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Z. K. MAIZUS, Corresponding Member of the Academy of Sciences of the USSR N. M. EMANUEL, and V. N. YAKOVLEVA

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Abstract

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Z. K. MAIZUS, Corresponding Member of the Academy of Sciences of the USSR
N. M. EMANUEL, and V. N. YAKOVLEVA

THE MECHANISM OF CHAIN INITIATION IN THE OXIDATION REACTION OF *n*-DECANE

Despite the broad development of work in the field of chain processes of hydrocarbon oxidation in the liquid phase, the mechanism of chain initiation in these reactions has still not been finally established. According to existing views, chain initiation in the early stages of hydrocarbon oxidation occurs mainly through interaction of the hydrocarbon molecule RH with oxygen (^{1})

$$\mathrm{RH} + \mathrm{O}_2 \rightarrow \mathrm{R}^{\cdot} + \mathrm{HO}_2^{\cdot} - q_1. \qquad (1)$$

From the energetic point of view, such a process is more favorable than formation of the radical $\mathrm{R}^{\cdot}$ by decomposition of the hydrocarbon molecule at the R—H bond, since it requires a smaller expenditure of energy by the amount of the energy of the bond formed in HO_2, equal to 47 kcal/mole. Chain initiation by reaction (1) is confirmed by experimental data obtained in studying the kinetics of acetaldehyde oxidation in the gas phase (^{2},^{3}).

In a recently published paper (^{4}), considerations are advanced that, in the oxidation of hydrocarbons in the liquid phase, reaction (1) is superseded by the trimolecular reaction

$$2\mathrm{RH} + \mathrm{O}_2 \rightarrow \mathrm{R}^{\cdot} + \mathrm{H}_2\mathrm{O}_2 + \mathrm{R}^{\cdot} - q_2, \qquad (2)$$

for which the value $q_2 = 2(Q_{\mathrm{RH}} - 72)$ is less than $q_1 = Q_{\mathrm{RH}} - 47$, while the frequency of triple collisions in the liquid phase is practically equal to the frequency of binary collisions.

The present work is an experimental investigation of the mechanism of chain initiation in the process of liquid-phase oxidation of *n*-decane. In order to choose between reactions (1) and (2) as processes of formation of free radicals at the beginning of oxidation, it is necessary to establish the dependence of the rate of chain initiation (W_0) on the concentration of the initial substances. In the first case we should obtain a straight line in the coordinates (W_0, $[RH]$), and in the second–in the coordinates (W_0, $[RH]^2$), and in both cases a rectilinear dependence on the concentration of O_2.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

To determine the value of W_0, we used the inhibitor method. The inhibitor (α-naphthol) was added to the initial decane (thoroughly purified of traces of hydroperoxides), and, beginning from the moment oxygen was admitted, the concentration of α-naphthol was measured spectrophotometrically after coupling it with para-nitrobenzenediazonium chloride in a 0.1 N solution of NaOH at the absorption maximum of the azo compound formed, 585 mμ. The magnitude of the rate of chain initiation is many times smaller than the rate of radical formation in the developed reaction. Therefore, an appreciable consumption of inhibitor at the beginning of the reaction can be observed only at relatively high process temperatures (150°). The consumption of α-naphthol in the oxidation of n-decane follows a zero-order reaction up to $\sim$ 30—40% conversion (Fig. 1). This linear segment of the kinetic curve was used to determine the rate of inhibitor consumption.

If the inhibitor is consumed only in the reaction of interaction with radicals, then the rate of inhibitor consumption should not depend on its

concentration. The magnitude of the rate of inhibitor consumption in this case serves as a direct measure of the rate of radical formation in the system. It was precisely such an absence of dependence of the rate of consumption of α-naphthol on its concentration that we observed when measuring the rate of chain branching in the oxidation process of n-decane at a temperature of 130° ([5]).

However, in the present work (at 150°) we found that the rate of consumption of α-naphthol at the beginning of the n-decane oxidation process increases with increasing inhibitor concentration (see Fig. 1). This indicates that,

Fig. 1. **A**—dependence of the rate of consumption of α-naphthol in the oxidation process of n-decane by molecular O_2 at 150°: on the concentration of α-naphthol introduced into the reaction (1), on the square of the concentration of α-naphthol (2), on the square of the concentration of α-naphthol during oxidation of n-decane with a mixture of 53% O_2 and 47% N_2 (3); **B**—kinetic curve of α-naphthol consumption.

Fig. 2. Dependence of the total rate of inhibitor consumption W_{InH} (1, outer scale) and of the chain-initiation rate W_0 (2, inner scale) on the partial pressure of oxygen. The open triangles in 2 were obtained experimentally; the filled ones were calculated from 1 by equation (3).

at the initial moment of n-decane oxidation the rate of radical formation is so small that it becomes comparable with the rate of oxidation of the inhibitor itself by molecular oxygen. Apparently this is the general reason why, when inhibitors are used, in some studies direct oxidation of the inhibitor is not observed ([6]), whereas in others such oxidation is significant ([7]).

Figure 3

Figure 2: Figure 3

In the latter case the expression for the rate of inhibitor consumption must be written in the form:

$$-\frac{d[\mathrm{InH}]}{dt} = W_0 + k_i[\mathrm{InH}]^n[\mathrm{O}_2]. \tag{3}$$

From the methodological standpoint this circumstance somewhat complicates the use of the inhibitor method for determining the rate of chain initiation, while at the same time allowance for the inhibitor-oxidation reaction makes it possible to obtain new information on the mechanism of inhibitor transformation in liquid-phase oxidation reactions of hydrocarbons.

The character of curve 1 in Fig. 1 indicates that inhibitor consumption in the system follows a reaction of second order with respect to the inhibitor. Indeed, a linear dependence is observed between the rate of inhibitor consumption and the square of its concentration (straight line 2 in Fig. 1), and the order of this reaction with respect to the inhibitor, determined from the slope of the straight line in the coordinates

$$\left(\lg \frac{d[\mathrm{InH}]}{dt},\ \lg[\mathrm{InH}]\right)$$

is 1.95.

As follows from equation (3), the segment cut off by straight line 2 (see Fig. 1) on the ordinate axis is the true value of the chain-initiation rate in the oxidation reaction of *n*-decane at 150°,

$W_0 = -2\frac{d[\mathrm{InH}]}{dt} = 2.6 \cdot 10^{-9}\ \mathrm{mol/l \cdot sec}$,

and the slope of this straight line gives the value

$k_i[\mathrm{O}_2] = 3 \cdot 10^{-3}\ \mathrm{l/mol \cdot sec}$.

Having experimentally determined the concentration of oxygen dissolved in decane under the conditions of our experiments, $[\mathrm{O}_2] = 2.4 \cdot 10^{-2}$ mol/l, we thus find the interaction constant of α-naphthol with oxygen,

Fig. 3. Dependence of the chain-initiation rate in the oxidation reaction of *n*-decane at 150° on the concentration of *n*-decane in a solution of *p*-dichlorobenzene (1), and on the square of the concentration of *n*-decane in a solution of *p*-dichlorobenzene (2). In the right-hand corner the dependence of $\lg W_0$ on $\lg[\mathrm{RH}]$ is shown, making it possible to determine the order of the chain-initiation-rate reaction with respect to the hydrocarbon.

$k_i = 1.2 \cdot 10^{-1}$ $\mathrm{l}^2/\mathrm{mol}^2 \cdot \mathrm{sec}$. We arrive at the same value of k_i from another series of experiments, in which the oxidation of n-decane was carried out not with pure O_2, but with a mixture of 53% O_2 and 47% N_2 (straight line 3). The observed dependence of the inhibitor-consumption rate on its concentration, at first glance, contradicts the zero order of the inhibitor-consumption rate. However, after analyzing equation (3), one may conclude that the initial portion of the kinetic curve of inhibitor consumption is approximated by a straight line. Indeed, if we denote $k_i[O_2] = k_x$, $W_0/k_x = a^2$ and integrate equation (3) at $n = 2$ and under the conditions that at $t = 0$, $[\mathrm{InH}] = [\mathrm{InH}]_0$, we obtain

$$[\mathrm{InH}] = a\,\mathrm{tg}\{a[C - k_x t]\},$$

where

$$C = \frac{1}{a}\,\mathrm{arctg}\,\frac{[\mathrm{InH}]_0}{a}.$$

Substituting into this expression the values of a and k_x found from the experimental data, we come to the conclusion that, at those inhibitor concentrations with which we are working, the inhibitor-consumption rate may be rectilinear up to 40–50% conversion of the inhibitor. The true values of W_0, obtained for two different concentrations of dissolved oxygen (see Fig. 1), make it possible to solve one of the main problems of the present work—to determine the order of the chain-initiation reaction in the oxidation of n-decane with respect to O_2. With increasing partial pressure of oxygen, the chain-initiation rate increases linearly (Fig. 2, straight line 2). The dependence of the overall inhibitor-consumption rate in the system on the oxygen concentration (straight line 1) is also expressed by a straight line. This makes it possible, on the basis of equation (3), to calculate values of W_0 for a large number of values of $[O_2]$, which lie well on straight line 2, confirming the first order of the chain-initiation reaction with respect to O_2. To solve the second problem—determining the order of the chain-initiation reaction in the oxidation of n-decane with respect to the con-

the hydrocarbon concentration, the value of W_0 was measured in various mixtures of n-decane with an inert solvent—n-dichlorobenzene—at the same initial concentration of α-naphthol.

In this case, the rate of oxidation of α-naphthol is a constant quantity, while the rate of its consumption in the reaction with free radicals increases with increasing concentration of n-decane in the system. This dependence is presented graphically in Fig. 3. As can be seen from the figure, and also from determination of the reaction order from the slope of the straight line in the coordinates $(\lg W_0,\ \lg[RH])$, the reaction of chain initiation during oxidation of n-decane is second order with respect to the concentration of n-decane.

The intercept cut off by the straight line on the ordinate axis represents the rate of oxidation of α-naphthol by molecular oxygen in a solution of n-dichlorobenzene. The rate constant for oxidation of the inhibitor, $k_i = 5.2 \cdot 10^{-1}$ $\mathrm{liter}^2/\mathrm{mole}^2 \cdot \mathrm{sec}$, for the process of oxidation of α-naphthol in

n-dichlorobenzene somewhat exceeds the value of k_i for oxidation of α-naphthol in n-decane, which apparently is associated with the influence of the polarity of the solvent.

The results of the present work confirm the assumption concerning the trimolecular character of the chain-initiation reaction in liquid-phase oxidation of hydrocarbons.

Institute of Chemical Physics
Academy of Sciences of the USSR

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