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Abstract

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THE MECHANISM OF CHAIN BRANCHING IN THE REACTION OF OXIDATION OF METHYL ETHYL KETONE IN THE LIQUID PHASE

The degenerate-branched character of the processes of liquid-phase oxidation of hydrocarbons is currently associated with the accumulation in the system of peroxides, the molecules of which decompose comparatively readily into radicals. Recently, direct experimental proof was obtained that it is hydroperoxides in particular that are the principal chain-branching product (^{1}). By the inhibitor method, the rate of chain branching at different stages of oxidation of *n*-decane was measured, and a linear dependence of the branching rate on the concentration of hydroperoxide in the system was established. However, hydroperoxides are not always the only branching substances in reactions of liquid-phase oxidation of hydrocarbons. Thus, for example, in the oxidation of cyclohexane in a steel vessel it was shown that chain branching is due not only to radical decomposition of cyclohexyl hydroperoxide, but also occurs with the participation of cyclohexanone (^{2}).

In the present work, in studying the oxidation of methyl ethyl ketone in the liquid phase, it has been established that degenerate branching of chains occurs through decomposition into radicals of two intermediate compounds: ketohydroperoxide and diacetyl. This conclusion is also of interest for establishing the mechanism of liquid-phase oxidation of low-molecular hydrocarbon gases, since methyl ethyl ketone is an intermediate product of the oxidation of liquefied *n*-butane (^{3}).

In the literature on liquid-phase oxidation there are practically no data on the oxidation of methyl ethyl ketone by molecular oxygen. Only works are known in which its oxidation by trifluoroacetic acid (^{4}), oxygen compounds of manganese (^{5}), chromic acid (^{6}), and others was studied. We carried out the oxidation of methyl ethyl ketone by atmospheric oxygen in the liquid phase at a pressure of 50 atm and temperatures of 100–145° in an autoclave-type apparatus (^{7}).

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Analysis of the oxidation products (acetic acid, ethyl acetate, diacetyl, ethanol, peroxides, CO and CO_2) was performed both by ordinary chemical methods and with the aid of a specially developed paper-chromatography procedure ([8]–[10]).

The general form of the kinetic curve for the consumption of methyl ethyl ketone (Fig. 1) and the linear character of its semilogarithmic anamorphosis indicate that the oxidation reaction of methyl ethyl ketone follows the kinetic law of first-order reactions. Naturally, we are dealing with a complex process that imitates the kinetic law of a reaction of simple type, as is often observed in the case of branched-chain reactions at a high initial concentration of active centers. That this is in fact so is shown by the chain character of the oxidation of methyl ethyl ketone established in the present work, and also by the anomalously low value of the pre-exponential factor in the expression for the reaction-rate constant $k = 5.2 \cdot 10 \exp(-11200/RT)$ sec^{-1}.

To prove the chain nature of the process, α-naphthol, known to be a strong inhibitor, was added to the initial methyl ethyl ketone.

by oxidation. In the presence of α-naphthol, a noticeable induction period appears, the duration of which increases with increasing inhibitor concentration (Fig. 2).

Fig. 1. Kinetic curves for the consumption of methyl ethyl ketone and the accumulation of reaction products at $T = 145°$, pressure 50 atm, and air feed rate 20 l/h.
1—consumption of methyl ethyl ketone; 1′—semilogarithmic anamorphosis of curve 1; 2—accumulation of acetic acid; 3—CO_2; 4—CO; 5—ethyl acetate; 6—diacetyl; 7—ketohydroperoxides (right-hand scale); 8—ethanol (right-hand scale).

Fig. 2. Kinetic curves for the oxidation of methyl ethyl ketone at $T = 145°$ and pressure 50 atm.
1—without addition of inhibitor; 2—with addition to the initial methyl ethyl ketone of α-naphthol in an amount of $1.59 \cdot 10^{-3}$ mol/l; 3 and 4—with addition of $9.54 \cdot 10^{-3}$ mol/l α-naphthol. 2′, 3′, and 4′—corresponding consumption of inhibitor during the induction period of methyl ethyl ketone oxidation.

The kinetics of inhibitor consumption during the induction period makes it possible to determine the rate of chain initiation in the oxidation of methyl ethyl ketone, $w_0 = 1.5 \cdot 10^{-6}$ mol/l $\cdot$ s at 145°. This value considerably exceeds the corresponding values of w_0 in analogous oxidation reactions of acetone and cyclohexanol ([11], [12]). In the developed oxidation process, the rate of chain initiation increases in comparison with w_0 owing to degenerate branching. The magnitude of the initiation rate during the course of the reaction was determined by measuring the rate of consumption of the inhibitor introduced into the reacting mixture at different time intervals from the beginning of oxidation.

It is evident from Fig. 3 that oxidation of methyl ethyl ketone proceeds only by a chain path, since from the moment the inhibitor is introduced the consumption of methyl ethyl ketone ceases completely.

The increase in the rate of chain initiation during the oxidation of methyl ethyl ketone is relatively small. Thus, on the portion of the kinetic curve corresponding to the main reaction time (from 0.5 to 5 h), the rate of initiation increases only by a factor of 2. This apparently is the reason why, in our case, the rate of the chain process is described by a law of the simple type. Indeed, on the basis of the expression for the dependence of the rate of hydrocarbon oxidation on the initiation rate ([13]), one can obtain an expression for the oxidation rate of methyl ethyl ketone in the form

$$w = \frac{k_2}{\sqrt{k_5}}[\mathrm{RCOR_1}]\, w_\mathrm{i}^{1/2},$$

When the initiation rate changes twofold during the course of the process, the value $w_\mathrm{i}^{1/2}$ increases only by a factor of 1.3, which leads practically to a linear dependence of the reaction rate on the concentration of methyl ethyl ketone, i.e., to first order of the reaction.

The rate of chain branching during the oxidation of methyl ethyl ketone increases in proportion to the concentration of ketohydroperoxide accumulating in the system only at the very beginning of the reaction. Then a considerable excess is observed of the total rate of radical formation in the system (measured from the consumption of inhibitor) over the value corresponding to the decomposition of ketohydroperoxide into free radicals. This indicates that, along with ketohydroperoxide, other intermediate oxidation products of methyl ethyl ketone participate in the chain-branching reaction.

It could be assumed that the second branching product is diacetyl, which is found in the reaction products in appreciable amounts and which, by its nature, is capable of decomposing relatively easily into two free radicals ([14]). Indeed, when small amounts of diacetyl are added to the oxidizing methyl ethyl ketone, the rate of chain branching, beginning from the moment at which the diacetyl additive is introduced, increases. For a quantitative characterization of the chain-branching reaction, the dependence of the branching rate on the total concentration of the two branching products, ketohydroperoxide and diacetyl, was obtained.

Fig. 3. Kinetic curves for the oxidation of methyl ethyl ketone in the presence of α-naphthol at $T = 145°$ and $p = 50$ atm. The time of inhibitor introduction

is indicated by an arrow.
1 –without α-naphthol; 2 –in the presence of $3.1 \cdot 10^{-2}$ mole/liter α-naphthol; 3 –$5.2 \cdot 10^{-2}$ mole/liter α-naphthol; 4 –$5.2 \cdot 10^{-2}$ mole/liter α-naphthol. A – kinetic curve for the change in the rate of chain initiation during the process.

The rate of chain initiation corresponding to a definite moment of reaction time can be expressed as

$$w_1 = k_1[D]_1 + k_2[P]_1 = k_1\left\{[D]_1 + \frac{k_2}{k_1}[P]_1\right\}, \tag{1}$$

where $[D]$ and $[P]$ are the concentrations of diacetyl and ketohydroperoxide, and k_1 and k_2 are the rate constants for the decomposition of these substances into radicals. If, at the same moment, some additional amount of diacetyl is introduced into the reacting mixture, then equation (1) takes the form

$$w_2 = k_1[D]_2 + k_2[P]_1 = k_1\left\{[D]_2 + \frac{k_2}{k_1}[P]_1\right\}. \tag{2}$$

Dividing equation (1) by equation (2), we obtain

$$\frac{w_1}{w_2} = \frac{[D]_1 + \frac{k_2}{k_1}[P]_1}{[D]_2 + \frac{k_2}{k_1}[P]_1}.$$

Fig. 4. Dependence of the rate of chain initiation in the oxidation reaction of methyl ethyl ketone on the total concentration of diacetyl and ketohydroperoxide, $T = 145^\circ$; $p = 50$ atm.

From this it is easy to obtain k_2/k_1, since all the remaining quantities are known from experimental data. Substituting the value of k_2/k_1 into equation (1), we obtain the dependence of the chain-branching rate on the total concentration of branching products (Fig. 4). The linear character of this dependence indicates that no substances other than ketohydroperoxide and diacetyl take part in chain branching. The slope of the straight line in Fig. 4 gives the value of the rate constant for the decomposition of diacetyl into radicals, $k_1 = 1.0 \cdot 10^{-5}$ sec^{-1} (at 145°).

In experiments to study the mechanism of decomposition of pure diacetyl, specially synthesized by us for this purpose, a value close to k_1 was obtained, and an expression for the temperature dependence $k_1 = 2.9 \cdot 10^{13} \exp(-35400/RT)$ sec^{-1}. The pre-exponential factor in this expression corresponds to its value for a truly monomolecular reaction, which confirms the mechanism of chain branching as a reaction of decomposition of the diacetyl molecule into two radicals.

The values of k_1 and k_2/k_1 also make it possible to determine the rate constant for decomposition of methyl ethyl ketone hydroperoxide into radicals, $k_2 = 1.4 \cdot 10^{-4}$ sec^{-1}. The value of k_2 is an order of magnitude greater than k_1 for the same experimental conditions, which would seem to lead to the predominant role of ketohydroperoxide as the branching product. In reality, however, this difference in the decomposition rate constants is compensated by the considerably larger amounts of diacetyl formed in the reaction, as compared with ketohydroperoxide.

The chain length, obtained from the ratio w/w_{branch}, rapidly decreases in the course of oxidation of methyl ethyl ketone from 360 links at the beginning of the reaction to 12 links at the end of the process.

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REFERENCES

1. D. G. Knorre, Z. K. Maizus, N. M. Emanuel, DAN, **123**, 123 (1958).
2. I. V. Berezin, N. F. Kazanskaya, V. F. Trivalov, DAN, **126**, 809 (1959).
3. N. M. Emanuel, DAN, **110**, 245 (1956).
4. W. D. Emmons, G. B. Lucas, J. Am. Chem. Soc., **77**, 2287 (1955).
5. J. S. F. Pode, W. A. Waters, J. Chem. Soc., **1956**, 717.
6. W. A. Waters, J. Chem. Soc., **1946**, 1151.
7. E. A. Blumberg, Z. K. Maizus, N. M. Emanuel, in: *Oxidation of Hydrocarbons in the Liquid Phase*, Publishing House of the Academy of Sciences of the USSR, 1959, p. 125.
8. G. E. Zaikov, Zhurn. analit. khim., **15**, 104 (1960).
9. G. E. Zaikov, Zhurn. analit. khim., **15**, 639 (1960).
10. G. E. Zaikov, Zhurn. analit. khim., **16**, No. 6 (1961).
11. E. T. Denisov, in: *Kinetics and Catalysis*, Publishing House of the Academy of Sciences of the USSR, 1960, p. 92.
12. E. T. Denisov, DAN, **130**, 1065 (1960).

13. D. G. Knorre, Z. K. Maizus, L. K. Obukhova, N. M. Emanuel, Usp. khim., **26**, 416 (1957).

14. R. P. Taylor, F. E. Blacet, Ind. Eng. Chem., **48**, 1505 (1956).

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