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Kinetics of 2-Methylbutene-2 Epoxidation with 2-Methylbutane Hydroperoxide

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Abstract—The kinetics of 2-methylbutene-2 epoxidation with 2-methylbutane hydroperoxide was studied in the presence of a molybdenum catalyst. The mathematical description of the hydroperoxide consumption and 2-methyl-butene-2 oxide formation was derived, and the most probable scheme of the process was suggested. The main kinetic constants were calculated.

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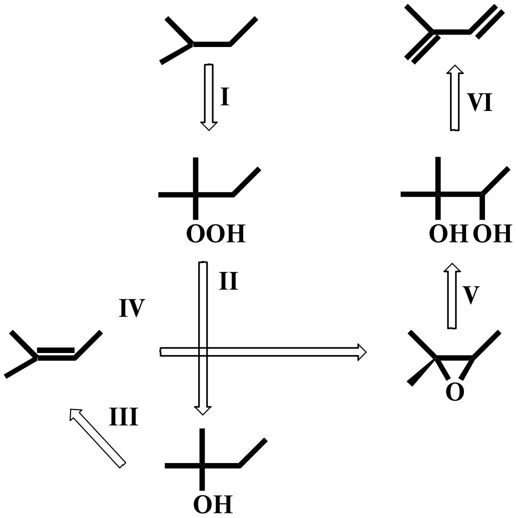
The synthesis of isoprene from isopentane via the reaction sequence involving 2-methylbutene-2 oxide (OMB) is one of the most promising isoprene manufacturing processes [1, 2] (Scheme 1):



Scheme 1.

The specific feature of the process is the fact that the successive transformations of 2-methylbutane hydroperoxide (HPMB) into 2-methylbutanol-2 (MBOL) (route II) and the OMB synthesis from 2-methylbutene-2 (OL) (route IV) are combined in one process, i.e., in the hydroperoxide epoxidation of olefin. This is shown in the scheme by crossing of the arrows referring to routes II and IV. The scheme also involves the stages of HPMB synthesis (route I); OMB hydration to 2-methylbutanediol (MBD) (route V); and the dehydration of the alcohols, namely, the conversion of MBOL into the olefin and MBD into isoprene, the final product. The key stage of the overall process shown in the scheme is epoxidation, which determines the isoprene production efficiency in many respects. Various molybdenum compounds were used as catalysts [3, 4].

In this work, we studied the general features of 2-methulbutene-2 epoxidation with 2-methylbutane hydroperoxide in the presence of a molybdenum-containing catalyst. Revealing the trends in the characteristics of the process and its mathematical description are of great importance for both the design of a reaction unit for the commercial production of isoprene according to the scheme given above and the epoxidation theory. Moreover, it is quite unclear whether the steric factor has an effect on the reaction mechanism, as the reactants bear bulky substituents.

EXPERIMENTAL

Experiments were carried out at a temperature of 30–40°C in a steady system with the use of a temperature-controlled glass vessel (50 ml) equipped with a heating jacket, a thermostat, a stirring device, a condenser, and a thermometer. The thermocatalytic decomposition of hydroperoxide was not observed at these temperatures, and OMB is formed almost quantitatively, thereby simplifying the study of the kinetics of the process in question. The reaction was carried out in isopentane. As a catalyst, we used a freshly prepared solution of bis(2-methylbutanediol-2,3) molybdate in MBD with 3.5 wt % of molybdenum, which was obtained by solution of molybdenum anhydride in MBD according to the procedure described in [5]. HPMB was synthesized according to the procedure described in [6]. 2-Methylbutene-2 was synthesized by the dehydration of MBOL in the presence of a KU-2

FPP catalyst. All the compounds were identified by IR, NMR, electronic absorption spectroscopy, and elemental analysis.

The progress of the reaction course was monitored by following the hydroperoxide consumption, because the selectivity for the oxide was 93–97% in all cases. The epoxidation reaction mixture was analyzed for HPMB by iodometric titration. The concentration of homogeneous molybdenum was determined by titration with an ammonium metavanadate solution in the presence of phenylanthranylic acid after molybdenum conversion into the pentavalent form by heating with an acidic phenylhydrazine solution. The concentration of OMB in the reaction mixture was determined by titration: an aliquot was added to a saturated $MgCl_2$ solution containing a 0.02 N HCl solution, held for 15 min at an ambient temperature, and the residual HCl was titrated with a KOH solution.

Kinetic Studies of the Process

Many publications are devoted to the kinetics of the hydroperoxide epoxidation of olefins, and the process itself has been employed in industry for a long time [1, 7]. Despite some disagreements in the interpretation of the details, most researchers agree with the general scheme of epoxidation, which involves the fast equilibrium formation of a catalyst complex with hydroperoxide and its slow reaction with the olefin:

$$[\mathrm{ROOH}] + [\mathrm{cat}] \xleftrightarrow{K_1} [\mathrm{cat} \cdot \mathrm{ROOH}] \qquad \text{(I)}$$

$$[\mathrm{cat} \cdot \mathrm{ROOH}] + [\mathrm{OL}] \xrightarrow{\kappa 0} [\mathrm{cat}] + [\mathrm{ROH}] + [\mathrm{oxide}]. \qquad \text{(II)}$$

The reaction course is complicated by the formation of various catalyst complexes with reaction products, which causes the so-called simple, quadratic, and crossed inhibition:

$$[\mathrm{ROH}] + [\mathrm{cat}] \xleftrightarrow{K_2} [\mathrm{cat} \cdot \mathrm{ROH}] \qquad \text{(III)}$$

$$2[\mathrm{ROH}] + [\mathrm{cat}\,] \xleftrightarrow{K_3} [\mathrm{cat} \cdot 2\mathrm{ROH}] \qquad \text{(IV)}$$

$$[\mathrm{ROH}] + [\mathrm{ROOH}] + [\mathrm{cat}] \xleftrightarrow{K_4} [\mathrm{cat} \cdot \mathrm{ROOH} \cdot \mathrm{ROH}]. \qquad \text{(V)}$$

The formation of these complexes in the reaction mixture was established not only by the analysis of kinetic data, but also by physicochemical methods [8–10]. According to published data, the rate equation for olefin epoxidation by hydroperoxides described above (reactions (I)~(V)) is a linear-fractional function

$$-\frac{d[\mathrm{ROOH}]}{dt} = \frac{k_0 \cdot K_1 \cdot [\mathrm{cat}] \cdot [\mathrm{OL}] \cdot [\mathrm{ROOH}]}{1 + K_1[\mathrm{ROOH}] + K_2[\mathrm{ROH}] + K_3[\mathrm{ROH}]^2 + K_4[\mathrm{ROOH}] \cdot [\mathrm{ROH}]}, \qquad (1)$$

where the terms in the denominator of Eq. (1) correspond to the formation of various complexes of the reactants and the products with the catalyst (so-called catalyst complexation function).

Taking into account the material balance relation, i.e., $[\mathrm{ROH}] = [\mathrm{ROOH}]_0 - [\mathrm{ROOH}]$, Eq. 1 can be represented as a function of a single variable (2):

$$-d[\mathrm{ROOH}]/dt = [\mathrm{ROOH}]/(\alpha + \beta[\mathrm{ROOH}] + \gamma[\mathrm{ROOH}]^2), \qquad (2)$$

where

$$\alpha = (1 + K_2[\mathrm{ROOH}]_0 + K_3[\mathrm{ROOH}]_0^2)/k_0K_1[\mathrm{cat}] \cdot [\mathrm{OL}]) \qquad (3)$$

$$\beta = (K_1 - K_2 - 2K_3[\mathrm{ROOH}]_0 + K_4[\mathrm{ROOH}]_0)/k_0K_1[\mathrm{cat}] \cdot [\mathrm{OL}]) \qquad (4)$$

$$\gamma = (K_3 - K_4)/(k_0K_1[\mathrm{cat}] \cdot [\mathrm{OL}])). \qquad (5)$$

We used this description of the process as a working hypothesis for revealing the following problems:

(i) formulation of the mathematical description of the hydroperoxide consumption and formation of OMB and suggestion of the more probable mechanism of the process;

(ii) solution of the problem regarding whether the reaction of interest obeys the most widespread scheme of metal complex catalysis, as the reaction centers of both reactants OL and HPMB possess bulky substituents.

In order to simplify the solution of this problem, we studied the reaction kinetics until ~50% hydroperoxide conversion, thereby diminishing the effect of the quadratic and crossed inhibition.

RESULTS AND DISCUSSION

Kinetic investigations were carried out by several series of single-factor experiments, with only one parameter being changed in each series. The series were as follows: (1) the influence of the catalyst concentration on the reaction rate at constant concentrations $[\mathrm{HPMB}]_0$ and $[\mathrm{OL}]_0$ and a temperature of $T =$ 45°C (Table 1); (2) the influence of the initial olefin concentration $[\mathrm{OL}]_0$ at constant $[\mathrm{HPMB}]_\mathrm{o}$ and catalyst $[\mathrm{cat}]_0$ concentrations and a temperature of $T =$ 45°C (Table 2); (3) two series with varying initial concentration $[\mathrm{HPMB}]_\mathrm{o}$ at different olefin concentrations: $[\mathrm{OL}]_0 = 7.2$ and 4 mol/l at a constant catalyst concentration of $[\mathrm{cat}]_0 = 2 \times 10^{-3}$ mol/l and a temperature of $T = 45$°C (Table 3); and (4) the influence of the temperature on the behavior of the hydroperoxide

Table 1. Effect of the catalyst concentration on the time variation of the hydroperoxide concentration (mol/l) at $[HPMB]_0 =$ 1.6 mol/l, $[OL]_0 = 7.2$ mol/l, and the temperature $T = 45°C$

Time, min	[cat], mol/l		
	1×10^{-3}	2×10^{-3}	3.0×10^{-3}
0	1.6	1.6	1.6
5	1.4	1.25	1.1
10	1.25	1.1	0.9
15	1.15	0.92	0.7
20	1.05	0.8	0.6
25	0.97	0.72	–
35	0.85	–	–

concentration with time at constant $[HPMB]_0$ and $[OL]_0$ concentrations and $[cat]_0 = 2 \times 10^{-3}$ mol/l (Table 4).

First, we processed the rate curves of the experiments on the influence of the catalyst concentration on the epoxidation rate. Based on the assumption that the catalyst concentration is involved as a factor in the rate equation and is not a function of time (the catalyst is stable during the reaction), i.e., the rate equation has the form of Eq. (6):

$$-d[\mathrm{HPMB}]/dt = [\mathrm{cat}] \cdot f([\mathrm{HPMB}]), \qquad (6)$$

the following equation can be derived in the integral form after the separation of the variables:

$$\int_{[\mathrm{HPMB}]_0}^{[\mathrm{HPMB}]} d[\mathrm{HPMB}]/f([\mathrm{HPMB}]) = [\mathrm{cat}] \cdot t, \qquad (7)$$

where $[HPMB]_0$ and [HPMB] are the initial and current concentrations of HPMB, and t is the reaction time.

Equation (7) shows that at the constant initial concentration of hydroperoxide ($[HPMB]_0$), i.e., at the equality of the left parts of Eq. (7), all kinetic curves in a single-factor experimental series concerning the effect of the catalyst concentration should give the same curve in the [HPMB] vs. $[cat]t$ coordinates. For the convenience of the treatment of all of the experimental series, we plotted the diagrams for the time variation of the current HPMB concentrations in the [HPMB] vs. $[cat]/[cat]_0t$ or [HPMB] vs. λt coordinates, where $\lambda = [cat]/[cat]_0$, [cat] is the catalyst concentration in a given run, and $[cat]_0 = 0.002$ mol/l is the catalyst concentration at which all other experimental series were carried out.

Superimposing all kinetic curves of the series concerning the influence of the catalyst (Table 1) in the same diagram in the [HPMB]–λt coordinates shows the left-hand part of Eq. 7 to be proportional to λ, indicating that the reaction is first-order in the catalyst (Fig. 1) [11].

It may be supposed that similar to the catalyst concentration, the olefin concentration is involved in the rate equation as a factor and is time-invariant providing that $[HPMB]_0 \ll [OL]_0$. However, the above-described treatment of rate curves for the series of experiments specified in Table 2 did not give positive results. The data points plotted in the [HPMB]–$[OL]_0t$ coordinates did not fall on the same line. The reaction slowed down with progress—the lower the excess of olefin over HPMB, the stronger the deceleration. On the other hand, the initial reaction rates (W_0) in this experimental series (Table 2) were proportional to the initial olefin concentration. The following linear dependence (8) was observed over the entire range of $[OL]_0$ examined.

$$W_0 = (0.014 \pm 0.001) \times [\mathrm{OL}]_0,\ \mathrm{mol\ l^{-1}\ min^{-1}}. \qquad (8)$$

The first order of the reaction with respect to the olefin is also confirmed by the results of the treatment of the rate curves of OL consumption, determined as a difference between the current and initial HPMB concentrations, in semilogarithmic coordinates (at $[HPMB]_0 \gg [OL]_0$). The rate constant of the pseudo-first-order olefin consumption is (0.015 ± 0.001) $\mathrm{min^{-1}}$ in this case, which coincides with the value deter-

Table 2. Effect of the initial concentration of olefin (OL) on the time variation of the HPMB concentration ($[HPMB]_0 =$ 1.5 mol/l, $[cat]_0 = 2 \times 10^{-3}$, $T = 45°C$

Time, min	Initial concentratione OL, mol/l						
	0.1	0.3	0.5	1.0	2.0	3.0	5.0
0	1.5	1.5	1.5	1.5	1.5	1.5	1.5
10	1.49	1.44	1.43	1.4	1.3	1.3	1.16
20	1.48	1.43	1.39	1.3	1.18	1.07	0.91
30	1.47	1.42	1.35	1.25	1.1	0.96	0.81
40	1.46	1.41	1.32	1.2	1.03	0.9	0.74
50	1.45	1.41	1.3	1.18	1.02	0.9	

Table 3. Effect of the initial concentration of hydroperoxide on the time variations of its concentration at $[\mathrm{OL}]_0 = 4$ and 7.2 mol/l, $[\mathrm{cat}]_0 = 2 \times 10^{-3}$ mol/l at 45°C

Time, min	[OL] = 4 mol/l			[OL] = 7.2 mol/l			
	[HPMB], mol/l						
0	0.95	1.5	1.7	0.5	0.83	1.2	1.6
5	0.8	1.3	1.5	0.35	0.63	0.97	1.25
10	0.72	1.16	1.35	0.3	0.48	0.76	1.1
15	0.65	1.1	1.3	0.25	0.4	0.65	0.95
20	0.6	1	1.22	0.22	0.38	0.58	0.85
25	0.57	0.98	1.18	0.2	0.35	0.53	0.76
30	0.55	0.96	1.16				

mined by the method of initial rates. The comparison of these results allows us to conclude that the olefin interacts with the products formed during the reaction, causing a change in the performance of the catalyst. Mathematically, this means that the olefin concentration ([OL]) is involved not only as a factor in the function $f([\mathrm{HPMB}])$ in Eqs. (6) and (7). To clarify the role of olefin in this process, it is necessary to express the function $f([\mathrm{HPMB}])$ in the explicit form. For this purpose, we treated the experimental series on the effect of the initial HPMB concentrations given in Tables 2 and 3.

The integral form of Eq. (2), Eq. (9), can easily be analyzed by a linear regression method:

$$\alpha\frac{\ln([\mathrm{HPMB}]_0/[\mathrm{HPMB}])}{t} + \beta\frac{([\mathrm{HPMB}]_0 - [\mathrm{HPMB}])}{t} + \gamma\frac{([\mathrm{HPMB}]_0^2 - [\mathrm{HPMB}]^2)}{t} = 1, \tag{9}$$

where the functional values of α, β, and γ are given above (Eqs. (3)–(5)).

Table 4. Effect of the temperature on the time variation of hydroperoxide at $[\mathrm{HPMB}]_0 = 1.7$ mol/l, $[\mathrm{OL}]_0 = 7.2$ mol/l, and $[\mathrm{cat}]_0 = 2 \times 10^{-3}$ mol/l

Time, min	Temperature, °C		
	30	35	40
0	1.7	1.7	1.7
5	1.57	1.50	1.48
10	1.51	1.40	1.33
20	1.40	1.20	1.05
30	1.30	1.00	0.80
40	1.20	0.88	0.68

The statistical treatment of the arrays of data for the experimental series dealing with the effect of the initial concentration of HPMB on the reaction (Table 3) showed that the coefficient at the third term γ in Eq. (9) is insignificant. On one hand, this result confirmed our assumption that the so-called quadratic and crossed inhibition did not manifest themselves at hydroperoxide conversions below 50%. On the other hand, data processing becomes much simpler, since the quadratic term in the denominator in Eqs. (1) and (2) disappears. In principle, the appearance of the insignificant factor γ might indicate the equality of the equilibrium constants K_3 and K_4 (see the functional dependence of γ in Eq. (5)). However, a more concrete answer can be given from the analysis of the dependences for α and β.

Further, we treated the data by linearization, which is a more illustrative statistical method. With allowance for the insignificance of γ, Eq. (2) is reduced to Eq. (10) (notations [ROOH] and [HPMB] are the same):

$$-d[\mathrm{HPMB}]/dt = [\mathrm{HPMB}]/(\alpha^* + \beta^* \cdot [\mathrm{HPMB}]), \tag{10}$$

where

$$\alpha^* = (1 + K_2\,[\mathrm{HPMB}]_0)/(k_0 \cdot K_1 \cdot [\mathrm{cat}] \cdot [\mathrm{OL}])$$

$$\beta^* = (K_1 - K_2)/(k_0 \cdot K_1 \cdot [\mathrm{cat}] \cdot [\mathrm{OL}])$$

and, after integration, it can be presented in a more convenient form (Eq. (10a)) for data processing by regression analysis:

$$Y = 1/\beta^* + (-\alpha^*/\beta^*) \cdot X, \tag{10a}$$

where X and Y are the variables

$$Y = ([\mathrm{HPMB}]_0 - [\mathrm{HPMB}])/t,$$

$$X = \ln([\mathrm{HPMB}]_0/[\mathrm{HPMB}])/t.$$

Indeed, processing the experimental data from Table 3 in $Y \sim X$ coordinates yields a set of linear dependences (Fig. 2, curves *1*–*4*). All of these straight lines cross at the same point on the ordinate axis, and the slope linearly depends on $[\mathrm{HPMB}]_0$. These findings indicate the following:

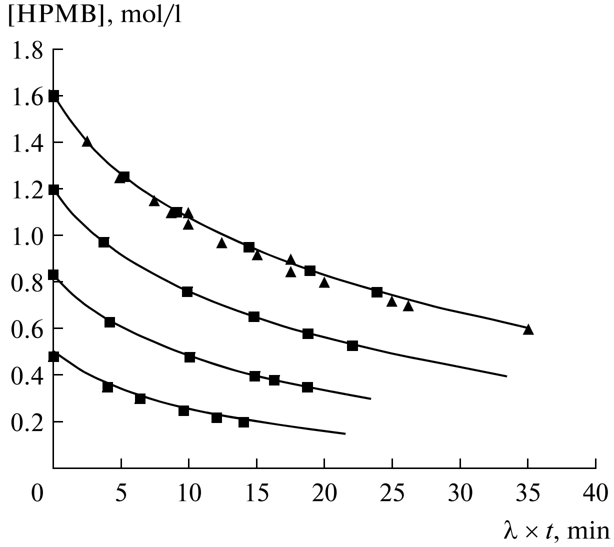


Fig. 1. Experimental data points and calculated rate curves for the experimental series: effect of the hydroperoxide initial concentration (data from Table 3, ■) and the effect of the catalyst concentration (data from Table 1, ▲). λ is a dimensionless value (see text).

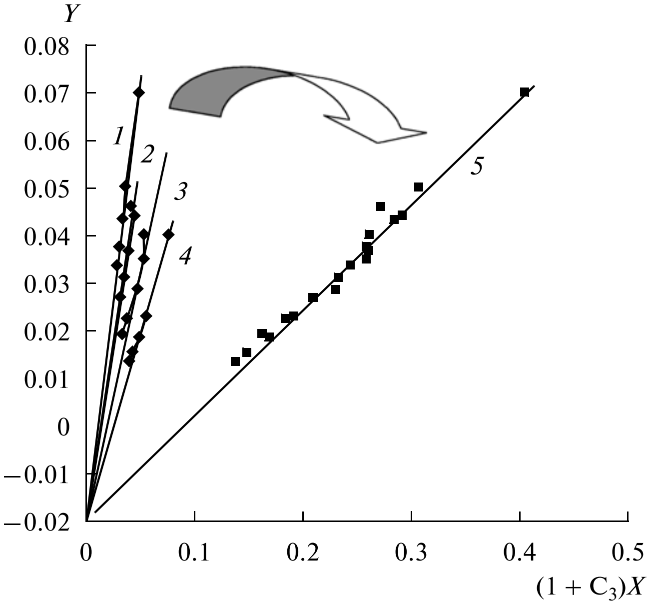


Fig. 2. Results of the treatment of the experimental series on the effect of the hydroperoxide initial concentration (Table 3). The designation of the diagram axes is given in the text. (*1*)–(*4*) corresponds to the experiments with $[HPMB]_0$) = 1.6, 1.2, 0.85, and 0.5 mol/l at $C_3 = 0$; (*5*) involves all experiments of this series at $C_3 = 5.4$.

—the crossing of the straight lines at one point on the ordinate axis shows that the constant β* does not depend on the initial substrate concentration $[HPMB]_0$; i.e., there are no terms with constants K_3 and K_4, and

—the linear relation of the slope to $[HPMB]_0$ confirms the reaction scheme involving only equilibriums (I), (II), and (III) and the absence of the influence of the quadratic and crossed inhibition.

In order to more precisely determine the constants for Eq. (10a), we processed the whole array of data of this experimental series (Table 2) in somewhat altered coordinates:

$$Y = C_1 + C_2(1 + C_3[HPMB]_0)X, \qquad (11)$$

where C_1, C_2, and C_3 are the constants for this experimental series.

One can see that there is a unique dependence between the coefficients C_1, C_2, and C_3 and the parameters α* and β* Eq. (10). From the fitting procedure, we estimated the coefficient C_3 and obtained a single linear dependence, which comprised all data of the experimental series (Fig. 2, *5*). In the range $5.2 < C_3 < 5.6$, the confidence of approximation (R^2 of the linear regression determined by a standard Excel 93-2003 program) was maximum $R^2 = 0.98$. Within this approximation for the confidence level ($R^2 = 0.98$), the numerical values of C_1, C_2, and C_3 of linear Eq. (11) were estimated (Table 5). It is noteworthy that the values of these coefficients did not change after the introduction of the data on the effect of the catalyst concentration to the analysis.

A similar treatment of the data of the experimental series on the influence of $[HPMB]_0$ at another olefin concentration (Table 3) gave identical results (Table 5). The confidence level of the approximation was also high ($R^2 = 0.975$).

From the comparison of the values of C_1, C_2, and C_3 and the functional dependences of the α* and β* parameters of Eq. (10), the values of the effective rate constant and equilibrium constants were calculated for 45°C (Table 5). The rate constant k_0 and the constant K_1 for the equilibrium formation of the catalyst complex with hydroperoxide were the same in both cases, whereas the equilibrium constant for the formation of the catalyst complex with alcohol (K_2) depended on the olefin concentration in the reaction mixture.

In order to more precisely investigate the dependence of K_2 on the olefin concentration, we analyzed the experimental data obtained at $[OL]_0 = 3$ and 5 mol/l (Table 2). For this purpose, we minimized the function $F(K_2)$, which was derived by integrating differential equation (10):

$$\begin{aligned} F(K_2) &= (1 + K_2 \cdot [HPMB]_0) \cdot X \\ &+ (K_1 - K_2) \cdot Y - (k_0 \cdot K_1 \cdot [cat] \cdot [OL]) = 0, \end{aligned} \qquad (12)$$

where *X* and *Y* are the variables defined above (Eq. 10a).

The optimization was carried out by the least-squares method in parameter K_2 at constant values of

Table 5. Constants C_1, C_2, and C_3 of Eq. (11) and kinetic constants of Eq. (10)

T, °C	[OL], mol/l	C_1	C_2	C_3	k_0, min^{-1}	K_1, l mol^{-1}	K_2, l mol^{-1}
45	7.2	–0.020 ± 0.001	0.2 ± 0.01	5.3 ± 0.2	25 ± 1	0.3 ± 0.03	5.4 ± 0.2
45	5.0				25	0.3	6.0 ± 0.5
45	4.0	–0.009 ± 0.0005	0.15 ± 0.01	7.0 ± 0.5	25 ± 1	0.27 ± 0.03	7.0 ± 0.2
45	3.0				25	0.3	8.0 ± 0.8
30–45	0–7.2				$\Delta H_0 =$ 10000 ± 500	$\Delta H_1 =$ 1000 ± 300	$\Delta H_2 =$ 4000 ± 50

k_0 and K_1 obtained earlier. The results are listed in Table 5.

Thus, we found that the inhibition of the process by virtue of the equilibrium formation of the catalyst complex with the reaction products weakens with an increase in the methylbutene concentration in the solution. Without going into the reasons behind this phenomenon, it may be stated that it is due to the enhanced stability of molybdenum compounds in the presence of olefins [12]. Furthermore, it has been found [13, 14] that catalyst activation does not occur unless the system simultaneously contains both hydroperoxide and olefin.

To determine the temperature dependence of the kinetic constants, we analyzed the experimental data obtained at different temperatures (Table 4) and minimized the function $F(\Delta H_0, \Delta H_1, \Delta H_2)$, which was obtained by the integration of differential Eq. (10):

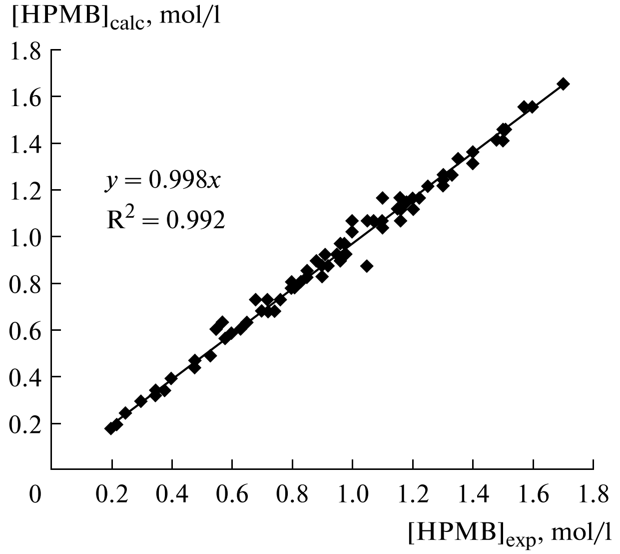


Fig. 3. Correlation of calculated $[\mathrm{HPMB}]_{\mathrm{calc}}$ and experimental $[\mathrm{HPMB}]_{\mathrm{exp}}$ values of the current concentration of HPMB for all experimental series under study.

$$F(\Delta H_0, \Delta H_1, \Delta H_2) = (1 + K_2[\mathrm{HPMB}]_0)\cdot X + (K_1 - K_2)\cdot Y - (k_0K_1[\mathrm{cat}]\cdot[\mathrm{OL}]), \quad (13)$$

where X and Y are the variables defined above and ΔH_0, ΔH_1, and ΔH_2 are the temperature coefficients of the exponential dependence of the constants k_0, K_1, and K_2, respectively.

The function $F(\Delta H_0, \Delta H_1, \Delta H_2)$ was optimized by the least-squares technique with ΔH_0, ΔH_1, ΔH_2 as fitting parameters at fixed values of the rate constants and equilibrium constants determined earlier for a temperature of 45°C [k_0(318 K), K_1(318 K), and K_2(318 K):

$$k_0 = \exp\{\ln k_0(318\ \mathrm{K}) + \Delta H_0(1/318 - 1/T)\}.$$

$$K_1 = \exp\{\ln K_1(318\ \mathrm{K}) + \Delta H_1(1/318 - 1/T)\}.$$

$$K_2 = \exp\{\ln K_2(318\mathrm{K}\ ) + \Delta H_2(1/318 - 1/T)\}.$$

The calculated data are listed in Table 5. The adequacy of the mathematical description of the process under study was confirmed as follows:

—the curves calculated with the use of Eq. (10) and the kinetic constants k_0, K_1, and K_2 fit well with the experimental data for all of the experimental series under consideration and

—the confidence level of approximation (R^2) for the correlation of all experimental (Tables 1–3) and calculated values of [OMB] is $R^2 = 0.99$ (Fig. 3).

The analysis of the rate curves for the reaction of HPMB with OL showed that this reaction follows the general trends characteristic of the hydroperoxide epoxidation of olefins. The rapidly formed catalytic complex of HPMB with the catalyst interacts with OL to give OMB and the corresponding alcohol. The alcohol also forms a complex with the catalyst, inhibiting the entire epoxidation process. The distinctive feature of this process is the fact that the latter equilibrium resulting in the simple inhibition of the reaction by the products shifts to the left with an increase in the olefin concentration in the solution. As a result, the reaction rate changes out of proportion to the olefin concentration, although the first order of the reaction in the olefin is clearly observed in the initial portion of the rate curves. The phenomenon of the unusual effect of the olefin accounts for the enhanced stability of the molybdenum compounds in the presence of olefins [12] and, in some cases, the catalyst activation [13, 14]. This phenomenon is likely due to the so-called steric factor, because the reactants possess bulky substituents, and is not observed for simple olefins. The revealed features of the process and its mathematical description make it possible to more competently design a reactor unit for the commercial production of isoprene according to the developed scheme.

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