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Kinetics of the Reaction Between Ethylallyl Ethylacrylate and *tert*-Butyl Hydroperoxide in the Presence of Molybdenum Catalysts[*]

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The reaction of ethylallyl ethylacrylate with *tert*-butyl hydroperoxide in the presence of molybdenum catalysts (Mo_2B and Mo_2B_5) was studied. The general kinetic model for the process is proposed, which adequately explains the hydroperoxide consumption up to 80% conversion. The equilibrium constants of the complex formation were calculated. It was shown that Mo/B ratio in the catalyst affects the catalyst–hydroperoxide complex stability.

Key words: epoxidation, molybdenum catalyst, hydroperoxide

The catalytic epoxidation of unsaturated compounds with hydroperoxides is one of the effective methods of epoxide production [1–3]. The ability of the unsaturated compounds to take part in the epoxidation reaction depends to a large extent on the compound structure [4]. Alkylallyl esters of the alkylacrylic acids contain two double bonds, so that they are less reactive due to the influence of a strong electron accepting group. The synthesis of epoxide derivatives of such esters was reported mainly with the aid of peroxyacids [5,6]. This approach has drawbacks main of which is an explosive hazard of peroxyacids. At the same time, ethylallyl ethylacrylate epoxidation with *tert*-butyl hydroperoxide in the presence of the active olefin epoxidation catalyst $MoO_2(acac)_2$ does not yield a positive result [7], while the heterogeneous ammonium paramolybdate is much more effective [8].

In this work we study the interaction of ethylallyl ethylacrylate (EAEA) with *tert*-butyl hydroperoxide (TBHP) in the presence of heterogeneous Mo_2B and Mo_2B_5 catalysts.

EXPERIMENTAL

Ethylallyl ethylacrylate was synthesized by Tishchenko reaction from α-ethylacrolein in the presence of aluminum isopropoxide as a catalyst. TBHP was obtained from hydrogen peroxide and *tert*-butanol in the presence of sulfuric acid [9]. The Mo_2B and Mo_2B_5 catalysts of pure grade with specific

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area 0.31 and 0.66 m^2/g, found from nitrogen desorption, were obtained from Donetsk Plant of Chemicals and used as received. The reaction was carried out in a glass thermostated container under nitrogen atmosphere. Toluene was used as a solvent. The introduction of the catalyst into the mixture (10 ml) of EAEA, TBHP and toluene was considered as the start of reaction. Under these conditions, 2,3-epoxy-2-ethylpropyl ethylacrylate (epoxide), which was characterized in [7], was formed. Additional experiments revealed that the reaction does not proceed without the catalyst and TBHP is almost not consumed under reaction conditions in the course of 1 hr. The TBHP content was determined by a iodometric titration. Other components were analyzed by using gas-liquid chromatography. A 3 m × 4 mm column filled with 10% Apiezon L on Chromatone N-AM was used for the separation on a "Tswet-100" apparatus at 450 K. Helium (carrier) consumption was 3.6 l/hr.

RESULTS AND DISCUSSION

The TBHP consumption in the course of epoxidation in the presence of Mo_2B and Mo_2B_5 is given in Fig. 1. One can see, that the rate of hydroperoxide consumption is quite significant. In the presence of Mo_2B, the dependence looks typical of autocatalytic reactions. The rate increase at beginning of the reaction can be related to the accumulation of catalyst homogeneous phase, that is the real catalyst of the reaction or it can be related to the surface activation processes. To reveal the reason for the induction period, the reaction was carried out up to the end of induction period. Then, the heterogeneous catalyst was filtered off and the process was continued without the heterogeneous catalyst. In this case, the hydroperoxide consumption is negligible. Then, the filtered catalyst was used in the new reaction mixture. In this case, induction period decreases and after it the process proceeds in a fashion similar to the initial reaction after induction period. The catalysts recovered right after induction period and after reaction completion exhibit the same activity.

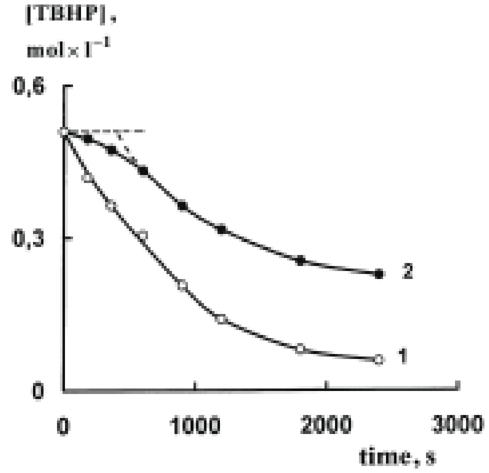

Figure 1. TBHP consumption in the presence of Mo_2B_5 (1) and Mo_2B (2). ($[EAEA]_0 = 2.2\ mol \cdot l^{-1}$, $[X_0] = 8\ g \cdot l^{-1}$, $T = 363$ K).

In the beginning of the epoxidation process in the presence of a heterogeneous catalyst, a catalyst surface modification takes place and, consequently, this leads to the increase of the process rate. Afterwards, the TBHP consumption is mediated by the activated catalyst. That is why the kinetic data were extrapolated to the initial concentration of TBHP after induction period and the initial rate (W_o) found (Fig. 1, dotted line) in the conditions when the catalyst is completely activated at the initial concentration of TBHP.

The effect of EAEA amount, TBHP concentration, and Mo_2B and Mo_2B_5 presence on the initial rate of TBHP consumption are shown in Fig. 2; the effect of the catalysts, the epoxide and the alcohol amount, introduced into the reaction vessel, on the initial rate of TBHP consumption, are shown in Fig. 3. The results show that the initial rate of the process does not essentially depend on the EAEA amount for both catalysts (Mo_2B and Mo_2B_5). The introduction of the epoxide (EP) to the reaction mixture, before the reaction start, leads to the decrease in the initial rate of the reaction. This means that epoxide is an inhibitor of the reaction.

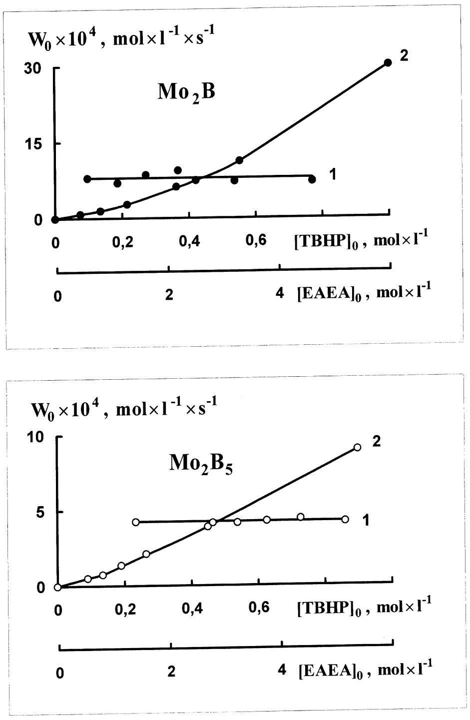

Figure 2. The effect of EAEA (1) and TBHP (2) initial concentrations in the presence of Mo_2B_5 (T = 363 K) and Mo_2B (T = 383 K) on the initial rate of the reaction.

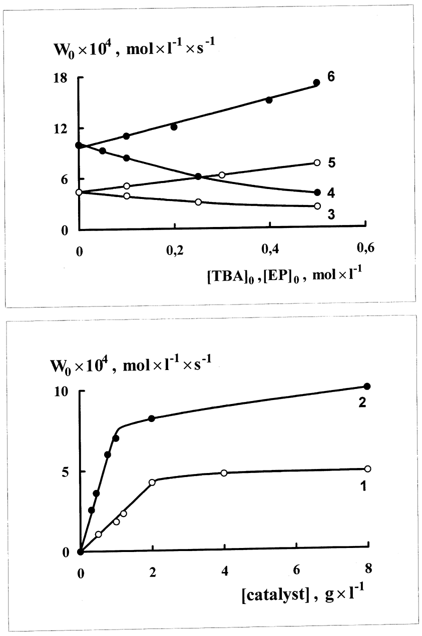

Figure 3. The effect of the initial concentration of catalysts (1, 2), of the epoxide (3, 4), and of the TBA (5, 6) in the presence of Mo_2B_5 (1, 3, 5) (T = 363 K) and Mo_2B (2, 4, 6) (T = 383 K) on the initial rate of the reaction.

The plot of $1/W_0$ *vs*. $[EP]_0$ is shown in Fig. 4. It can be seen, that the dependence is almost linear in the presence of Mo_2B_5 and is nonlinear in the presence of Mo_2B. The nonlinear dependence of $1/W_0$ on $[EP]_0$ in the presence of Mo_2B may suggest that in the presence of the catalyst the epoxide partially transforms under the influence of the reagents to a more powerful inhibitor of the process. The introduction of *tert*-butyl alcohol (TBA) to the reaction mixture results in an almost linear increase in the initial rate of the reaction in the presence of both catalysts (Fig. 3).

When the equimolar mixture of the epoxide and the alcohol is introduced into the reaction mixture, the effect of the catalysts on the reaction path is different. In the presence of Mo_2B_5, the addition of the equimolar mixture does not influence the kinetics of the process, while in the presence of Mo_2B the process becomes slower, though to a smaller extent than in the presence of the same amount of epoxide.

The results for EAEA TBHP epoxidation in the presence of Mo_2B and Mo_2B_5 heterogeneous catalysts can be explained according to the scheme already formulated for reaction in the presence of ammonium molybdate [8]. At the very beginning of the process, the active form of the catalyst (X_0) is formed. The active form produces EAEA–catalyst complex:

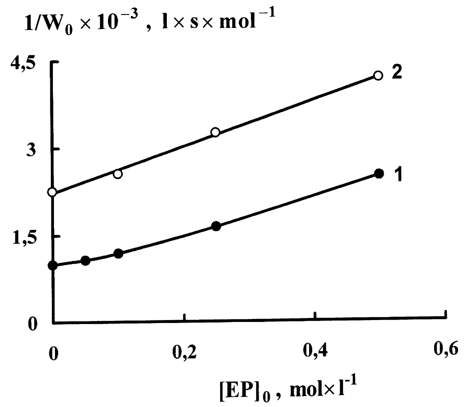

Figure 4. The plot of $1/W_0$ *vs.* $[EP]_0$ in the presence of Mo_2B_5 (2) and Mo_2B (1).

$$\mathrm{EAEA} + X_0 \rightleftarrows X$$

The zero order of the reaction with respect to the ester suggests that the equilibrium is shifted to a large extent to the right and all catalyst present initially is bound into the complex with the ester.

The complex X reacts with other substances in the reaction mixture, forming catalytically active complexes TBHP–catalyst–EAEA (X_1) and TBA–catalyst–EAEA (X_3) and inactive complex epoxide–catalyst–EAEA (X_2):

$$X + \mathrm{TBHP} \overset{K_1}{\rightleftarrows} X_1; \quad X + \mathrm{EP} \overset{K_2}{\rightleftarrows} X_2; \quad X + \mathrm{TBA} \overset{K_3}{\rightleftarrows} X_3$$

The product formation proceeds according to:

$$X_1 + \mathrm{TBHP} \xrightarrow{k_{e1}} \text{products} \quad (1) \qquad X_2 + \mathrm{TBHP} \xrightarrow{k_{e2}} \text{products} \quad (2)$$

It is possible that TBHP–catalyst–EAEA (X_1) complex produces epoxide by inner-sphere reaction, which has not been accounted for in [8], and the following reaction should be added to the general scheme:

$$X_1 \xrightarrow{k_{e3}} \text{products} \quad (3)$$

The kinetic analysis in the quasi-stationary approximation leads to the following general equation for the reaction rate:

$$W = \frac{k_{e1}K_1[\mathrm{TBHP}] + k_{e2}K_3[\mathrm{TBA}] + k_{e3}K_1}{1 + K_1[\mathrm{TBHP}] + K_2[\mathrm{EP}] + K_3[\mathrm{TBA}]}[\mathrm{TBHP}][X_0]$$

Taking into account that there is a linear dependence of the initial reaction rate on the alcohol concentration, the K_3[TBA] value in the denominator can be neglected. Then, general equation for the reaction rate reads as follows:

$$W = \frac{k_{e1}K_1[TBHP] + k_{e2}K_3[TBA] + k_{e3}K_1}{1 + K_1[TBHP] + K_2[EP]}[TBHP][X_0]$$

The initial reaction rate should follow equation under conditions $[TBA]_0 = [EP]_0 = 0$:

$$W_0 = \frac{k_{e1}K_1[TBHP]_0 + k_{e3}K_1}{1 + K_1[TBHP]_0}[TBHP]_0[X_0] \qquad (4)$$

The reaction order with respect to the hydroperoxide found from $\ln W_0 = f(\ln[TBHP]_0)$ dependence can range from 0 to 2. The limiting conditions are defined by the ratios of epoxide formation rate in reactions (1) and (3) and the stability of X_1 (TBHP–catalyst–EAEA) complex. The limiting conditions and possible reaction orders (n) are given in Table.

The experimental reaction order found from $\ln W_0 = f(\ln[TBHP]_0)$ in the presence of Mo_2B is 1.40, while in the presence of Mo_2B_5 is 1.26. Thus, in both cases $1 < n < 2$, which corresponds to the limiting condition 2 or 4 (Table). If the case 2 is adopted, which means that catalyst has average ability to form X_1 complex and almost no epoxide is formed by inner-sphere mechanism, then the following equation should describe the initial reaction rate dependence on the initial concentration of TBHP:

$$W_0 = \frac{k_{e1}K_1[TBHP]_0^2}{1 + K_1[TBHP]_0}[X_0]$$

One can transform the equation to a linear form, and find the solution:

$$\frac{[TBHP]_0^2}{W_0} = \frac{1}{k_{e1}K_1[X_0]} + \frac{1}{k_{e1}[X_0]}[TBHP]_0$$

Table. Possible reaction orders according to equation (4) under various limiting conditions.

	Limiting condition	Order n
1	$k_{e1} >> k_{e3}$; $K_1[TBHP]_0 << 1$	2
2	$k_{e1} >> k_{e3}$; $K_1[TBHP]_0 \approx 1$	$1 < n < 2$
3	$k_{e1} >> k_{e3}$; $K_1[TBHP]_0 >> 1$	1
4	$k_{e1} \approx k_{e3}$; $K_1[TBHP]_0 << 1$	$1 < n < 2$
5	$k_{e1} \approx k_{e3}$; $K_1[TBHP]_0 >> 1$	$0 < n < 1$
6	$k_{e1} << k_{e3}$; $K_1[TBHP]_0 \approx 1$	$0 < n < 1$
7	$k_{e1} << k_{e3}$; $K_1[TBHP]_0 >> 1$	0

In Fig. 5, one can see that this dependence describes the reaction well in the presence of Mo_2B_5 and unsatisfactory in the presence of Mo_2B.

The limiting condition 4 (Table) envisages comparability of the rate of epoxide formation by the inner-sphere and the outer-sphere mechanisms and low stability of X_1 complex. In this case, the dependence of the initial reaction rate on the initial concentration of TBHP should be expressed by the equation:

$$W_0 = (k_{e1}K_1[TBHP]_0 + k_{e3}K_1)[TBHP]_0[X_0],$$

with the form for graphic solution as follows:

$$\frac{W_0}{[TBHP]_0} = k_{e1}K_1[TBHP]_0[X_0] + k_{e3}K_1[X_0]$$

Fig. 6. shows that linear dependence $W_0/[TBHP]_0 = f([TBHP]_0)$ is observed in a wide range of TBHP initial concentration only for the reaction in the presence of Mo_2B. For Mo_2B_5, the deviation from linearity is observed, especially at low initial concentrations of hydroperoxide. Taking the above into account, the general equation for epoxidation process in the presence of Mo_2B_5 can be written as follows:

$$W = \frac{k_{e1}K_1[TBHP] + k_{e2}K_3[TBA]}{1 + K_1[TBHP] + K_2[EP]}[TBHP][X_0] \tag{5}$$

From the linear correlations $[TBHP]_0^2/W_0$ – $[TBHP]_0$, $1/W_0$ – $[EP]_0$ and W_0 – $[TBA]_0$, the equilibrium constants (K_1 and K_2) of complex formation – Mo_2B_5 with hydroperoxide (K_1) and epoxide (K_2) blocked by ester – are calculated at 363 K; they

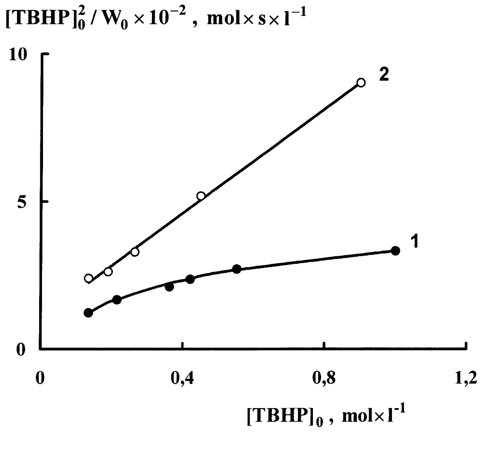

Figure 5. The plot of $[TBHP]_0^2/W_0$ *vs.* $[TBHP]_0$ in the presence of Mo_2B_5 (2) and Mo_2B (1).

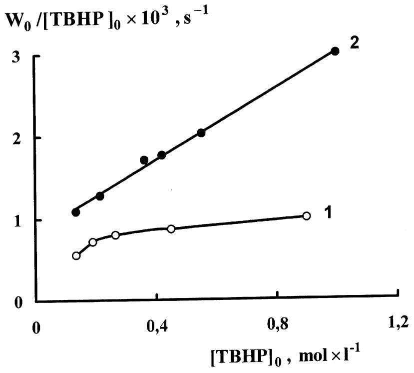

Figure 6. The plot of W_0/[TBHP]$_0$ *vs.* [TBHP]$_0$ in the presence of Mo_2B_5 (1) and Mo_2B (2).

are equal to 9.5 and 8.6 l·mole^{-1}, respectively, and effective constants $k_{e1}K_1 = 4.8\cdot10^{-3}$ $l^2/(mol\cdot g\cdot s)^{-1}$ and $k_{e2}K_3 = 3.4\cdot10^{-3}$ $l^2/(mol\cdot g\cdot s)^{-1}$. The general equation for Mo_2B can be written in the following form:

$$W = \frac{k_{e1}K_1[TBHP] + k_{e2}K_3[TBA] + k_{e3}K_1}{1 + K_2[EP]}[TBHP][X_0] \tag{6}$$

From the W_0/[TBHP]$_0$ – [TBHP]$_0$ and W_0 – [TBA]$_0$ linear correlations, the effective constants $k_{e1}K_1$, $k_{e2}K_3$, and $k_{e3}K_1$ are calculated at 383 K and they are equal $2.0\cdot10^{-3}$ $l^2/(mol\cdot g\cdot s)^{-1}$, $2.9\cdot10^{-3}$ $l^2/(mol\cdot g\cdot s)^{-1}$, and $9.2\cdot10^{-4}$ $l/(g\cdot s)^{-1}$ respectively. The constants are calculated at the catalyst content 1 g·l^{-1} – concentration at which the dependence of the initial reaction rate on the catalyst concentration levels off. Taking into account, that $1/W_0$ – [EP]$_0$ dependence is nonlinear, K_2 value was found by minimization of the deviation between the experimental and calculated according to (8) kinetic curves. K_2 is found by this approach to be 0.47 l·mol^{-1}.

The integral forms of (5) and (6) are as follows:

$$\left[\frac{K_1 - K_2}{(k_{e1}K_1 - k_{e2}K_3)[X_0]} - \frac{1 + K_2([TBHP]_0 + [EP]_0)}{(k_{e2}K_3([TBHP]_0 + [TBA]_0)[X_0]}\right]\times$$

$$\times \ln\left[\frac{k_{e2}K_3([TBHP]_0 + [TBA]_0) + (k_{e1}K_1 - k_{e2}K_3)[TBHP]_0}{k_{e2}K_3([TBHP]_0 + [TBA]_0) + (k_{e1}K_1 - k_{e2}K_3)[TBHP]}\right] + \tag{7}$$

$$+ \frac{1 + K_2([TBHP]_0 + [EP]_0)}{k_{e2}K_3([TBHP]_0 + [TBA]_0)[X_0]} \ln\frac{[TBHP]_0}{[TBHP]} = t$$

and

$$\left[\frac{K_2}{(k_{e1}K_1 - k_{e2}K_3)[X_0]} + \frac{1 + K_2([TBHP]_0 + [EP]_0)}{(k_{e3}K_1 + k_{e2}K_3([TBHP]_0 + [TBA]_0))[X_0]}\right] \times$$

$$\times \ln\left[\frac{k_{e3}K_1 + k_{e2}K_3([TBHP]_0 + [TBA]_0) + (k_{e1}K_1 - k_{e2}K_3)[TBHP]}{k_{e3}K_1 + k_{e2}K_3([TBA]_0 + k_{e3}K_1[TBHP]_0}\right] + \tag{8}$$

$$+ \frac{1 + K_2([TBHP]_0 + [EP]_0)}{(k_{e3}K_1 + k_{e2}K_3([TBHP]_0 + [TBA]_0))[X_0]} \ln\frac{[TBHP]_0}{[TBHP]} = t$$

Theoretical kinetic curves of TBHP consumption calculated according to (7) for Mo_2B_5 and (8) for Mo_2B (after induction period) are similar to experimental data (up to 80%) TBHP conversion (for example, in Fig. 7 theoretical kinetic curves calcu-

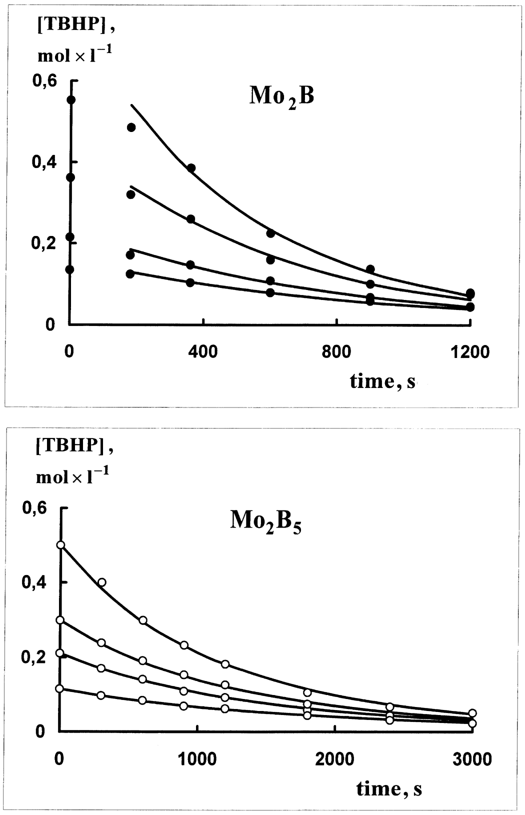

Figure 7. Theoretical kinetic curves calculated for different initial concentrations of TBHP and experimental TBHP consumption in the presence of Mo_2B ($[X_0] = 1\ g{\cdot}l^{-1}$, $T = 383$ K) and Mo_2B_5 ($[X_0] = 2.2\ g{\cdot}l^{-1}$, $T = 363$ K). ($[EAEA]_0 = 2.2\ mol{\cdot}l^{-1}$, $[TBA]_0 = 0\ mol{\cdot}l^{-1}$, $[EP]_0 = 0\ mol{\cdot}l^{-1}$).

lated for different initial concentrations of TBHP) that testify the adequacy of the admitted reaction model.

CONCLUSIONS

The obtained results show that ethylallyl ethylacrylate epoxidation with *tert*-butyl hydroperoxide in the presence of Mo_2B_5 and Mo_2B can be described by the same kinetic model. The increase of Mo/B ratio in the catalyst leads to the weakening of catalyst interaction with the hydroperoxide and increase of the contribution of reaction (3) in the overall reaction rate. As the result, analytical equations that describe the reaction rate in the presence of the different catalysts are different.

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