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## Abstract

## Full Text

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## ACTIVATION ENERGY OF THE REACTION OF CHAIN FORMATION AND CONSUMPTION OF ALCOHOLS DURING THE OXIDATION OF *n*-DECANE

In studies on the mechanism of oxidation of *n*-decane it was established that alcohols are formed from hydroperoxides by two routes: during the nonchain decomposition of *n*-decane hydroperoxides into radicals

$$\mathrm{RO_2H} \longrightarrow \mathrm{RO^\bullet} + \dot{\mathrm{O}}\mathrm{H},$$

$$\mathrm{ROOH} + \mathrm{RH} \longrightarrow \mathrm{RO^\bullet} + \dot{\mathrm{R}} + \mathrm{H_2O}, \qquad (1)$$

$$\mathrm{RO^\bullet} + \mathrm{RH} \longrightarrow \mathrm{ROH} + \dot{\mathrm{R}}$$

and during the chain decomposition of hydroperoxides induced by radicals, leading to the formation of alcohols and ketones,

$$\mathrm{RO_2^\bullet} + \mathrm{ROOH} \xrightarrow{w_{\text{form}}} \text{alcohols},$$

$$\mathrm{RO_2^\bullet} + \mathrm{ROOH} \longrightarrow \text{ketones}. \qquad (2)$$

The consumption of alcohols occurs only by the chain route [1]

$$\mathrm{RO_2^\bullet} + \mathrm{ROH} \xrightarrow{w_{\text{cons}}} \ldots \qquad (3)$$

The rate of nonchain formation of alcohol by reaction (1) was determined from the rate of decomposition of hydroperoxides in the presence of an inhibitor. A quantitative correspondence was established between the consumption of hydroperoxides and the formation of alcohols [1]. The study of the kinetic laws governing the chain conversion of hydroperoxides and alcohols requires special methods that make it possible to measure the rates of formation and consumption of intermediate products during the oxidation process. For paraffin hydrocarbons of normal structure this task is complicated by the formation in the mixture of several isomers with different positions of the functional group [2–4].

Figure 1. Kinetic curves for the accumulation of hydroperoxides during the oxidation of n-decane in an open system when pure n-decane is fed and when a mixture of decane with decanol-2 is fed.

**Fig. 1.** Kinetic curves for the accumulation of hydroperoxides during the oxidation of *n*-decane in an open system when pure *n*-decane is fed and when a mixture of decane with decanol-2 is fed.
1 $-T = 130^\circ$, $v = 3.1 \cdot 10^{-3}$ min$^{-1}$;
2 $-T = 150^\circ$, $v = 7.5 \cdot 10^{-3}$ min$^{-1}$;
3 $-T = 145^\circ$, $v = 7.95 \cdot 10^{-3}$ min$^{-1}$.
The moment of transition from feeding pure decane to feeding decane containing alcohol is marked by an arrow.

For measuring the rate of chain formation and consumption of alcohols in the process of oxidation of *n*-decane, a method was applied for determining the reaction rates of intermediate products when the process is carried out in an open system [5]. This method makes it possible to determine the rate of consumption of individual isomers. In our previous work [6], the rates of consumption of decanol-2, decanol-4, and decanol-5 were measured in the oxidation reaction of *n*-de-

of decane and it was shown that all isomeric decanols are subsequently converted at identical rates. This made it possible to calculate the rate of formation of the sum of the alcohols independently of its isomeric composition.

If the oxidation of *n*-decane is carried out in an open system, feeding first pure *n*-decane into the reactor and, after the establishment of the steady state, decane containing a certain small amount of alcohol, then the change in the steady-state concentration of alcohols in this case makes it possible to determine the rate and the effective rate constant for alcohol consumption, which is the product of the true rate constant and the radical concentration

$$k_2[\mathrm{RO_2}] = \left\{ \frac{[C]_0}{[C]_2 - [C]_1} - 1 \right\} v \tag{4}$$

($[C]_1$ and $[C]_2$ are the steady-state concentrations of alcohols established upon feeding pure *n*-decane and decane containing $[C]_0$ mol/l of alcohol, respectively; $v$ is the specific rate of feed and withdrawal of products). One and the same value of $k_2[\mathrm{RO_2}]$ for all isomeric decanols made it possible to calculate the rate of formation of the sum of the alcohols

$$W_{\text{form}} = \{k_2[\mathrm{RO_2}] + v\}[C]_1.$$

Figure 2. Kinetic curves of alcohol accumulation during oxidation of n-decane in an open system upon feeding n-decane and a mixture of decane with decanol-2.

**Fig. 2.** Kinetic curves of alcohol accumulation during oxidation of *n*-decane in an open system upon feeding *n*-decane (1, 2, 3) and a mixture of decane with decanol-2 (1a, 2a, 3a).
1 $-T = 130^\circ$, $v = 3.1 \cdot 10^{-3}$ min$^{-1}$;
1a $-T = 130^\circ$, $v = 3.1 \cdot 10^{-3}$ min$^{-1}$, $[C]_0 = 0.202$ mol/l;
2 $-T = 145^\circ$, $v = 7.95 \cdot 10^{-3}$ min$^{-1}$;
2a $-T = 145^\circ$, $v = 7.95 \cdot 10^{-3}$ min$^{-1}$, $[C]_0 = 0.205$ mol/l;
3 $-T = 150^\circ$, $v = 7.5 \cdot 10^{-3}$ min$^{-1}$;
3a $-T = 150^\circ$, $v = 7.5 \cdot 10^{-3}$ min$^{-1}$, $[C]_0 = 0.230$ mol/l.

The rate of formation of alcohols, determined from the experimental data, is composed of the rate of chain formation of alcohol and the rate of formation of alcohol as a result of radical decomposition of hydroperoxides (the rate of chain branching) by reaction (1). Consequently:

$$W_{\text{form}} = k_1[\mathrm{RO_2}][\mathrm{ROOH}] + k_3[\mathrm{ROOH}].$$

Hence

$$k_1[\mathrm{RO_2}] = \frac{(k_2[\mathrm{RO_2}] + v)[C]_1}{[\mathrm{ROOH}]} - k_3. \tag{5}$$

Knowing the rate constant of the chain-branching reaction, one can determine the product of the true rate constant of alcohol formation by the chain route and the radical concentration, $k_1[\mathrm{RO_2}]$.

In the present work, the activation energies of the elementary reaction of chain formation of alcohols (reaction 2) and chain consumption of alcohols (reaction 3) have been determined. To solve this problem, it is not necessary to determine the radical concentration $[\mathrm{RO_2}]$ in the system, since, using the method of steady-state concentrations, the radical concentration can be expressed through the hydroperoxide concentration (the degree of conversion under the conditions of our experiments does not exceed 5%)

$$[\mathrm{RO_2}] = \sqrt{\frac{k_3}{k_6}[\mathrm{ROOH}]}$$

($k_6$ is the recombination constant of $\mathrm{RO_2}$ radicals). Then

$$k_1[\mathrm{RO_2}] = k_1\sqrt{\frac{k_3}{k_6}}[\mathrm{ROOH}]^{1/2}, \qquad k_2[\mathrm{RO_2}] = k_2\sqrt{\frac{k_3}{k_6}}[\mathrm{ROOH}]^{1/2}.$$

Consequently, from the data obtained by us, the combination of constants $K_I = k_1\sqrt{\frac{k_3}{k_6}}$ and $K_{II} = k_2\sqrt{\frac{k_3}{k_6}}$ can be determined. The temperature dependence of the quantities $K_I$ and $K_{II}$ will give the values of the activation energies $E_I$ and $E_{II}$, respectively equal to

$$E_I = E_1 + \frac{1}{2}E_3 - \frac{1}{2}E_6, \tag{6}$$

$$E_{II} = E_2 + \frac{1}{2}E_3 - \frac{1}{2}E_6. \tag{7}$$

Since the activation energy $E_3$ is known and is equal to 24.8 kcal/mol, while the activation energy $E_6$ is very small and may be taken as equal to 0, the true activation energies of the reactions of chain formation $E_1$ and chain consumption $E_2$ of alcohols can be obtained from this temperature dependence.

For determining the values $E_1$ and $E_2$ by the method described above, experiments were carried out to measure the effective rate constants of chain formation and chain consumption of alcohols at temperatures of 130, 140, 145, and 150°C.

All experiments were performed at different feed rates of *n*-decane in order to ensure, at low temperatures, a stationary alcohol concentration that was not too small, and at high temperatures, an oxidation depth that was not too great, when much water is formed in the system.

The stationary concentration of hydroperoxides remains the same in experiments with the feed of pure *n*-decane and of *n*-decane with 2-decanol at all experimental temperatures (Fig. 1). This means that the addition of alcohols does not affect the concentration of radicals in the system. From the values of the stationary concentrations of alcohols in experiments without added alcohol and with additions of a mixture of decane with 2-decanol (Fig. 2), at all four temperatures, the effective rate constants of chain formation ($k_1[\mathrm{RO_2}]$) and consumption ($k_2[\mathrm{RO_2}]$) of alcohols in the oxidation reaction of *n*-decane can be calculated by formulas (4) and (5).

Fig. 3. Dependence of the effective rate constant of alcohol consumption on temperature.

**Fig. 3.** Dependence of the effective rate constant of alcohol consumption $K_{II} = k_2\sqrt{k_3/k_6}$ on temperature.

In Fig. 3 is shown the dependence of the quantity

$$K_{II} = \frac{k_2[\mathrm{RO_2}]}{\sqrt{[\mathrm{ROOH}]}} = k_2\sqrt{\frac{k_3}{k_6}}$$

on temperature in Arrhenius coordinates. The activation energy $E_{II} = 22.6$ kcal, calculated from the slope of this straight line. According to formula (7),

$$E_2 = E_{II} - \frac{1}{2}E_3 + \frac{1}{2}E_6.$$

Since $E_3 = 24.8$ kcal/mol, and $E_6 \approx 0$ kcal/mol, the activation energy $E_2$ of the chain consumption of alcohol in the reaction $\mathrm{ROH} + \mathrm{RO_2} \rightarrow$ is equal to 10.2 kcal/mol. Calculated in an analogous way by formula (6), the activation energy of alcohol formation proved to be 9.8 kcal/mol. Comparison of the values $E_1$ and $E_2$ with the activation energy of the reaction $\mathrm{RO_2} + \mathrm{RH} \rightarrow$, equal in the case of oxidation of *n*-decane to 14.5 kcal/mol, indicates that the interaction of radicals with oxidation products—hydroperoxides and alcohols—proceeds with a lower activation energy than the interaction of $\mathrm{RO_2}$ with the hydrocarbon.

The elementary reaction of chain formation of alcohol, whose activation energy was measured in the present work, may be represented, ⋯

for example, in the following form:

$$\mathrm{R_1R_2CH\text{-}O\text{-}O^\bullet \cdots O\text{-}O\text{-}CHR_1R_2} \longrightarrow \mathrm{R_1R_2CH\text{-}O^\bullet} + \mathrm{R_1R_2CH\text{-}OH} + \mathrm{O_2}$$
$$\mathrm{R_1R_2CH\text{-}O^\bullet} + \mathrm{RH} \longrightarrow \mathrm{R_1R_2CH\text{-}OH} + \mathrm{R^\bullet}$$

For the chain consumption of alcohol, the mechanism proposed in work (8) is quite probable.

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