms and OH radicals in super-equilibrium concentrations confirms the correctness of this mechanism.

Since almost all hydroxyl radicals enter into the rapid reaction (1)^(2, 13, 14), one can, by using CD_3OH or CH_3OD as an additive, judge the site of attack by oxygen atoms on alcohol molecules from the ratio of the concentrations of OH and OD radicals or of the concentrations of H and D atoms. We used the spectra of H and D atoms observed with additions of CH_3OD and CD_3OH.*

In the case of CH_3OD additions, D atoms were not detected, whereas the ratio of the intensity of the hydrogen-atom lines to the noise intensity was 30-35. Hence, taking into account the number of components in the spectra of H and D atoms and the line widths, we obtain the concentration ratio $(H)/(D) \geq 15$, i.e., oxygen atoms react mainly with the methyl group of CH_3OD.

In the case of CD_3OH additions, H atoms were also observed along with D atoms. In this case $(D)/(H) \simeq 6$. The change in the fraction of atoms abstracted from the methyl group on going from CH_3OD to CD_3OH is evidently associated with the different strengths of the C—H and C—D bonds, as well as of the O—H and O —D bonds^(15) in methanol. These data show that oxygen atoms react mainly with hydrogen from the methyl group of the alcohol molecule; moreover, each of the C—H bonds reacts with oxygen to a greater extent than the O—H bond.

If the difference in activation energies for the reactions of abstraction by oxygen atoms of D and H atoms from the methyl group is taken to be 1.2 kcal/mole^(15), then from the value $(D)/(H) \simeq 6$, which pertains to the case of CD_3OH, we obtain for CH_3OH a concentration ratio of H atoms abstracted from the methyl and hydroxyl groups close to 11. With an analogous assumption concerning the D and H atoms in the hydroxyl group of the alcohol molecule, from the value $(D)/(H) \geq 15$, which pertains to CH_3OD, the concentration ratio of H atoms abstracted from the methyl and hydroxyl groups of CH_3OH proves to be > 8.

Thus, under the conditions of our experiments, oxygen atoms react with the methyl group of methanol more than 8 times faster than with the hydroxyl group.

Studying the chemiluminescence spectrum of the reaction of O atoms from a discharge with CH_3OD, Gay^(4) also came to the conclusion that H atoms are preferentially abstracted from the methyl group of the alcohol, on the basis that OD-radical lines were absent from the spectrum, whereas an OH line was observed. However, Gay does not indicate the temperature of the experiments, and at low temperatures the result he obtained can also be explained by the lower reactivity of D atoms compared with H atoms in the hydroxyl group of the alcohol.

The presence of appreciable amounts of H atoms in the case of CD_3OH additions means that it is impossible to explain the lowering of the first ignition limit of CO and O_2 mixtures in the presence of methanol by reaction (A), which would be followed by the reaction $O + CH_2O = OH + HCO$ and reactions (1) and (2). Indeed, in this case, with CD_3OH additions under the conditions of our experiments, only D atoms should have been formed in the flame.

Because of the small magnitudes of the alcohol additions, the amount of water formed in the course of reaction (A) is also small, and its endothermic reaction with atomic oxygen at such concentrations is imperceptible.

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

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