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Reaction Kinetics of the Hydroperoxide Epoxidation of 1-Octene in the Presence of Mo_2B

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Abstract—The kinetics of epoxidation of 1-octene by *tert*-butyl hydroperoxide in the presence of molybdenum boride (Mo_2B) was studied. The effects of reactant and reaction product concentrations on the process were examined. A kinetic scheme was proposed, and the kinetic parameters of the process were calculated.

INTRODUCTION

Previously [1], we found that in the epoxidation of ethylallyl ethylacrylate (EAEA), a compound with two double bonds and an ester group, by *tert*-butyl hydroperoxide (TBHP) in the presence of the molybdenum boride Mo_2B the order of reaction with respect to the hydroperoxide was higher than unity and the concentration of the unsaturated compound practically had no effect on the process. Based on the dependence of the initial rate of reaction on the initial concentrations of the reactants and reaction products, which were added before the reaction, a general kinetic scheme was proposed and the constants of particular steps of this process were calculated.

In this work, we studied the epoxidation of 1-octene (a linear α-olefin with no functional groups) by TBHP in the presence of Mo_2B (Cat) in order to extend the epoxidation regularities found to unsaturated compounds of a different nature.

EXPERIMENTAL

Commercial 1-octene of reagent grade was additionally purified by distillation.

Molybdenum bromide (Mo_2B) of reagent grade with a specific surface area of 0.31 m^2/g, which was determined by nitrogen desorption, was used as a catalyst.

The procedures used for the preparation and purification of the other reagents, experimental procedures, and the treatment of kinetic curves were described elsewhere [1].

RESULTS AND DISCUSSION

As in the case of the epoxidation of EAEA [1], the kinetic curves of TBHP consumption exhibited an induction period in the course of which the reaction rate increased (Fig. 1). It is likely that the observed increase in the rate at the beginning of reaction, as in the case of EAEA, was due to catalyst activation under the action of reaction mixture components [2, 3]. This is evident from the fact that the consumption of the hydroperoxide practically ceased after separation of the catalyst from the reaction mixture upon attaining a maximum rate of reaction (Fig. 1, curve *2*).

Taking into account the occurrence of an induction period, the initial rate of reaction (w_0) was determined by extrapolating the kinetic curve of hydroperoxide consumption on an activated catalyst to the initial concentration of TBHP.

Figure 1 (curve *3*) demonstrates the dependence of w_0 on the initial concentration of 1-octene. It can be seen that, as distinct from EAEA, a near-zero order of reaction with respect to the olefin was observed only at $[\text{octene}]_0 > 2.0$ mol/l. At 1-octene concentrations in the range 0–2.0 mol/l, the order of the reaction with respect to the olefin changed from 1 to 0. This fact suggests that

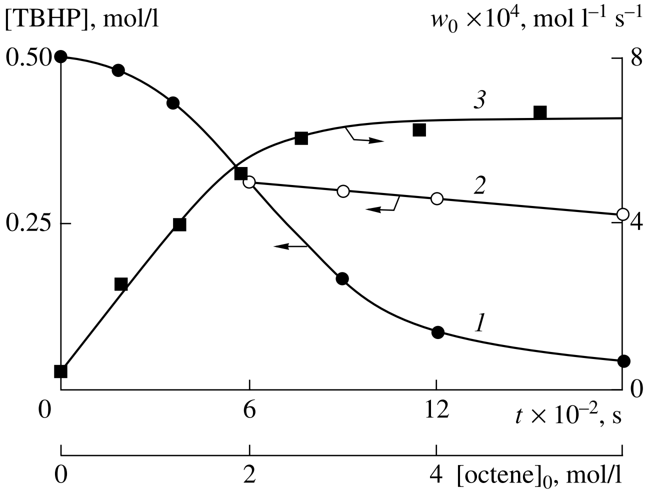

Fig. 1. Kinetic curves of TBHP consumption (*1*) in the presence of a heterogeneous catalyst species and (*2*) after the removal of this species; (*3*) the dependence of the initial rate of the epoxidation reaction on the initial octene concentration ([Cat] = 0.75 g/l) at $T = 360$ K.

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octene, as well as EAEA, forms a complex with the catalyst; however, the stability of this complex in the case of 1-octene is lower than that in the case of EAEA.

Figure 2 illustrates the dependence of w_0 on the concentrations of TBHP, the catalyst, and reaction products (*tert*-butanol (*tert*-BuOH) and 1,2-epoxyoctane (Ep)). The data indicate that, as in the case of EAEA, the order of reaction with respect to the catalyst is close to unity over the tested range of catalyst concentrations. The same reaction order with respect to the hydroperoxide was also observed, which is lower than that in the case of EAEA epoxidation ($n = 1.4$). The effects of the reaction products (an alcohol and an epoxide) were qualitatively the same as in the epoxidation of EAEA, the addition of the alcohol to the reaction medium resulted in a linear increase in the initial rate of reaction, whereas the addition of the epoxide resulted in a nonlinear decrease in the rate. The linear dependence of the initial rate on the amount of the epoxide added to the reaction mixture before the onset of reaction ($[\mathrm{Ep}]_0$) was observed on the $\frac{1}{w_0}$–$[\mathrm{Ep}]_0^2$ coordinates.

Thus, taking into account the qualitatively similar dependence of the initial rate of reaction on the initial concentrations of reactants and reaction products in the epoxidation of EAEA and 1-octene by TBHP in the presence of $\mathrm{Mo_2B}$, we can apply the general reaction scheme proposed previously for EAEA [1] to 1-octene. This reaction scheme includes the formation of a complex (X) of an active catalyst species (X_0) with an olefin (Ol)

$$\mathrm{Ol} + X_0 \xrightleftharpoons{K} X.$$

The complex X reacts with the epoxide and the alcohol to form catalytically inactive (Ol–Cat–2Ep (X_2)) and catalytically active (Ol–Cat–*tert*-BuOH (X_3)) complexes:

$$X + \mathrm{TBHP} \xrightleftharpoons{K_1} X_1;\ X + 2\mathrm{Ep} \xrightleftharpoons{K_2} X_2;$$

$$X + tert\text{-}\mathrm{BuOH} \xrightleftharpoons{K_3} X_3.$$

The epoxide is formed in the following reactions:

$$X_1 + \mathrm{TBHP} \xrightarrow{k_{e1}} \text{products}; \tag{I}$$

$$X_3 + \mathrm{TBHP} \xrightarrow{k_{e2}} \text{products}; \tag{II}$$

$$X_1 \xrightarrow{k_{e3}} \text{products}, \tag{III}$$

where k_{e1}, k_{e2}, and k_{e3} are the rate constants of epoxidation.

According to the above reaction scheme, the rate of hydroperoxide consumption is described by the general equation

$$w = \frac{(k_{e1}K_1[\mathrm{TBHP}] + k_{e2}K_3[tert\text{-}\mathrm{BuOH}] + k_{e3}K_1)K[\mathrm{Ol}][\mathrm{TBHP}][\mathrm{Cat}]_0}{1 + K[\mathrm{Ol}](1 + K_1[\mathrm{TBHP}] + K_2[\mathrm{Ep}]^2 + K_3[tert\text{-}\mathrm{BuOH}])}.$$

It is likely that, in the region of high initial olefin concentrations (>2 mol/l), the term $K[\mathrm{Ol}](1 + K_1[\mathrm{TBHP}] + K_2[\mathrm{Ep}]^2 + K_3[tert\text{-}\mathrm{BuOH}])$ in the denominator becomes much greater than unity and the order of reaction with respect to the olefin approaches zero, as was observed experimentally. In the specified range of olefin concentrations, the reaction rate equation has the form

$$w = \frac{(k_{e1}K_1[\mathrm{TBHP}] + k_{e2}K_3[tert\text{-}\mathrm{BuOH}] + k_{e3}K_1)[\mathrm{TBHP}][\mathrm{Cat}]_0}{1 + K_1[\mathrm{TBHP}] + K_2[\mathrm{Ep}]^2 + K_3[tert\text{-}\mathrm{BuOH}]}. \tag{1}$$

According to Eq. (1), the order of the reaction with respect to the hydroperoxide can vary within a range from 0 to 2 depending on the ratio between the equilibrium constants and the rate constants of individual steps. The order of the reaction with respect to the hydroperoxide was equal to unity, as found experimentally from the dependence of w_0 on $[\mathrm{TBHP}]_0$ under conditions when $[tert\text{-}\mathrm{BuOH}]_0 = [\mathrm{Ep}]_0 = 0$. This occurs in the following two cases: (1) $k_{e1} \ll k_{e3}$ and $K_1[\mathrm{TBHP}] \ll 1$ and (2) $k_{e3} \ll k_{e1}$ and $K_1[\mathrm{TBHP}] \gg 1$. It is more likely that, as in the case of EAEA epoxidation [1], the value of $K_1[\mathrm{TBHP}]$ is also lower than unity. Hence, it follows that in the interaction of 1-octene with TBHP in the presence of $\mathrm{Mo_2B}$, unlike EAEA epoxidation, epoxide formation by reaction (III) prevails over reaction (I). The equation that describes the dependence of the initial rate of reaction on the initial concentration of TBHP has the form

$$w_0 = k_{e3}K_1[\mathrm{TBHP}]_0[\mathrm{Cat}]_0.$$

This equation provides an opportunity to determine the apparent rate constant of 1-octene epoxidation via reaction (III) as $k_{e3}K_1$.

The linear dependence of w_0 on $[tert\text{-}\mathrm{BuOH}]_0$ suggests that the term $K_3[tert\text{-}\mathrm{BuOH}]$ in the denominator of Eq. (1) can also be ignored and $k_{e2}K_3$ can be determined from this dependence. The linear dependence of the initial rate of reaction on the initial epoxide concen-

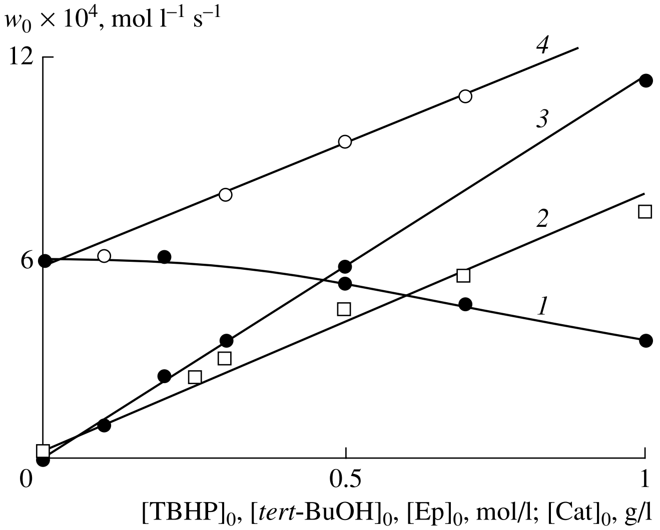

Fig. 2. Dependence of the initial rate of the epoxidation reaction on the initial concentrations of (*1*) the epoxide ($[\text{TBHP}]_0$ = 0.5 mol/l; [Cat] = 0.75 g/l), (*2*) the catalyst ($[\text{TBHP}]_0$ = 0.5 mol/l), (*3*) TBHP ([Cat] = 0.75 g/l), and (*4*) *tert*-butanol ($[\text{TBHP}]_0$ = 0.5 mol/l; [Cat] = 0.75 g/l); $[\text{octene}]_0$ = 2.5 mol/l; T = 360 K.

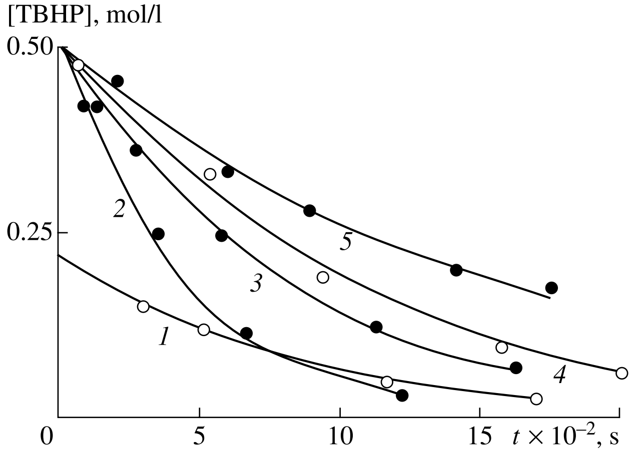

Fig. 3. Theoretical kinetic curves and experimental points for TBHP consumption with time at (*1*) $[\text{TBHP}]_0$ = 0.22 mol/l, $[\text{Cat}]_0$ = 0.75 g/l; $[\text{Ep}]_0$ = 0 mol/l, and $[tert\text{-BuOH}]_0$ = 0 mol/l; (*2*) $[\text{TBHP}]_0$ = 0.5 mol/l, $[\text{Cat}]_0$ = 0.75 g/l; $[\text{Ep}]_0$ = 0 mol/l, and $[tert\text{-BuOH}]_0$ = 0.7 mol/l; (*3*) $[\text{TBHP}]_0$ = 0.5 mol/l, $[\text{Cat}]_0$ = 0.70 g/l; $[\text{Ep}]_0$ = 0 mol/l, and $[tert\text{-BuOH}]_0$ = 0 mol/l; (*4*) $[\text{TBHP}]_0$ = 0.5 mol/l, $[\text{Cat}]_0$ = 0.55 g/l; $[\text{Ep}]_0$ = 0 mol/l, and $[tert\text{-BuOH}]_0$ = 0 mol/l; and (*5*) $[\text{TBHP}]_0$ = 0.5 mol/l, $[\text{Cat}]_0$ = 0.75 g/l; $[\text{Ep}]_0$ = 1.0 mol/l, and $[tert\text{-BuOH}]_0$ = 0 mol/l ($[\text{octene}]_0$ = 2.5 mol/l; T = 360 K).

tration on the $1/w_0$–$[\text{Ep}]_0^2$ coordinates allowed us to calculate K_2. The following values of these parameters at 360 K were found:

$$k_{e3}K_1 = 15.2 \times 10^{-4}\ \text{l g}^{-1}\ \text{s}^{-1};$$

$$k_{e2}K_3 = 19.3 \times 10^{-4}\ \text{l}^2\ \text{mol}^{-1}\ \text{g}^{-1}\ \text{s}^{-1};$$

$$K_2 = 0.82\ \text{l}^2/\text{mol}^2.$$

In general, a differential equation that describes the rate of reaction of the epoxidation of 1-octene (at concentrations higher than 2 mol/l) by TBHP in the presence of Mo_2B has the form

$$-\frac{d[\text{TBHP}]}{dt} = \frac{(k_{e3}K_1 + k_{e2}K_3[tert\text{-BuOH}])[\text{TBHP}][\text{Cat}]_0}{1 + K_2[\text{Ep}]^2}. \qquad (2)$$

Taking into account the high selectivity of epoxide formation based on the hydroperoxide consumed (higher than 90%), we can assume that current epoxide and alcohol concentrations are $[\text{Ep}] = [tert\text{-BuOH}] = [\text{TBHP}]_0 - [\text{TBHP}]$. Substituting this expression in Eq. (2) and integrating, we obtain the equation

$$\begin{aligned}
&\frac{1 + K_2([\text{TBHP}]_0 + [\text{Ep}]_0)^2}{(k_{e3}K_1 + k_{e2}K_3([\text{TBHP}]_0 + [tert\text{-BuOH}]_0))[\text{Cat}]_0}\ln\frac{[\text{TBHP}]_0}{[\text{TBHP}]}\\
&-\left[\frac{K_2(k_{e3}K_1 + k_{e2}K_3([\text{TBHP}]_0 + [tert\text{-BuOH}]_0))}{(k_{e2}K_3)^2[\text{Cat}]_0} - \frac{2K_2([\text{TBHP}]_0 + [\text{Ep}]_0)}{k_{e2}K_3[\text{Cat}]_0}\right.\\
&\left.+\frac{1 + K_2([\text{TBHP}]_0 + [\text{Ep}]_0)^2}{(k_{e3}K_1 + k_{e2}K_3([\text{TBHP}]_0 + [tert\text{-BuOH}]_0))[\text{Cat}]_0}\right] \qquad (3)\\
&\times\ln\left[\frac{k_{e3}K_1 + k_{e2}K_3([\text{TBHP}]_0 + [tert\text{-BuOH}]_0) - k_{e2}K_3[\text{TBHP}]_0}{k_{e3}K_1 + k_{e2}K_3([\text{TBHP}]_0 + [tert\text{-BuOH}]_0) - k_{e2}K_3[\text{TBHP}]}\right]\\
&-\frac{K_2}{k_{e2}K_3[\text{Cat}]_0}([\text{TBHP}]_0 - [\text{TBHP}]) = t,
\end{aligned}$$

where $[\mathrm{Ep}]_0$ and $[\textit{tert}\text{-BuOH}]_0$ are the concentrations of the epoxide and the alcohol introduced into the reaction mixture before the onset of the reaction.

It can be seen in Fig. 3 that the theoretical kinetic curves of TBHP consumption calculated from Eq. (3) with the use of parameters determined from the dependence of the initial rate of reaction on the initial concentrations of the reactants, the catalyst, and the reaction products after an induction period are practically consistent with experimental data.

Based on the experimental data, we can conclude that the chemical kinetic reaction schemes of 1-octene and EAEA epoxidation by TBHP in the presence of Mo_2B are identical. However, the nature of the olefin affects the ratio between the rate constants of individual reaction steps and, correspondingly, the final rate equation that describes the dependence of the rate of reaction on the concentrations of reactants.

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