ON THE INTERACTION BETWEEN OZONE AND METHYL HYDROPEROXIDE

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ON THE INTERACTION BETWEEN OZONE AND METHYL HYDROPEROXIDE

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In a study of the oxidation of methane by oxygen atoms formed during the thermal decomposition of ozone, we showed (1) that ozone, as a molecule, does not react directly with methane up to the temperature of its decomposition. In carrying out this work it was found that in the scrubber, where the intermediate reaction products were trapped with the aid of distilled water, an interaction occurred between undecomposed ozone and the methyl hydroperoxide formed, which at low temperatures is one of the main reaction products. Under identical experimental conditions, as the duration of the experiment increased, the yield of methyl hydroperoxide per 1 cm^3 of the mixture passed invariably decreased. The curve obtained for the peroxide yield as a function of the time of the experiment is presented in Fig. 1. As is seen from the curve, after an 8-hour experiment the peroxide yield had fallen by more than a factor of 3. The decrease of methyl hydroperoxide in solution was attributed to the reaction

$$CH_3OOH + O_3 \rightarrow CH_3OH + 2O_2, \qquad (1)$$

similarly to what occurs in the reaction of hydrogen peroxide with ozone (2), leading to the formation of a water molecule and two oxygen molecules according to the overall scheme

$$H_2O_2 + O_3 \rightarrow H_2O + 2O_2. \qquad (2)$$

Methyl alcohol, which is the presumed product of the interaction according to reaction (1), was not identified by us at that time. It was to be expected that an analogous interaction would take place not only in the liquid, but also in the gas phase. The present work is devoted to describing the results obtained in studying the kinetics of the interaction between ozone and methyl hydroperoxide in the gas phase. The initial methyl hydroperoxide was synthesized by the method of methylating hydrogen peroxide with dimethyl sulfate in an alkaline medium (3). In this way an approximately 80% aqueous solution of methyl hydroperoxide was obtained. The latter contained no hydrogen peroxide, as was established with the aid of quadrivalent titanium.

Fig. 1 and Fig. 2: experimental curves

Figure 1: Fig. 1 and Fig. 2: experimental curves

Fig. 3: lg K versus 1000/T

Figure 2: Fig. 3: lg K versus 1000/T

The experiments were carried out as follows. Into an evacuated flask of 8.5 l capacity, kept in a thermostat at the specified temperature, specified amounts of hydroperoxide and then of ozonized oxygen were rapidly introduced. The ozone concentration in all experiments exceeded the peroxide concentration by a factor of 5-6. In order to stop further interaction between the reagents, after a specified holding time the gas from the reaction vessel was rapidly transferred into another evacuated flask placed in melting ice. To separate the unreacted peroxide from the ozone, the mixture from the second flask was slowly pumped through two traps connected in series, kept at temperatures of −100° and liquid nitrogen. Blank experiments established that by this procedure the peroxide is separated quantitatively from the ozone.

The results of the experiments are presented in Fig. 2. The points on curves *1, 2, 3, 4,* and *5* show the experimental values of the concentrations of methyl hydroperoxide as a function of the holding time of the reacting mixture at temperatures of 25, 34, 43, 52, and 64°, respectively. The solid curves were obtained by calculation, on the assumption that, with a large excess of ozone in the mixture, the decrease in the concentration

Fig. 1. Decrease in the concentration of methyl hydroperoxide in solution, referred to 1 cm^3 of the exhaust gases, as a function of the duration of the experiment

Fig. 2. Kinetics of the decrease of methyl hydroperoxide at different temperatures.
1—25°, *2*—34°, *3*—43°, *4*—52°, *5*—64°

of methyl hydroperoxide with time should be described by a monomolecular law. As can be seen from Fig. 2, the points, within the possible experimental errors, fit the corresponding curves well.

Fig. 3

From the kinetic curves of Fig. 2 the following values of the reaction-rate constant were obtained.

T, °C	K, sec.
25	$7.7 \cdot 10^{-4}$
34	$1.12 \cdot 10^{-3}$
43	$1.5 \cdot 10^{-3}$

T, °C	K, sec.
52	$2.12 \cdot 10^{-3}$
64	$2.8 \cdot 10^{-3}$

From the temperature dependence of the reaction-rate constant, the activation energy of the reaction of ozone with methyl hydroperoxide was determined. Fig. 3 gives the dependence of $\lg K$ on $1/T$. As can be seen from this figure, the experimental points fit a straight line well; from the tangent of the angle of inclination of this line, a value $E = 7000$ cal/mole was obtained for the activation energy.

From the series of kinetic curves presented in Fig. 2 it is seen that if, at 25°, about 15 min is required for the peroxide concentration to decrease by a factor of 2, then at 64° this time decreases to 2.5 min, and with a 25-minute holding period practically all the peroxide undergoes decomposition under the action of ozone.

In addition to the experiments described, a special investigation was carried out to determine the principal products of the reaction of ozone with methyl hydroperoxide. Analysis of the products showed, in accordance with the

the assumption stated above, that under the action of ozone the peroxide is converted mainly into methyl alcohol. In the reaction products about 80% methyl alcohol and about 6% formaldehyde were found. No analysis for other products was carried out. The alcohol was determined by Gulyaeva' s modified method (^{4}), based on esterification of methyl alcohol with nitrous acid. Formaldehyde was determined polarographically.

Recently a series of papers by Schubert and Pease (^{5}) has appeared in the literature, in which the results are described of an investigation of the oxidation reaction of a number of hydrocarbons initiated by ozone. Carrying out experiments under static conditions with holding times reaching many tens of minutes, or under flow conditions with long contact times, the authors established that in the temperature range studied, 25-270°, the main reaction products are the corresponding alcohols, which, as they suppose, are obtained by direct interaction of an ozone molecule with a hydrocarbon according to the following chain scheme:

$$\mathrm{RH} + \mathrm{O_3} \rightarrow \mathrm{RO} + \mathrm{HO_2},$$

$$\mathrm{RO} + \mathrm{RH} \rightarrow \mathrm{ROH} + \mathrm{R},$$

$$\mathrm{R} + \mathrm{O_2} \rightarrow \mathrm{RO_2}.$$

In the authors' opinion, the radicals HO_2 and RO_2 perish at low temperatures without entering into further reaction with hydrocarbons. In the light of the investigations described in the present communication, and also of the work (^{1}) devoted to the reaction of oxidation of methane by oxygen atoms formed during the thermal decomposition of ozone, the results of the experiments of Schubert and Pease may be explained differently.

The primary products of the oxidation of hydrocarbons in the presence of slowly decomposing ozone are the hydroperoxides of the corresponding hydrocarbons. However, the authors fail to detect them because during the holding time of the reacting gases in the vessel they are, under the action of undecomposed ozone, converted completely into alcohols.

Comparison of the rate constant for the consumption reaction of methyl hydroperoxide in the interaction of the latter with ozone with the constant for ozone consumption in its interaction reaction with methane showed that the former is considerably greater than the latter.

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