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Abstract

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ON THE MECHANISM OF DECOMPOSITION OF INTERMEDIATE HYDROPEROXIDES DURING THE OXIDATION OF *n*-DECANE IN THE LIQUID PHASE

In studying the oxidation reaction of *n*-decane, we established that the total rate of decomposition of intermediate hydroperoxides practically coincides with the rate of formation of the sum of the oxidation products (^{1}). This meant that hydroperoxides are the only primary intermediate substances in the process of liquid-phase oxidation of *n*-decane. This conclusion provides an idea of the first stage of the complex reaction of oxidation of saturated hydrocarbons and poses the problem of studying the mechanism of the further transformations of hydroperoxides that lead to the formation of the remaining oxidation products.

A number of facts obtained in studying the decomposition of hydroperoxides in the absence of oxygen (i.e., under conditions in which the formation of new hydroperoxide molecules is excluded) attest to the complex character of the reaction. These facts gave grounds for assuming that the free radicals formed upon cleavage of the O–O bond in the hydroperoxide molecule induce chain decomposition of hydroperoxides (^{2}, ^{3}, ^{4}). The experimentally measured rate of hydroperoxide decomposition was regarded as the total rate of two processes—monomolecular and chain.

In the present work, to prove the existence of chain decomposition of *n*-decyl hydroperoxides in *n*-decane and to determine the quantitative relationship between the molecular and chain pathways of decomposition, we used the method of suppressing the induced decomposition of hydroperoxides by additions of inhibitors. Such a procedure was applied in studying the dependence of the decomposition rate on the structure of substituted benzoyl peroxides (^{5}), in the oxidation reaction of cyclohexane (^{6}), and in other works.

In our work, α-naphthol was used as the inhibitor; it was introduced into *n*-decane oxidized by a stream of oxygen at 130°. The inhibitor was introduced at different stages in the development of the reaction. On the kinetic curve for the accumulation of hydroperoxides (Fig. 1, 1), after the introduction of α-naphthol a sharp break is observed, associated with the fact that the addition

Fig. 1. Kinetic curves of the change in hydroperoxide concentration in the oxidation reaction of n-decane at 130°: 1—without inhibitor; 2, 3, 4—in the presence of α-naphthol. The time of introduction of α-naphthol is shown by an arrow

Figure 1: Fig. 1. Kinetic curves of the change in hydroperoxide concentration in the oxidation reaction of n-decane at 130°: 1—without inhibitor; 2, 3, 4—in the presence of α-naphthol. The time of introduction of α-naphthol is shown by an arrow

of the inhibitor interrupts the chain reaction of hydroperoxide formation. After introduction of the inhibitor, the concentration of hydroperoxides does not remain constant, as it would if their decomposition proceeded only by a chain pathway; rather, an appreciable consumption of hydroperoxides is observed. Consequently, the decomposition of hydroperoxides proceeds to a certain extent without the participation of radicals, i.e., by a nonchain pathway. The rate constant of nonchain decomposition does not depend on the initial concentration of hydroperoxides or on the presence in the system of other oxidation products. Indeed, from curves 2, 3, and 4 (Fig. 1), corresponding to different times of introduction of α-naphthol, we find the same value for the decomposition rate constant,

$$k = 1.7 \cdot 10^{-3}\ \text{min}^{-1}.$$

Consequently, the rate constant of nonchain decomposition of hydroperoxides measured by the inhibitor method is the rate constant of the elementary act of decomposition of hydroperoxide into radicals.

Since the absolute value of the rate constant for nonchain decomposition of hydroperoxides is much smaller than the overall decomposition constant measured in work ([1]), it was necessary to compare the decomposition of hydroperoxides in the presence of an inhibitor and under conditions not preventing chain decomposition.

Fig. 1. Kinetic curves of the change in hydroperoxide concentration in the oxidation reaction of n-decane at 130°: 1—without inhibitor; 2, 3, 4—in the presence of α-naphthol. The time of introduction of α-naphthol is shown by an arrow.

For this purpose, at the same initial concentration of hydroperoxides, the supply of oxygen was stopped, and in a nitrogen atmosphere two parallel experiments were carried out to measure the kinetics of hydroperoxide consumption in the presence of an inhibitor and without it. The kinetic curves shown in Fig. 2 indicate that the decomposition of hydroperoxides is strongly retarded by additions of inhibitor, i.e., under the conditions of oxidation of n-decane there occurs decomposition of hydroperoxides induced by free radicals.

Fig. 2. Kinetic curves of consumption of n-decyl hydroperoxide in n-decane in a nitrogen atmosphere at 130°: 1, 2, 3—without inhibitor; 1′, 2′, 3′—in the presence of α-naphthol. Crosses on curves 1′, 2′, 3′ indicate the concentration of hydroperoxides in experiments on the decomposition of n-decyl hydroperoxide in n-decane in the presence of α-naphthol in an O_2 atmosphere

Figure 2: Fig. 2. Kinetic curves of consumption of n-decyl hydroperoxide in n-decane in a nitrogen atmosphere at 130°: 1, 2, 3—without inhibitor; 1′, 2′, 3′—in the presence of α-naphthol. Crosses on curves 1′, 2′, 3′ indicate the concentration of hydroperoxides in experiments on the decomposition of n-decyl hydroperoxide in n-decane in the presence of α-naphthol in an O_2 atmosphere

Hence a conclusion follows concerning the mechanism of inhibition. Usually, in studying the inhibition of oxidation reactions it is assumed that naphthols react with the radicals RO_2 that carry the chain reaction. However, during the decomposition of hydroperoxides in a nitrogen atmosphere, RO_2 radicals are absent. Consequently, α-naphthol reacts not only with RO_2 radicals, but also with other free radicals, for example RO radicals formed during the decomposition of hydroperoxides.

The ratio between the rates of chain and nonchain decomposition of *n*-decyl hydroperoxide during the oxidation of *n*-decane is not constant. It changes in parallel with the change in the overall rate of hydroperoxide decomposition with the depth of oxidation. A quantitative characteristic of this ratio may be the chain length of hydroperoxide decomposition, which can be estimated from the ratio of the rate constants for uninhibited decomposition and decomposition in the presence of α-naphthol at the same initial hydroperoxide concentration. The value of the chain length of decomposition of *n*-decyl hydroperoxide in *n*-decane at 130°, measured in this way, varies from 20 links at the beginning of the reaction (hydroperoxide concentration 0.6%) to 3 links at a hydroperoxide concentration of 2.1%. Fig. 2 also presents the results of experiments on the kinetics of nonchain decomposition of *n*-decyl hydroperoxide in *n*-decane in the presence of oxygen, which completely coincide with the data obtained in a nitrogen atmosphere. This shows that the presence of oxygen is not reflected in the nonchain decomposition of hydroperoxides. Data on measurement of the rate constant for decomposition of *n*-decyl hydroperoxide as a function of inhibitor concentration are shown in Fig. 3. With an increase in the concentration of α-naphthol, the rate constant for decomposition of hydroperoxides in a nitrogen atmosphere first drops sharply, then, beginning from a certain value of inhibitor concentration, remains constant. This value is the greater, the higher the initial concentration of hydroperoxides. The value of the constant

Fig. 2. Kinetic curves of consumption of *n*-decyl hydroperoxide in *n*-decane in a nitrogen atmosphere at 130°: 1, 2, 3—without inhibitor; 1′, 2′, 3′—in the presence of α-naphthol. Crosses on curves 1′, 2′, 3′ indicate the concentration of hydroperoxides in experiments on the decomposition of *n*-decyl hydroperoxide

Fig. 3

Figure 3: Fig. 3

in n-decane in the presence of α-naphthol in an O_2 atmosphere.

with an excess of inhibitor is the constant of non-chain decomposition of hydroperoxides, which should not depend on the conditions under which the process is carried out. Similar experiments carried out in an oxygen atmosphere (blackened points in Fig. 3) lead to the same limiting value of the rate constant for the decomposition of hydroperoxides.

The absolute value of the rate constant of non-chain decomposition of hydroperoxides in different experiments varies within the limits from 1.7 to 1.9 $\cdot 10^{-3}$ min^{-1}; it is close to the value of the rate constant for the chain-branching reaction in the oxidation of n-decane, measured by us earlier, $k = 1.1 \cdot 10^{-3}$ min^{-1} (^{7}).

Fig. 3. Dependence of the rate constant for decomposition of n-decyl hydroperoxides in n-decane in a nitrogen atmosphere at 130° on inhibitor concentration. Concentration of hydroperoxides: 1 –0.63%, 2 –1.21%, and 3 –2.1%. Shaded points correspond to analogous experiments in an O_2 atmosphere.

Some discrepancy between the values of the constants may lead to the assumption that, along with non-chain decomposition of hydroperoxides into radicals, molecular decomposition of hydroperoxides also occurs, with formation of ketones and water. To test this assumption, special experiments were carried out on the decomposition of n-decyl hydroperoxides isolated from oxidized n-decane by the method described in (^{8}), in the presence of α-naphthol. Ketones were completely absent from the products of this reaction. The somewhat smaller value of the rate constant for chain branching is apparently connected with the so-called "cage effect." It is highly probable that a small fraction of the radicals R formed in the interaction of RO with the solvent reacts with the OH radical without leaving the "cage."

The formation of RO radicals during non-chain decomposition of hydroperoxides is confirmed by experiments measuring the concentration of alcohol in the products of decomposition of n-decyl hydroperoxides in the presence of phenol ($8.5 \cdot 10^{-8}$ mole/l) as inhibitor. Under these conditions the kinetic curves for hydroperoxide consumption and alcohol formation coincide completely, i.e., the entire amount of alcohol is formed from hydroperoxides through further transformations of the radicals RO, as is seen from the following:

Time from the start of the experiment, min.	45	70	110	200	260
Amount of decomposed hydroperoxide, mole %	0.1	0.24	0.40	0.61	0.96
Amount of alcohol formed, mole %	0.1	0.26	0.38	0.64	0.94

Thus, it may be concluded that the chain-branching reaction in the oxidation of *n*-decane is the non-chain decomposition of *n*-decyl hydroperoxides into radicals, and that one of these radicals is the RO radical.

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