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Abstract

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On the Mechanism of Chain Branching in the Oxidation Reaction of *n*-Decane

In most works devoted to the study of the mechanism of hydrocarbon oxidation, it is assumed that pronounced chain branching is due to the formation of free radicals from molecules of intermediate hydroperoxides ([1]).

Direct experimental proof of this view was given only recently in work ([2]).

Using the inhibitor method in the oxidation reaction of *n*-decane, the rate of chain branching was measured, and it was shown that it increases linearly with increasing concentration of hydroperoxides in the system. In other words, hydroperoxides are the principal branching agent.

This conclusion was also confirmed by the results of work on the kinetics of the decomposition of *n*-decyl hydroperoxides in the presence of α-naphthol ([3]). It was shown that the rate constant for decomposition of the hydroperoxide molecule into radicals is close in magnitude to the chain-branching rate constant measured by the inhibitor method. However, the mechanism of the chain-branching reaction remained unclear. Most authors believe that the primary decomposition of hydroperoxide proceeds according to the scheme

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{OH}\cdot . \tag{1}$$

At the same time, N. N. Semenov ([4]) and a number of other authors indicate that the formation of free radicals in a reaction between two saturated molecules may be energetically more favorable than simple monomolecular decomposition into radicals. This occurs in cases where at least one of the bonds being broken is not very strong, while the bond being formed has a high dissociation energy. From this point of view, one might expect that the formation of free radicals from hydroperoxides—pronounced branching—also occurs through the bimolecular interaction of two saturated molecules according to the scheme

$$2\mathrm{ROOH} \rightarrow \mathrm{RO_2}\cdot + \mathrm{RO}\cdot + \mathrm{H_2O} \tag{2}$$

or

$$\mathrm{ROOH} + \mathrm{RH} \rightarrow \mathrm{R}\cdot + \mathrm{RO}\cdot + \mathrm{H_2O}, \qquad (3)$$

since the energies of the bonds being broken, R—H and RO—OH, are less than the energy of the H—O bond formed in water. In favor of reaction (2), for example, is the fact that, as a rule, a linear dependence is observed between the rate of the oxidation reaction and the concentration of hydroperoxides. If branching were due to the monomolecular decomposition of hydroperoxide by reaction (1), then in this case the reaction rate would have to be proportional to the square root of the hydroperoxide concentration.

It has already been suggested in the literature that at not very low hydroperoxide concentrations its decomposition proceeds by reaction (2) (^{5}).

The heat effect of the bimolecular decomposition reaction of hydroperoxides is $Q = -9$ kcal, i.e., it is 26 kcal more exothermic than the reaction $\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{OH}\cdot$, for which the heat effect is $Q = -35$ kcal.

It seems more probable that pronounced branching occurs as a result of the interaction of hydroperoxides with the solvent. The heat effect of this reaction depends on the strength of the R—H bond in the hydrocarbon molecule, and in a number of cases reaction (3) may prove more favorable than the bimolecular interaction of two hydroperoxide molecules (especially since, in the medium of the hydrocarbon being oxidized, the concentration of hydrocarbon is considerably greater than the concentration of hydroperoxides). Thus, already in the case of *n*-decane, in which the strength of the C—H bond is 92 kcal, the heat effect of the reaction is

$$Q = Q_{\mathrm{H-OH}} - Q_{\mathrm{RO-OH}} - Q_{\mathrm{R-H}} = 116 - 35 - 92 = -11 \text{ kcal},$$

i.e., reaction (3) is 24 kcal more exothermic than reaction (1). In the case of hydrocarbons with a bond strength below 81 kcal, such a reaction should proceed with a positive heat effect.

In some works there are indirect indications of the possibility of a bimolecular reaction of hydroperoxide with a hydrocarbon. In work (^{2}) it was shown that the chain-branching reaction in the oxidation of *n*-decane proceeds according to a first-order law with respect to hydroperoxide, with a rate constant

$$k = 6.8 \cdot 10^8 \exp(-24800/RT).$$

The magnitude of the pre-exponential factor is considerably smaller than the value that could be expected for a monomolecular decomposition reaction of hydroperoxides. The supposition that the primary decomposition of hydroperoxide proceeds by a bimolecular mechanism was also made in a recently published work devoted to the study of the influence of the solvent on the rate constant of the elementary decomposition reaction of tetralin hydroperoxide (^{6}).

Fig. 1. Dependence of the branching rate on hydrocarbon concentration in solutions. Chlorobenzene—decane (1); chlorobenzene—isodecane (2); chlorobenzene—ethylbenzene (3); and chlorobenzene—methyl oleate (4). Hydroperoxide concentration 0.03 mol/l. Temperature 130°

Figure 1: Fig. 1. Dependence of the branching rate on hydrocarbon concentration in solutions. Chlorobenzene—decane (1); chlorobenzene—isodecane (2); chlorobenzene—ethylbenzene (3); and chlorobenzene—methyl oleate (4). Hydroperoxide concentration 0.03 mol/l. Temperature 130°

The aim of the present work was to elucidate the mechanism of chain branching in the oxidation reaction of *n*-decane.

Fig. 1. Dependence of the branching rate on hydrocarbon concentration in solutions. Chlorobenzene—decane (1); chlorobenzene—isodecane (2); chlorobenzene—ethylbenzene (3); and chlorobenzene—methyl oleate (4). Hydroperoxide concentration 0.03 mol/l. Temperature 130°.

Since reactions (1) and (3) differ from one another by the participation of a hydrocarbon in one of them, in the case where branching proceeds by reaction (3), a dependence of the rate of hydroperoxide decomposition on the hydrocarbon concentration should be observed.

Experiments were carried out to measure the branching rate in solutions of *n*-decyl hydroperoxides in chlorobenzene, chosen as an inert solvent, and in mixtures of chlorobenzene with *n*-decane. To prepare solutions of hydroperoxides in chlorobenzene, the hydroperoxides obtained in the oxidation of *n*-decane were converted into sodium salts, which were then decomposed with sulfuric acid and extracted from the aqueous layer with chlorobenzene.

The rate of chain branching was measured by the inhibitor method, described in work (2), from the slope of the straight line for the consumption of α-naphthol.

The concentration of α-naphthol in the solution was determined spectrophotometrically. The α-naphthol contained in the sample was extracted twice with 1 N NaOH and coupled with sulfo-acid phenyl diazonium, the color intensity of which was measured on an SF-4 spectrophotometer at the absorption maximum of the resulting azo compound, 520 mμ.

It was established that decomposition of hydroperoxides also occurs in pure chlorobenzene (apparently by the reaction ROOH → ·RO + OH·). With increasing concentration of *n*-decane in chlorobenzene, the rate of hydroperoxide decomposition (branching) increases linearly (Fig. 1, 1), which indicates first order of the reaction with respect to the hydrocarbon.

Thus, we come to the conclusion that chain branching in the oxidation of *n*-decane proceeds by two parallel routes (according to mono- and bimolecular laws).

The rate constant of monomolecular decomposition, determined from experiments on the decomposition of *n*-decyl hydroperoxides in pure chlorobenzene, is $k_1 = 0.28 \cdot 10^{-5}$ sec^{-1}. The value of the rate constant of the bimolecular reaction of hydroperoxides with *n*-decane is determined from the slope of straight line 1 and proves to be equal to $k_2 = 1.65 \cdot 10^{-6}$ mole$^{-1} \cdot$ sec$^{-1} \cdot$ l.

Thus, the rate constant of branching measured in work$^{(2)}$ is effective and may be represented as the sum of the constants k_1 and k_2, according to the equation $k_{\text{eff}} = k_1 + k_2[\text{RH}]$.

Assuming that in oxidized *n*-decane [RH] = 5.2 mole/l, and substituting the values of the rate constants obtained in the present work, we find the effective rate constant of the branching reaction

$$k_{\text{eff}} = 1.1 \cdot 10^{-5}\ \text{sec}^{-1}.$$

This value agrees satisfactorily with the value of the branching rate constant measured in work$^{(2)}$, $k = 1.9 \cdot 10^{-5}$ sec^{-1}.

In order to study the dependence of the branching rate on the solvent, experiments were carried out to measure the rate of hydroperoxide decomposition in chlorobenzene solutions with different amounts of isodecane, ethylbenzene, and methyl oleate.

From the slopes of straight lines 1, 2, 3, and 4 (Fig. 1), the following rate constants of the bimolecular branching reaction were obtained:

System	$k_2\, 10^6$ mole$^{-1} \cdot$ sec$^{-1} \cdot$ l
Chlorobenzene—decane	1.65
Chlorobenzene—isodecane	2.40
Chlorobenzene—ethylbenzene	4.10
Chlorobenzene—methyl oleate	16.6

It is evident that the value of the rate constant of the branching reaction is greater the more readily the given hydrocarbon is oxidized, i.e., the lower the strength of the CH bond in the hydrocarbon (decane—92 kcal, isodecane—88 kcal, ethylbenzene—77 kcal).

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