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## Abstract

## Full Text

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# REACTIVITY OF ISOMERIC DECANOLS—INTERMEDIATE PRODUCTS OF THE OXIDATION OF *n*-DECANE

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Establishing the relation between the reactivity of a substance and its structure is one of the main tasks of modern chemical kinetics. The study of quantitative kinetic characteristics of various reactions is in many cases limited by the lack of information on the reactivity of intermediate compounds participating in later stages of the process. Thus, in the oxidation of hydrocarbons with a long carbon chain, the formation of a large number of isomeric oxygen-containing compounds is possible, and the final composition of the reaction products depends on their reactivity. Using *n*-decane ([1]) as an example, it has been shown that in the process of liquid-phase oxidation of paraffinic hydrocarbons, hydroperoxides, alcohols, ketones, and acids are formed. Information on the reactivity of these intermediate products for different positions of the functional group is very limited.

From studies on the oxidation of *n*-decane ([2]) and *n*-heptane ([3]), it follows that the primary reaction products—isomeric hydroperoxides—are formed in approximately equal amounts. The derivatives of ketones isolated from the reaction mixture under these conditions also contain equal amounts of isomers with respect to the position of the carbonyl group. This fact was confirmed by direct quantitative determination of decan-2-one and decan-3-one in the oxidation products of *n*-decane by gas-liquid chromatography ([4]).

Thus, it may be considered established that ketones are formed from preceding products at a rate identical for all isomers. Since ketones may be formed both from hydroperoxides and from alcohols ([1]), this indicates that the reactivity of alcohols does not depend on the position of the OH group. However, direct data for alcohols had not yet been obtained. The method proposed by us ([5]) for determining the rate constants of formation and consumption of intermediate products of complex reactions by carrying out the process in open systems provides new possibilities for the quantitative determination of the reactivity of substances participating in a reaction.

In the present work this method was used to determine the reactivity of *n*-decanols, which are positional isomers, in the process of oxidation of *n*-decane.

Figure 1

Figure 1: Figure 1

The essence of the method is that, for a given open system, two equations can be obtained for two values of the stationary concentration of the intermediate product at the same concentration, in both cases, of free radicals (or of a substance supplying radicals, for example, hydroperoxides). The simultaneous solution of these equations makes it possible to determine the value of the rate constant for consumption of the intermediate product. A simple change in the feed rate of the starting substance does not allow such equations to be obtained, since in the complex reactions under consideration a change in the feed rate leads to a simultaneous change in the concentration of free radicals. The conditions necessary for the method under consideration are achieved in the following way.

Into the reaction vessel, with a certain specific rate $v$, pure starting substance is fed until a steady-state concentration $[\bar{C}]_1$ of the intermediate product is established, the rate of consumption of which is to be measured. Then, at the same rate, starting substance containing small amounts of this product is fed, and its new steady-state concentration $[\bar{C}]_2$ is measured. The value $v$ is defined as the volume of liquid fed per unit time per unit volume of the reaction vessel.

**Fig. 1.** Steady-state concentrations of alcohols (*I*) and hydroperoxides (*II*) during the oxidation of *n*-decane in an open system at 140° and $v = 2.7 \cdot 10^{-3}$ min$^{-1}$. Section 1—feed of pure *n*-decane, 2—mixture of *n*-decane with decanol-2 in an amount of 0.205 mole/l, 3—mixture of *n*-decane with the same amount of decanol-4, 4—mixture of *n*-decane with decanol-5.

The steady state of the system for experiments with and without additions of the intermediate product can be described by the equations

$$k_1[\mathrm{RO_2}][A] - k_2[\mathrm{RO_2}][\bar{C}]_1 - v[\bar{C}]_1 = 0$$

$$k_1[\mathrm{RO_2}][A] - k_2[\mathrm{RO_2}][\bar{C}]_2 - v[\bar{C}]_2 + v[C]_0 = 0,$$

where $[C]_0$ is the concentration of the intermediate product in the starting substance fed into the vessel. Hence

$$k_2[\mathrm{RO_2}] = \left(\frac{[C]_0}{[\bar{C}]_2 - [\bar{C}]_1} - 1\right) v^*. \tag{1}$$

The rate of formation of the intermediate product is determined by the formula

$$W_{\text{form.}} = (k_2[\mathrm{RO_2}] + v)\bar{C}_1. \tag{2}$$

If, in the reaction under study, the formation of several isomers of the intermediate product is possible, for example decanols 2, 3, 4, and 5 during the oxidation of $n$-decane, then formula (2) will be applicable only in the case where all isomers are consumed at equal rates.

To compare the reactivity of isomeric decanols in the process of oxidation of $n$-decane, experiments were carried out to determine the rate constants for the consumption of decanol-2, decanol-4, and decanol-5. Decane was oxidized in an ideally mixed vessel, described in work (6), at a temperature of 140°.

The feed rate of pure decane and of decane containing decanols corresponded to $v = 2.7 \cdot 10^{-3}$ min$^{-1}$. After establishment of the first steady state (pure decane) (Fig. 1, 1), feeding of decane containing 0.205 mole/l decanol-2 was begun. After establishment of the new steady state (Fig. 1, 2), the feed of the solution of decanol-2 in decane was stopped and the same solution of decanol-4 (Fig. 1, 3) and then decanol-5 (Fig. 1, 4) was fed.

As is seen from Fig. 1, the concentration of hydroperoxides during the feed of pure decane and of all three mixtures of decane with isomeric decanols remains one and the same. This indicates that none of the isomeric alcohols affects the concentration of radicals in the system and, consequently, formula (1) can be used to determine the rate constant of their consumption. From the same figure it is seen that the steady-state concentration of alcohols established during feeding of the solution of decanol-2 in decane does not change on transition to the two other alcohols—decanol-4 and decanol-5. This obser-

* The formula was derived on the assumption that the intermediate product itself does not affect the rate of its formation.

makes it possible to conclude that decanol-2, decanol-4, and decanol-5 are consumed in the oxidation reaction of $n$-decane at the same rate, i.e., the reactivity of isomeric alcohols of normal structure does not depend on the position of the hydroxyl group in the carbon chain.

From the experimental data the value $k_2[\mathrm{RO}_2]$ was calculated; it proved to be $2.6 \cdot 10^{-3}$ min$^{-1}$, which agrees well with the value determined earlier for decanol-2, $k_2[\mathrm{RO}_2] = 2.3 \cdot 10^{-3}$ min$^{-1}$ ($^5$). The identical value of the rate constant for the consumption of all decanols formed in the oxidation of $n$-decane makes it possible, using formula (2), to determine the total rate of formation of alcohols in this reaction:

$$W_{\text{form.}} = 7.4 \cdot 10^{-4} \text{ mol/l} \cdot \text{min.}$$

In ($^7$) it was shown that, in the oxidation of $n$-decane, alcohols are formed both through radical decomposition and through chain decomposition of hydroperoxides. In this case the rate of formation of alcohols is

$$W_{\text{form.}} = (k_3 + k_1[\mathrm{RO}_2])[\mathrm{ROOH}],$$

where $k_3$ is the rate constant for the decomposition of hydroperoxides into radicals, and $k_1$ is the rate constant for the chain formation of alcohol from hydroperoxides. Knowing the concentration of hydroperoxides in the system and the value of $W_{\text{form.}}$, we obtain

$$k_3 + k_1[\mathrm{RO_2}] = 6.15 \cdot 10^{-3}\ \mathrm{min}^{-1}.$$

The value $k_3 = 2.9 \cdot 10^{-3}\ \mathrm{min}^{-1}$ was measured in ([8]) by the inhibitor method. Hence

$$k_1[\mathrm{RO_2}] = 3.25 \cdot 10^{-3}\ \mathrm{min}^{-1}.$$

Comparison of these constants shows that the rates of chain and radical decomposition of hydroperoxides under the conditions of our experiments are approximately the same.

Thus, the information obtained on the reactivity of isomeric decanols is not only of independent interest, but also provides substantial assistance in solving the problem of establishing the mechanism of individual stages in the process of hydrocarbon oxidation.

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