MECHANISM OF THE REACTION OF CHAIN PROPAGATION IN PROCESSES OF LIQUID-PHASE OXIDATION IN THE PRESENCE OF COPPER STEARATE

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UDC 541.124:542.943

The influence of salts of metals on the composition of the oxidation products of organic substances has permitted a number of authors to hypothesize the participation of the catalyst in the reaction of chain propagation [1-4]. This question has been investigated quantitatively for the example of the oxidation of n-decane, catalyzed by cobalt stearate [5]. A comparison of the rates of consumption of hydroperoxide and the accumulation of the sum of the remaining oxidation products indicated that hydroperoxides formed in the oxidation process are not the only primary intermediate products of oxidation. In the presence of a catalyst, together with the reaction $\text{RO}_2^+ + \text{RH} \rightarrow \text{ROOH} + \text{R}$, a substantial role is played by the direct conversion of the radical $\text{RO}_2^+$ to alcohols, ketones, and acids.

This work is devoted to a further study of the regulating function of salt catalysts, i.e., to the influence of homogeneous catalysts on the reaction of chain propagation in processes of liquid-phase oxidation. It had to be established whether the peculiarities of chain propagation in oxidation catalyzed by CoSt$_2$ are also characteristic of other metals salts. In connection with this, we selected copper stearate, the role of which in the mechanism of chain branching was investigated in detail in [6-8], as a homogeneous catalyst of the oxidation of n-decane.

EXPERIMENTAL METHOD

In a study of the decomposition of n-decyl hydroperoxide, catalyzed by CuSt$_2$, it was shown that in the presence of CuSt$_2$, hydroperoxide decomposes in two ways, molecular and radical [6]. To establish the pathways of the conversion of other reaction products we used the method of introducing an inhibitor during the process. CuSt$_2$ was introduced into n-decane, oxidized to a definite degree, and then an inhibitor (2,6-di-tert-butyl-4-methylphenol) was introduced after 15-20 min. Figure 1 presents the kinetic curves of the accumulation of the oxidation products of n-decane in the case of successive introduction of CuSt$_2$ and the inhibitor into the system. The introduction of CuSt$_2$ greatly accelerates the accumulation of alcohols, ketones, and acids. After the introduction of the inhibitor, the accumulation of these products stops entirely.

![Fig. 1. Kinetic curves of the accumulation of ketones (1), alcohols (2), and acids (3) in the case of successive introduction into the system of CuSt$_2$ (marked by an arrow with a dark circle) and 2,6-di-tert-butyl-4-methylphenol (the moment of introduction is marked by an arrow with a light circle). The concentration of CuSt$_2$ is $2.4 \cdot 10^{-3}$ M, that of the inhibitor $2.1 \cdot 10^{-2}$ M; temperature 140°C.](image)
This is evidence that in the presence of CuSt$_2$ all the oxidation products are formed and consumed only by a chain mechanism.

To measure the rates of formation and consumption of alcohols, ketones, and acids, the oxidation of n-decane in the presence of CuSt$_2$ was conducted at 140° in an open system [9] in a glass oxidizing cell, constructed according to the principle of an ideal mixing reactor. Mixing was accomplished with a stream of oxygen, delivered to the vessel at a rate of 1.6 liters/h. Before the beginning of the experiment, 16 ml of n-decane, containing $3 \cdot 10^{-3}$ M CuSt$_2$, was delivered to the reaction vessel. During the experiment a solution of CuSt$_2$ in n-decane ($3 \cdot 10^{-3}$ M), containing various amounts of the oxidation product whose rate of consumption was to be measured, was delivered to the vessel at a constant rate, equal to 0.26 h$^{-1}$ (volume of the reaction zone 16 ml).

The oxidate collected from the vessel was analyzed for its content of hydroperoxides, alcohols, ketones, and acids. The hydroperoxides were analyzed iodometrically. Alcohols were determined in the form of the corresponding nitrates according to the absorption intensity at 360 nm on an SF-4A spectrophotometer [1]. The reaction of oxime formation in the interaction of carbonyl compounds with NH$_2$OH.HCl was used for the quantitative determination of ketones. The HCl liberated was titrated with an alcohol solution of KOH according to bromophenol blue at the temperature $-70^\circ$ [1]. Acids were titrated with alcoholic alkali according to phenolphthalein.

The method of conducting the reaction in open systems permits a determination of the rate of consumption of the substance $A$ in the system according to the difference of the equilibrium concentrations of this substance, established at various concentrations of $A$ in the solution delivered to the vessel, $[A]_0$ [10]. The effective rate constants of consumption of the product $A$ ($k_{eff}$)$_A$ = $k_A$[RO$_2$] were determined according to the formula [10]

$$
\frac{(k_{eff})_A}{(u/V)} + 1 = \frac{[A]_b}{[A]_0 - [A]_b},
$$

where $u$ is the volume rate of delivery of the solution to the vessel; $V$ is the volume of the reaction zone; $[A]_b$ is the equilibrium concentration of $A$, established in the system at a concentration of $A$ in the solution delivered to the vessel equal to $[A]_b$; $[A]_0$ is the equilibrium concentration of $A$ when $[A]_0 = 0$.

To determine ($k_{eff}$)$_{ROH}$ and the rate of consumption of alcohol $W_{c}^{ROH}$, experiments were conducted delivering solutions not containing alcohol and containing 0.17, 0.34, and 0.51 M sec-decyl alcohol to the vessels (Fig. 2). As can be seen from Fig. 2, a change in the alcohol concentration in the solution delivered to the vessel substantially changes the values of the equilibrium concentrations of alcohols (curve 2), ketones (curve 3), and acids. The equilibrium concentration of hydroperoxide (curve 1) is unchanged in this case. The latter circumstance permits us to conclude that the addition of alcohol does not influence the rate of initiation in the system.* Consequently, the concentration of RO$_2$ in the system may be considered constant during the experiment, and in determining $W_{c}^{ROH}$, we can use formula (1) [10].

*The observed dependence of $W_i$ on [ROH] is due to the fact that under the conditions of our experiments, alcohol is added to the already oxidized decane, containing substantial amounts of alcohols, ketones, and acids. As was shown in [7, 8], the rate of decomposition of hydroperoxide into free radicals in the presence of CuSt$_2$ ceases to depend on the concentration of these products when their content in the solution is high.