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The Kinetics of the Reaction between Cyclopentene and Aqueous Hydrogen Peroxide under Phase-Transfer Catalysis

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Abstract—The kinetics of the reaction between cyclopentene and an aqueous solution of hydrogen peroxide under phase-transfer catalysis conditions has been studied. The activation energies of the successive stages of cyclopentene epoxidation to 1,2-epoxycyclopentane and the hydration of the resulting epoxide to 1,2-cyclopentanediol have been found, and the orders of the reactions with respect to the reactants have been determined. A mathematical model of the process that adequately describes the available experimental data in the entire range of reactant concentrations has been proposed.

Keywords: cyclopentene, hydrogen peroxide, 1,2-epoxycyclopentane, 1,2-cyclopentanediol, phase-transfer catalysis, kinetics, reaction rate, mathematical model

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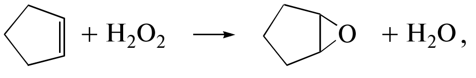
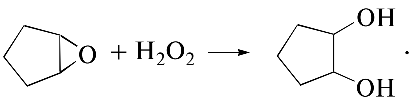
At present, the epoxidation of olefins with oxygen, organic hydroperoxides, and peracids are being implemented on an industrial scale, and hydrogen peroxide is becoming more commonly used as an oxidizing agent. This is caused by the fact that hydrogen peroxide is an effective and environmentally friendly oxidizing agent and the product of its reduction is water. A method for oxidizing unsaturated compounds with a dilute aqueous solution of hydrogen peroxide using tungsten and phosphorus heteropoly compounds in combination with phase-transfer catalysis was first proposed in the 1980s [1]; since then, the number of studies in this domain is increasing every year [2–5].

Oxygenated cyclopentene (CP) derivatives, such as epoxide, alcohols, and carbonyl compounds, are used in the synthesis of macromolecular compounds, fragrances, pharmaceuticals, and bactericides [6, 7]. We have developed a method for oxidizing CP with aqueous hydrogen peroxide [8], which makes it possible to obtain either 1,2-epoxycyclopentane or 1,2-cyclopentanediol with a high yield (over 95%) using a single setup. Methods for changing the ratios between the reaction rates of oxidation of CP (I) and hydration of the resulting epoxide (II) and thus controlling the direction of the process have been found:



(I)



(II)

The catalyst complex used in the process is formed in situ in the reaction mixture during mixing of tungsten salts, phosphoric acid, a phase-transfer catalyst (PTC) in a molar ratio of 1 : 1 : 0.36, and hydrogen peroxide. Haloalkanes or aromatic hydrocarbons are used as a solvent for the organic phase; hydrogen peroxide is taken in slight excess with respect to CP (1.3 : 1) to provide a more complete conversion of the olefin. This method is characterized by mild synthesis conditions, instrumentation simplicity, and high yields of the desired products [8].

The aim of this study is to examine the kinetics of the reaction between CP and an aqueous solution of hydrogen peroxide in the presence of a catalyst system of sodium tungstate and phosphoric acid in combination with a PTC and develop a mathematical model of this reaction.

EXPERIMENTAL

Materials

Cyclopentene (NII Yarsintez) was purified by fractional distillation (to 98%). Petroleum xylene (GOST (State Standard) 9410-78) used as a solvent was purified with sulfuric acid and dried by fractional distillation. Hydrogen peroxide (35% aqueous solution, reagent grade, GOST 177-88), sodium tungstate dihydrate (analytical grade, GOST 18289-78), 80% phosphoric acid (reagent grade, GOST 6552-80), and an Adogen 464 PTC (98%, Aldrich) were used without additional treatment.

Experimental Procedure

A 50-cm^3 temperature-controlled glass reactor equipped with a mechanical stirrer, a reflux condenser, a thermometer, and a sampler was charged with a separately prepared aqueous phase (sodium tungstate, phosphoric acid, hydrogen peroxide, water) having a specified pH value and an organic phase (PTC, xylene, CP). The pH value of the aqueous phase was adjusted by adding a 30% H_2SO_4 or NaOH solution. The reaction time was counted from the beginning of stirring.

The reaction progression was monitored from the conversion of hydrogen peroxide (iodometric method) and the accumulation of the epoxide (reaction with perchloric acid) in the reaction mixture [9]. The CP content was determined by the bromine–bromide method (Kaufman method) [9]; the content of 1,2-cyclopentanediol was found by GLC (a CHROM-5 chromatograph with a flame-ionization detector; a 1.5 m × 3 mm glass column packed with 15% PEG-20 M-coated Chromaton N-AW-DMCS with temperature programming in isothermal portions at 65 (2 min), 100 (4 min), and 195°C (8 min); the rate of temperature rise, 20°C/min; the carrier gas (nitrogen) flow rate of 30 cm^3/min, and the chart speed of 240 mm/h; the internal standard, hexanol-1). Samples were collected from the common reaction mixture under vigorous stirring. It has been shown that the sampling mode (from the common reaction mixture or from each phase separately) has no effect on the results.

RESULTS AND DISCUSSION

The reaction between CP and an aqueous hydrogen peroxide occurs in the two-phase liquid–liquid system; the ratio between the oxidation and hydration rates is controlled by changing the acidity of the aqueous phase. At pH 2.5 of the aqueous phase, the yield of 1,2-epoxycyclopentane is more than 94% because the rate of its hydration reaction (II) is extremely low, whereas a decrease in the pH value to 1.5 leads to a significant acceleration of the hydration of the epoxide and to an increase in the yield of 1,2-cyclopentanediol to 95%. The CP conversion is more than 98% in either case [8].

There are different points of view on the place of occurrence of epoxidation reaction (I): at the interface or in the entire volume of the organic phase. Based on the data of [2], it has been assumed that the transfer of oxygen to the double bond of the olefin takes place in the organic phase; however, it occurs from the catalytic peroxo complex formed in the aqueous phase at the initial instant rather than directly from the hydrogen peroxide. The peroxo complex is formed according to the reaction

$$\begin{aligned}&4Na_2WO_4 + H_3PO_4 + 8H_2O_2\\ &\rightleftharpoons Na_3[PO_4\{W(O)(O_2)_2\}_4] + 5NaOH + 7H_2O.\end{aligned} \qquad \text{(III)}$$

This equation does not describe the true state of formation of peroxo heteropoly compounds in the system to the full extent; however, the reduced PW_4 complex is dominant [5].

The catalyst complex is transferred into the organic phase, where the epoxidation of CP occurs, by a lipophilic PTC:

$$\begin{aligned}&Na_3[PO_4\{W(O)(O_2)_2\}_4] + 3QCl\\ &\rightleftharpoons Q_3[PO_4\{W(O)(O_2)_2\}_4] + 3NaCl.\end{aligned} \qquad \text{(IV)}$$

The catalyst complex, which underwent active-oxygen depletion during the oxidation of CP, restores its activity in contacting with hydrogen peroxide. Analyses have shown that the content of active oxygen of the peroxo complex in the organic phase is constant during the reaction; it is 0.5–0.6% in terms of hydrogen peroxide, which corresponds to the represented composition of the catalyst.

The effect of the stirring rate on the rate of reaction (I) was studied to find that the reaction rate remains constant at an intensity of stirring of more than 250 rpm. Hence, the epoxidation of CP occurs in the kinetic region in the organic phase. Further studies were carried out at a stirring rate of 400 rpm. It was shown that the products of reactions (I) and (II)—1,2-epoxycyclopentane and 1,2-cyclopentanediol—have no effect on the rate of the oxidation reaction, which is described by a first-order equation until the complete conversion of the reactants. In addition, a side reaction of decomposition of hydrogen peroxide can occur in the system.

Typical kinetic curves for cases where the pH of the aqueous phase is 2.5 or 1.5 are shown in Figs. 1a and 1b.

The reaction between CP and an aqueous solution of hydrogen peroxide under phase-transfer catalysis can be represented by the following scheme:

$$[Cat]_{aq.ph.} + 3[QCl]_{org.ph.} \xrightleftharpoons{K_1} [QCat]_{org.ph.} + 3[Cl^-]_{aq.ph.}$$

$$[CP]_{org.ph.} + [QCat]_{org.ph.} \xrightarrow{k_2} [ECP]_{org.ph} + [QCat]^*_{org.ph.}$$

$$[QCat]^*_{org.ph.} + [H_2O_2]_{aq.ph.} \xrightarrow{k_3} [QCat]_{org.ph.} + [H_2O]_{aq.ph.}$$

$$[ECP]_{org.ph.} \xrightleftharpoons{K_4} [ECP]_{org.ph.}$$

$$[H_2O_2]_{aq.ph.} \xrightarrow{k_5} [H_2O]_{aq.ph.} + 1/2[O_2]$$

$$[ECP]_{aq.ph.} + [H_2O]_{aq.ph.} \xrightarrow{k_6} [diol]_{aq.ph.},$$

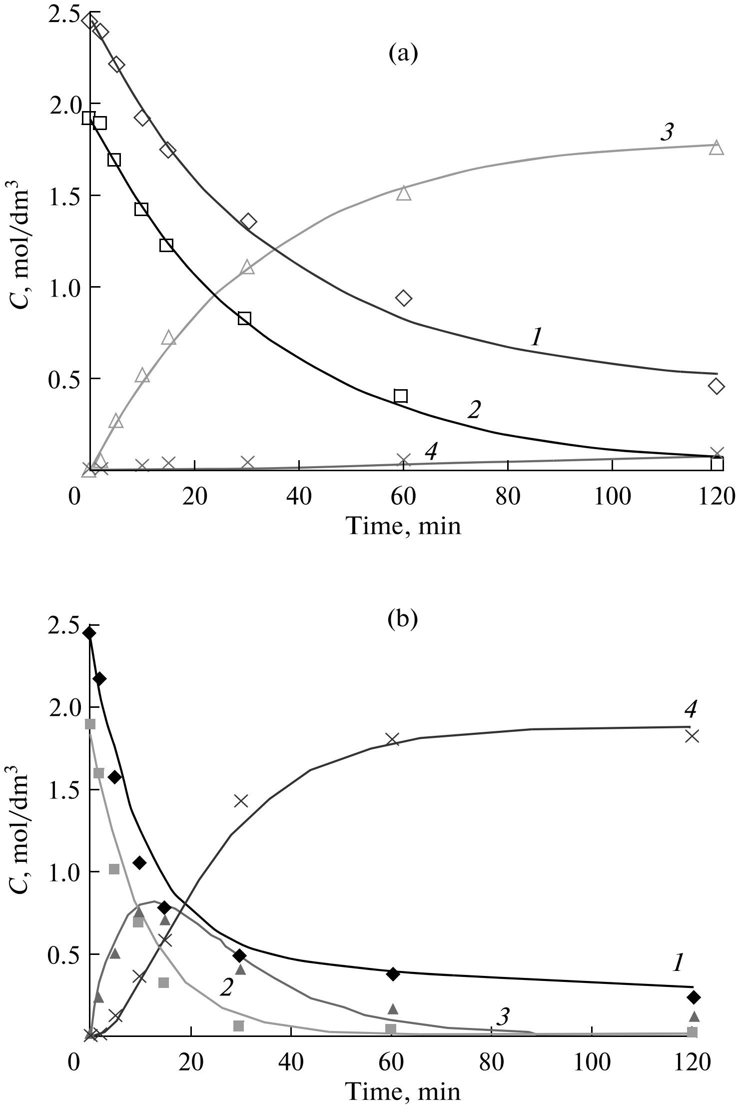


Fig. 1. Typical reactant consumption and product buildup rate curves for the reaction between cyclopentene and aqueous hydrogen peroxide. Solvent, xylene; aqueous phase : organic phase volume ratio, 1.6 : 1; initial concentrations in the total volume, mol/dm^3: CP, 1.91; hydrogen peroxide, 2.45; sodium tungstate, 0.037; Na_2WO_4 : H_3PO_4 : Adogen 464 molar ratio, 1 : 1 : 0.36: (a) 50°C, pH of the aqueous phase of 2.5 and (b) 60°C, pH of the aqueous phase of 1.5; (*1*) hydrogen peroxide, (*2*) cyclopentene, (*3*) 1,2-epoxycyclopentane, and (*4*) 1,2-cyclopentanediol. The symbols and the curve refer to the experimental and calculated data, respectively.

where K_1 and K_4 are the equilibrium (extraction) constants; k_2, k_3, k_5, and k_6 are the rate constants of the respective stages, dm^3 mol^{-1} min^{-1}, dm^3 mol^{-1} min^{-1}, min^{-1}, and dm^3 mol^{-1} min^{-1}, respectively; $[QCl]_{org.ph.}$, $[Cat]_{aq.ph.}$, $[QCat]_{org.ph.}$, and $[QCat]_{org.ph}{}^*$ are the concentrations of the PTC and the catalyst complex in the aqueous and organic phases, respectively (the asterisk (*) denotes the active-oxygen depleted complex), mol/dm^3; $[CP]_{org.ph.}$, $[H_2O_2]_{aq.ph.}$, $[ECP]_{org.ph.}$, $[ECP]_{aq.ph.}$, $[H_2O]_{aq.ph.}$, and $[diol]_{aq.ph.}$ are the concentrations of CP, hydrogen peroxide, 1,2-epoxycyclopentane, water, and 1,2-cyclopentanediol in the respective phases, mol/dm^3.

The following assumptions have been made: (i) the rate constant of reactivation of the peroxo complex k_3 is so high that it has no effect on the rate of other reactions; therefore, this reaction has been ignored; (ii) hydration reaction (II) occurs in the aqueous phase; according to solubility, 1,2-epoxycyclopentane is transferred to this phase in large excess water; therefore, the water concentration has been assumed constant and included into rate constant k_6, i.e., $k_{6\ eff}$; (iii) hydration reaction (II) is an acid-catalyzed reaction; its rate depends on the concentration of hydrogen ions; however, since we considered two cases where this concentration was constant (the pH of the

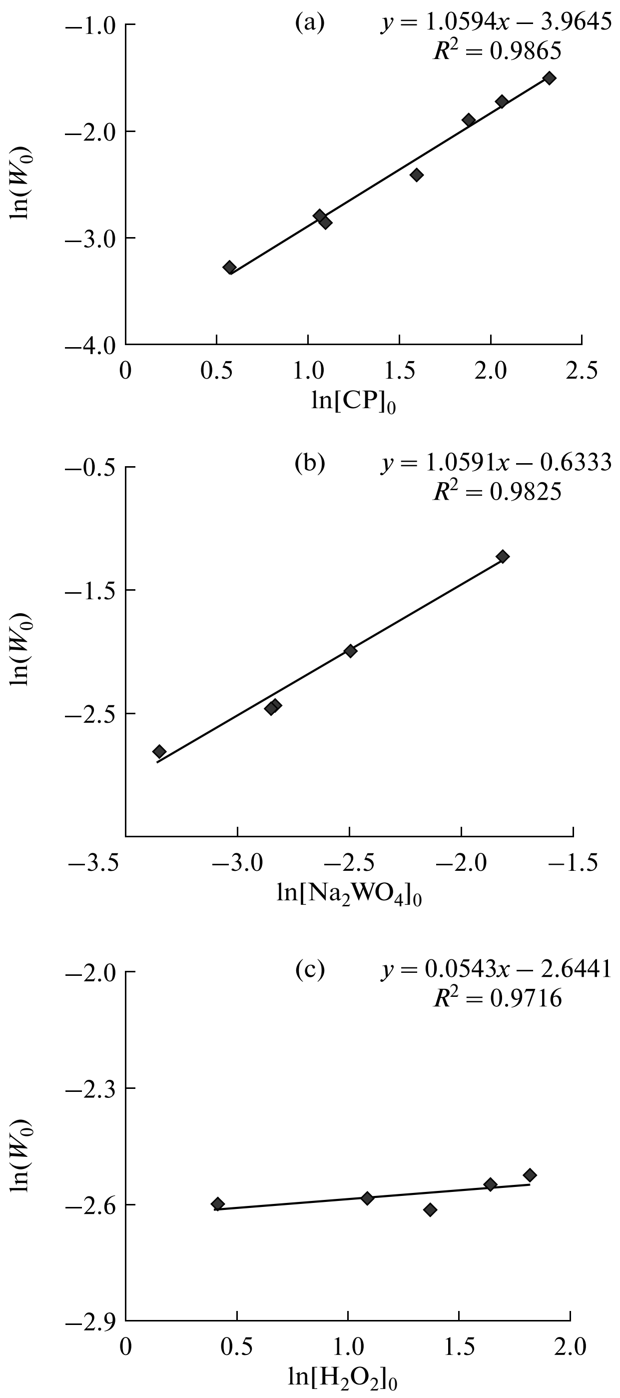


Fig. 2. Dependence of the initial rate of cyclopentene epoxidation with aqueous hydrogen peroxide on the initial concentrations of the reactants. Temperature, 50°C; solvent, xylene; pH of the aqueous phase, 2.5. Variation in the initial concentrations of (a) cyclopentene, (b) catalyst, and (c) hydrogen peroxide.

aqueous phase was 2.5 and 1.5 for synthesizing the epoxide and diol, respectively), the concentration of hydrogen ions was also included in rate constant $k_{6\,\mathrm{eff}}$.

According to the above conversion scheme, a system of differential equations (1–4) was derived to describe the consumption of the reactants and the accumulation of the reaction products in terms of the total volume of the reaction mixture:

$$\frac{d[\mathrm{CP}]}{dt} = -k_2[\mathrm{CP}][\mathrm{QCat}], \qquad (1)$$

$$\frac{d[\mathrm{H_2O_2}]}{dt} = -\frac{d[\mathrm{CP}]}{dt} - k_5[\mathrm{H_2O_2}], \qquad (2)$$

$$\frac{d[\mathrm{ECP}]}{dt} = k_2[\mathrm{CP}][\mathrm{QCat}] - k_{6\,\mathrm{eff}}[\mathrm{ECP}], \qquad (3)$$

$$\frac{d[\mathrm{diol}]}{dt} = k_6[\mathrm{ECP}][\mathrm{H_2O}] = k_{6\,\mathrm{eff}}[\mathrm{ECP}]. \qquad (4)$$

The rate-limiting step of the formation of 1,2-epoxycyclopentane is the epoxidation of CP by an active peroxo complex. The concentration of the peroxo complex [QCat] in the organic phase in the steady-state condition is constant; it is determined by extraction constant K_1.

In [2, 10], it has been shown that, in the case of using an Adogen 464 PTC, the catalyst complex is almost completely transferred to the organic phase after its formation and remains there during and after the reaction.

The expression for constant K_1 is written as follows:

$$K_1 = \frac{[\mathrm{QCat}]_{\mathrm{org.ph.}}\,[\mathrm{Cl^-}]^3_{\mathrm{aq.ph.}}}{[\mathrm{Cat}]_{\mathrm{aq.ph.}}\,[\mathrm{QCl}]^3_{\mathrm{org.ph.}}}. \qquad (5)$$

The current concentration of the PTC in the organic phase is determined by the difference between its initial concentration and the amount consumed for the formation of the complex according to reaction (IV): $[\mathrm{QCl}]_{\mathrm{org.ph.}} = [\mathrm{QCl}]_{\mathrm{org.ph.}} - 3[\mathrm{QCat}]_{\mathrm{org.ph.}}$

The current concentration of $\mathrm{Cl^-}$ ions in the aqueous phase is proportional to the concentration of the catalyst complex in the organic phase with allowance for the volume ratio of the organic and aqueous phases: $\left[\mathrm{Cl^-}\right]_{\mathrm{org.ph.}} = 3\left[\mathrm{QCat}\right]_{\mathrm{org.ph.}}\left(\frac{V_{\mathrm{org.ph.}}}{V_{\mathrm{aq.ph.}}}\right)$.

The concentration of the catalyst complex in the aqueous phase depends on the initial concentration of sodium tungstate, which is taken in deficiency with respect to the other components constituting the complex with allowance for the stoichiometry of reaction (III): $\left[\mathrm{Cat}\right]_{\mathrm{aq.ph.}} = \frac{1}{4}\left[W_0\right]_{\mathrm{aq.ph.}}$

After transformations of equation (5), constant K_1 can be expressed in terms of the initial concentrations of sodium tungstate and the PTC as well as the current concentration of the catalyst complex as follows:

$$K_1 = \frac{108\left(\frac{V_{\mathrm{org.ph.}}}{V_{\mathrm{aq.ph.}}}\right)^3[\mathrm{QCat}]^4_{\mathrm{org.ph.}}}{\left([\mathrm{QCl_0}]_{\mathrm{org.ph.}} - 3[\mathrm{QCat}]_{\mathrm{org.ph.}}\right)^3\,[W_0]_{\mathrm{aq.ph.}}}. \qquad (6)$$

Kinetic parameters of the reaction between cyclopentene and aqueous hydrogen peroxide

Parameter	Temperature of 50°C; pH of aqueous phase 2.5	Temperature of 60°C; pH of aqueous phase 1.5
K_1	$(63.7 \pm 1.5) \times 10^3$	
k_2, $dm^3\ mol^{-1}\ min^{-1}$	2.41 ± 0.01	9.97 ± 0.03
k_5, min^{-1}	$(0.50 \pm 0.03) \times 10^{-3}$	$(1.20 \pm 0.04) \times 10^{-3}$
k_{6eff}, min^{-1}	$(0.09 \pm 0.01) \times 10^{-3}$	$(78.0 \pm 2.5) \times 10^{-3}$
$E_{a(I)}$, kJ/mol	65.9 ± 4.0	
$E_{a(II)}$, kJ/mol	64.0 ± 2.7	
$S_{a(I)}$, J/(mol K)	-107 ± 8	
$S_{a(II)}$, J/(mol K)	-110 ± 10	

The constants in the above equations (1–4) were selected using two arrays of experimental data on the reaction between CP and an aqueous solution of hydrogen peroxide: one for a temperature of 50°C and a pH of the aqueous phase of 2.5 and the other for a temperature of 60°C and a pH of the aqueous phase of 1.5.

The concentration of the catalyst (sodium tungstate) in the aqueous phase was varied in a range of 0.028–0.177 mol/dm^3, while maintaining the $Na_2WO_4 : H_3PO_4$: PTC ratio of 1 : 1 : 0.36. The initial concentration of hydrogen peroxide was varied in a range of 1.52–6.18 mol/dm^3 in the aqueous phase, while the concentration of CP in the organic phase was varied from 1.78 to 10.24 mol/dm^3 (solventless reaction) at constant concentrations of the other substances. The individual orders of reactions (I) and (II) were determined from the change in the initial rates as a function of the initial concentrations of the analytes, all other parameters and concentrations being constant.

These data indicate that the individual orders with respect to CP and the catalyst are equal to unity (Figs. 2a, 2b), while the order with respect to hydrogen peroxide is close to zero (Fig. 2c). The last-mentioned fact indicates that the true oxidizing agent is the active catalytic intermediate transferred from the aqueous phase to the organic phase using a PTC rather than hydrogen peroxide. The studies on the effect of the pH of the aqueous phase on the thermocatalytic decomposition of hydrogen peroxide have shown that, at the presence of the $Q_3[PO_4\{W(O)(O_2)_2\}_4]$ catalyst complex at 50°C and a pH below 3, the rate constant of decomposition of hydrogen peroxide does not exceed 0.001 min^{-1}.

It was found that, at a pH of the aqueous phase of 1.5 and a temperature of 60°C, the order of reaction (II) with respect to the epoxide at 1,2-epoxycyclopentane concentrations of 2.62–6.94 mol/dm^3 in the organic phase is equal to unity. It was shown that 1,2-epoxycyclopentane hydration reaction (II) occurs in the aqueous phase and the distribution of the epoxide between the phases is determined by its total content in the reaction mass and solubility in water. The order of the reaction with respect to the epoxide equal to unity suggests that the transfer of the epoxide into the aqueous phase occurs much more rapidly than its reaction with water and has no effect on the hydration reaction rate; therefore, the constant of extraction of 1,2-epoxycyclopentane from the aqueous phase into the organic phase K_4 was ignored in the calculations.

The extraction constant K_1 was calculated from the determined concentration of peroxo groups (i.e., the $Q_3[PO_4\{W(O)(O_2)_2\}_4]$ complex) in the organic phase; it has a value of 63 700 and hardly depends on temperature in the examined range of 30–70°C. Further calculations and selection of the rate constants of the stages were conducted using this value.

The constants in Eqs. (1)–(4) were calculated and selected in a broad range of variation of the unknown quantities with minimization of the squared deviation of the experimental and calculated values. The rate constants found by graphical analytical methods were taken as an initial approximation.

In the temperature range of 30–70°C, the activation energies of reactions (I) and (II) were found to be 65.9 and 64.0 kJ/mol, respectively. The activation entropies calculated according to the Eyring equation were also close in value: –107 and –110 J/(mol K) for the epoxidation and hydration reactions, respectively.

The derived constants are listed in the table; the agreement between the experimental kinetic curves of reactant consumption and product accumulation for the synthesis of 1,2-epoxycyclopentane and 1,2-cyclopentanediol and the curves calculated according to the developed model is shown in Fig. 1.

The adequacy of the model was tested using the Fisher's test. The reproducibility variance was determined from five parallel experiments, and the residual variance was found from all the components and all the experimental data points in the control experiments. The following Fisher's test values were obtained: 0.71 and 1.25 for the synthesis of 1,2-epoxycyclopentane and 1,2-cyclopentanediol at the pH of the aqueous phase of 2.5 and 1.5, respectively. The two test values are lower than the tabulated value of 5.75 for the probability of 0.05 and the number of degrees of freedom of 25 and 4, respectively.

Thus, the developed mathematical model adequately describes the reaction between CP and an aqueous solution of hydrogen peroxide under phase-transfer catalysis at a pH of the aqueous phase of 2.5 and 1.5 over the entire range of concentrations of the reactants and the catalyst. The model can be used for engineering calculations of the synthesis of 1,2-epoxycyclopentane or 1,2-cyclopentanediol from cyclopentene and hydrogen peroxide.

REFERENCES

1. C. Venturello and R. D' Aloisio, Org. Chem. **53**, 1553 (1988).
2. T. V. Dovganyuk, V. V. Berentsveig, E. A. Karakhanov, and A. A. Borisenko, Neftekhimiya **30**, 602 (1990).
3. M. N. Timofeeva, Z. P. Pai, A. G. Tolstikov, et al., Izv. Akad. Nauk, Ser. Khim., No. 2, 458 (2003).
4. M. Wang and T. Huang, Ind. Eng. Chem. Res. **43**, 675 (2004).
5. N. Mizuno, K. Yamaguchi, and K. Kamata, Coord. Chem. Rev., No. 249, 1944 (2005).
6. L. I. Kas'yan, M. F. Seferova, and S. I. Okovityi, *Alicyclic Epoxy Compounds: Methods of Synthesis* (Dnepropetrovskii Univ., Dnepropetrovsk, 2003) [in Russian].
7. B. B. Snider and T. Liu, Org. Chem. **64**, 1088 (1999).
8. L. V. Mel'nik, A. E. Meshechkina, G. V. Rybina, et al., Pet Chem. **52**, 313 (2012).
9. S. Siggia and J. G. Hanna, *Quantitative Organic Analysis via Functional Groups* (Wiley, New York, 1979).
10. A. E. Meshechkina, L. V. Mel'nik, G. V. Rybina, et al., Russ. J. Appl. Chem. **85**, 661 (2012).

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