

Kinetics of the Acetic Acid Oxyethylation Catalyzed by Chromium Acetate

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Received March 22, 1999

Abstract—The effect of the product of the acetic acid oxyethylation (ethylene glycol monoacetate) on the kinetics of this reaction in the presence of chromium acetate is studied. Compared to base catalysis, catalysis with chromium acetate provided a higher selectivity in the formation of the monoaddition compound. It is found that an increase in the concentration of ethylene glycol monoacetate resulted in a drop in the reaction rate. The hypothetical mechanism of catalysis is proposed. The kinetic equation that adequately describes all experimental data is derived from this mechanism.

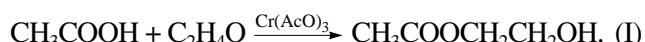
INTRODUCTION

Hydroxyalkyl esters of carboxylic acids are valuable products of organic synthesis. Thus, hydroxyalkyl esters of unsaturated acids (for example monoacrylates and monomethacrylates) find use as components of dyeing coatings, printer inks, and medicinal preparations [1]; whereas hydroxyalkyl esters of acetic acid are used as hardeners of sand blends in metallurgy [2], components of cooling agents for low-temperature processes [3], solvents for dyeing compositions [4–7], components of anticorrosive coatings [8, 9], and cement modifiers [10].

The addition of olefin oxides to carboxylic acids in the presence of bases (alkali and quaternary ammonium salts) is a conventional method for obtaining such products. A disadvantage of this method is a decrease in the selectivity to a target product with an increase in the conversion of the initial carboxylic acid, which is caused by the occurrence of a number of consecutive-parallel side reactions [11].

Information is available that the use of chromium compounds as catalysts significantly enhanced the selectivity in the addition of α -oxides to carboxylic acids [1].

To study the mechanism and kinetics of similar reactions, we chose the oxyethylation of acetic acid catalyzed by chromium acetate for our study:



EXPERIMENTAL

Kinetic experiments were carried out in a manometric setup described in detail in [12]. The effect of the catalyst on the selectivity of the reaction was studied in a stainless-steel autoclave equipped with a magnetic stirrer and a jacket with a circulating cooling agent. The rate of accumulation of reaction products was studied in experiments performed in a glass, airtight, batch, tem-

perature-controlled reactor with a rubber cover through which the samples were taken at intervals via a syringe. The composition of the reaction mixture was analyzed by GLC using a CHROM-5 chromatograph (Czechoslovakia) equipped with a 3000×3 -mm glass column packed with 15% di-(2-ethyl)hexyl sebacate supported on INERTON AW-PMCS (grains 0.20–0.25 mm in size). The temperature of the column, evaporator, and detector was 150°C. The flow rate of the carrier gas (nitrogen) was 27 cm³/min, the flow rates of air and hydrogen in the flame of a detector were 300 and 30 cm³/min, respectively. The volume of the sample was 1 μl .

RESULTS AND DISCUSSION

We showed earlier [13] that the rate of the reaction between ethylene oxide and acetic acid increases with an increase in the size of the ionic pair of a catalyst; that is, with an increase in the radius of a cation. We obtained the corresponding dependence of the reaction rate constant on the cationic radius of a catalyst and showed that chromium acetate drastically falls out of it. In our opinion, this was due to the occurrence of the reaction in the coordination sphere of the metal catalyst rather than to its occurrence by the classical base-catalyzed mechanism. The experiments were carried out in the autoclave at 130°C and at an ethylene oxide-to-acetic acid initial molar ratio of 1.05. The experimental results (see the table) showed that the catalysis with nucleophiles, which greatly differed in size, only slightly affected the selectivity of the process, whereas chromium acetate provided an almost quantitative yield of ethylene glycol monoacetate and a much higher selectivity than other catalysts of the base type. The high selectivity of the process pointed to the fact that the mechanism of opening the oxide cycle differed from the base-catalytic one [11], which was necessarily accompanied by the side reactions of polyoxyethylation and transesterification and consisted in the nucleo-

Effect of the catalyst on the selectivity to ethylene glycol monoacetate ($T = 130^\circ\text{C}$, $[\text{C}_2\text{H}_4\text{O}]_0/[\text{CH}_3\text{COOH}]_0 = 1.05$)*

Catalyst	Catalyst concentration, mol/l	Acetic acid conversion	Selectivity to ethylene glycol monoacetate with respect to acetic acid
Potassium acetate	0.176	0.98	0.60
Pyridine	0.167	0.97	0.53
Triethylbenzylammonium bromide	0.177	0.93	0.69
Tetraethylammonium bromide	0.182	0.97	0.51
Chromium acetate	0.021	0.99	0.97

* $[\text{C}_2\text{H}_4\text{O}]_0$ and $[\text{CH}_3\text{COOH}]_0$ are the initial molar concentrations of ethylene oxide and acetic acid, respectively.

philic attack of the acetate ion on the carbon atom of the oxide cycle activated by the hydrogen bond with protons present in the reaction mixture.

In our opinion, the above facts confirm our earlier conclusion [13] that the reaction proceeded in the coordination sphere of the metal.

Because ethylene glycol monoacetate is formed in the reaction between ethylene oxide and acetic acid with nearly 100% yield, the kinetic study of ethylene oxide consumption leads to a complete understanding of the mechanism of catalysis for this reaction. Previous kinetic studies of ethylene oxide addition to acetic acid in the presence of $\text{Cr}(\text{OAc})_3$ showed that this reaction is a first-order process with respect to ethylene oxide and the catalyst [13]. In this work, we performed a set of experiments varying the concentrations of the catalyst, acetic acid, and ethylene glycol monoacetate in the reaction mixture at three temperatures to reveal the effect of the reaction mixture composition on the process rate. The composition of the reaction mixture in the experiments performed at each of the three temperatures was varied over a wide range, simulating the accumulation of the reaction product starting from the pure initial substance ($[\text{CH}_3\text{COOH}] = 16.0 \text{ mol/l}$ and $[\text{EGMA}] = 0 \text{ mol/l}$) and finishing with a high conversion of the initial substance ($[\text{CH}_3\text{COOH}] = 0.166 \text{ mol/l}$ and $[\text{EGMA}] = 9.51 \text{ mol/l}$).

Experiments were carried out under conditions when the molar amount of ethylene oxide (EO) was greatly deficient with respect to acetic acid and ethylene glycol; these conditions provided the overall first order of the reaction. The results of each experiment were treated with the following rate law:

$$-\frac{d[\text{EO}]}{d\tau} = k_{\text{app}}[\text{EO}], \text{ mol l}^{-1} \text{ min}^{-1}, \quad (1)$$

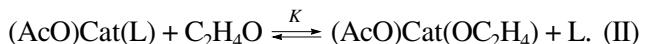
where $[\text{EO}]$ is the current concentration of ethylene oxide, mol/l , and k_{app} is the apparent rate constant of the first-order reaction, min^{-1} .

Figure 1 presents the reaction rate constants k_{app} calculated by this equation as functions of the reaction conditions. The experimental results showed that the

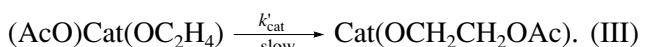
apparent rate constant depends on the concentration of the reaction product and decreases with an increase in the concentration. This is illustrated by a decrease in the slopes of the curves of k_{app} vs. catalyst concentration when the concentration of ethylene glycol monoacetate in the reaction mixture increased.

A study of the dependence of the reaction product composition on the reaction time showed that ethylene oxide was consumed only for the formation of ethylene glycol monoacetate while acetic acid was present in the reaction mixture. These experiments also showed that, when the concentration of acetic acid decreased to a some limit (~ 0.2 to 0.1 mol/l), the solution changed its color from green (typical of the initial $\text{Cr}(\text{OAc})_3$) to violet. It is known that Cr^{3+} forms complexes with the coordination number 6 in solutions. A change in the solution color pointed to a change in the ligand environment in the coordination sphere of the chromium complex [14].

It was shown that the mechanism of the reaction between epichlorohydrin and acetic acid in the presence of $\text{Cr}(\text{OAc})_3$ consisted in the activation of epoxide in the coordination sphere of chromium [1]. In acetic acid medium, three of six coordination sites in the initial complex are occupied by acetate ions, while others are occupied by acetic acid molecules. Assuming that this mechanism is general for epoxides, we propose the following mechanism of catalysis. At the first (fast) step, an ethylene oxide molecule replaced ligand (L) in the coordination sphere of the catalyst:



An ethylene oxide molecule activated by the coordination bond was then attacked by an acetate ion inside the coordination sphere of the catalyst to yield β -acetoxyethylate ion:



The resulting unstable (five-ligand) complex entered the exchange reaction with a component of the reaction mixture (L) that can be any molecule with an

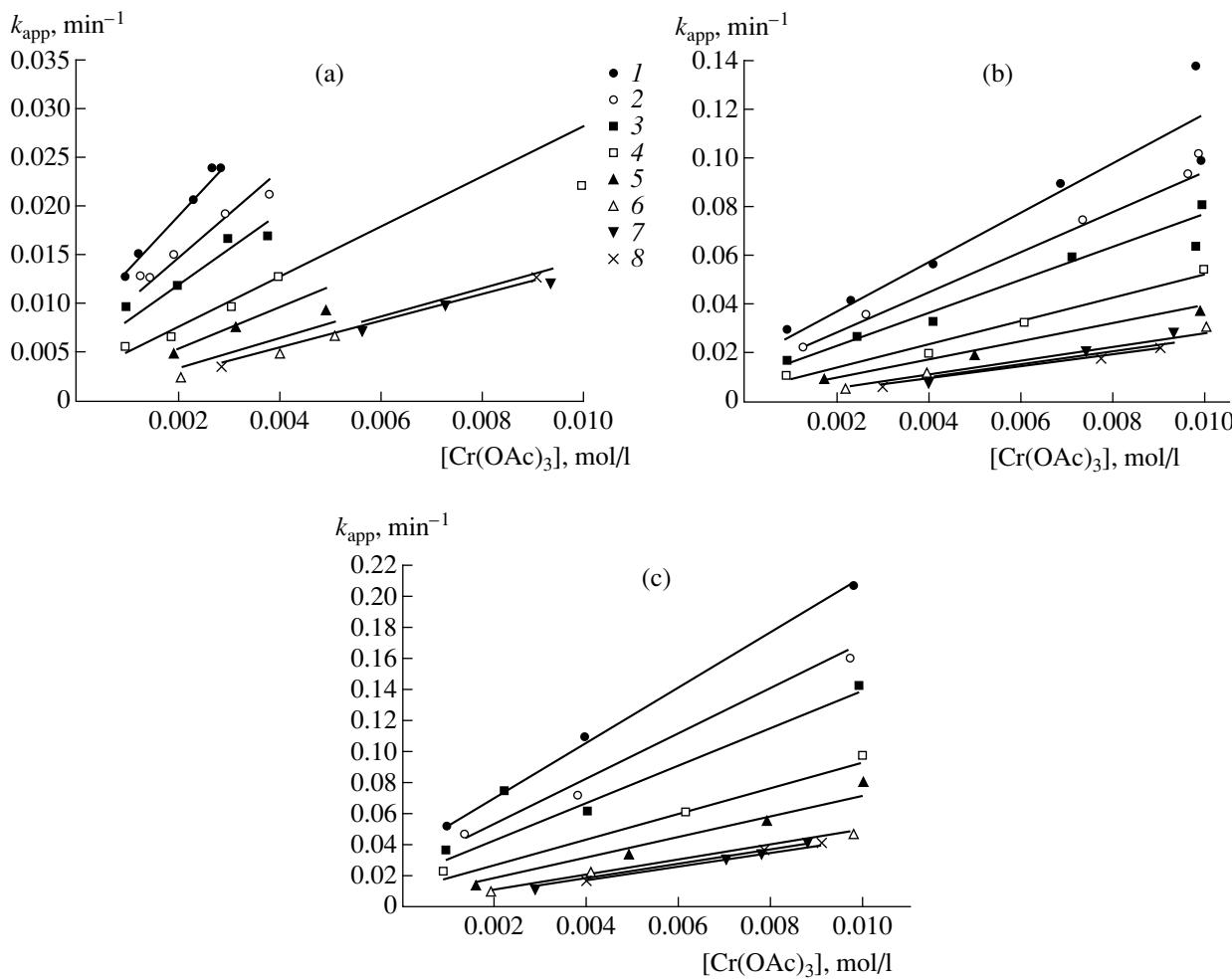
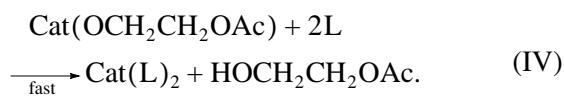
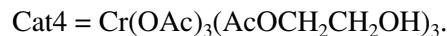


Fig. 1. Dependence of the apparent rate constant of acetic acid oxyethylation on the composition of the reaction mixture and $\text{Cr}(\text{OAc})_3$ concentration at (a) 90, (b) 100, and (c) 110°C ($[\text{CH}_3\text{COOH}]$, mol/l: (1) 16.00, (2) 12.50, (3) 10.50, (4) 6.60, (5) 4.20, (6) 1.10, (7) 0.49, (8) 0.17; $[\text{EGMA}]$, mol/l: (1) 0, (2) 2.40, (3) 3.55, (4) 5.70, (5) 7.12, (6) 8.90, (7) 9.32, (8) 9.51; symbols refer to the experiment and lines refer to the calculation).

active hydrogen atom, such as acetic acid and ethylene glycol monoacetate. This resulted in the formation of the reaction product (ethylene glycol monoacetate) and a new six-ligand catalytic complex:



Three coordination sites in the chromium complex that were not occupied by acetate ions were taken by other electron donors, acetic acid and ethylene glycol monoacetate. Therefore, four catalytic complexes can exist in equilibrium with each other (Cat1, Cat2, Cat3, and Cat4) that differ in ligand environment:



$$\begin{aligned} K_1 &= [\text{Cat2}][\text{AcOH}] / ([\text{Cat1}][\text{AcOCH}_2\text{CH}_2\text{OH}]) \\ K_2 &= [\text{Cat3}][\text{AcOH}] / ([\text{Cat2}][\text{AcOCH}_2\text{CH}_2\text{OH}]) \\ K_3 &= [\text{Cat4}][\text{AcOH}] / ([\text{Cat3}][\text{AcOCH}_2\text{CH}_2\text{OH}]) \\ [\text{Cat1}] + [\text{Cat2}] + [\text{Cat3}] + [\text{Cat4}] &= [\text{Cat}]_0 \end{aligned} \quad (2)$$

where K_1 , K_2 , and K_3 are the equilibrium constants; $[\text{Cat}]_0$ is the initial molar concentration of the catalyst; and $[\text{Cat1}]$, $[\text{Cat2}]$, $[\text{Cat3}]$, and $[\text{Cat4}]$ are the molar concentrations of the corresponding complexes.

It is clear that, when the reaction product was absent from the solution, the only catalytic complex was Cat1, whereas when ethylene glycol monoacetate appeared, the catalyst transformed in all four complexes via equilibria (2).

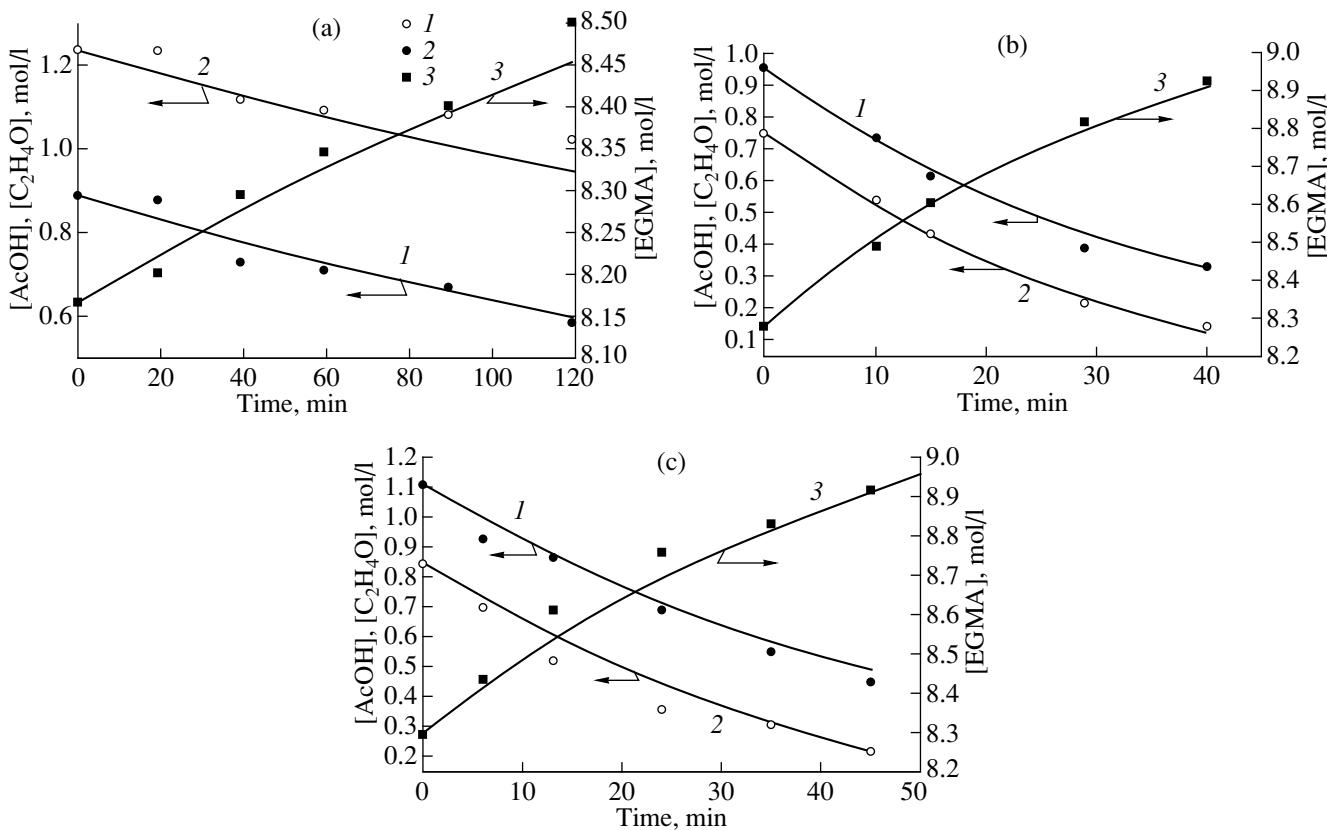


Fig. 2. Dependence of (1) ethylene oxide, (2) acetic acid, and (3) ethylene glycol monoacetate concentrations on time (experimental conditions: (a) $[Cat]_0 = 2.07 \times 10^{-3}$ mol/l, $T = 90^\circ\text{C}$; (b) $[Cat]_0 = 1.02 \times 10^{-2}$ mol/l, $T = 100^\circ\text{C}$; (c) $[Cat]_0 = 3.75 \times 10^{-3}$ mol/l, $T = 110^\circ\text{C}$; lines refer to calculated curves).

According to the mechanism proposed, the rate of the catalytic reaction was equal to the rate of the slow step (III) described by the first-order rate law:

$$w_{\text{cat}} = k'_{\text{cat}}[(\text{AcO})\text{Cat}(\text{OC}_2\text{H}_4)]. \quad (3)$$

Any of the four complexes formed from the initial catalyst complexes (Cat1, Cat2, Cat3, and Cat4) can appear in this equation as an intermediate catalytic complex $[(\text{AcO})\text{Cat}(\text{OC}_2\text{H}_4)]$. According to equilibrium (II), the concentration of the intermediate catalytic complex in Eq. (3) can be expressed as follows:

$$[(\text{AcO})\text{Cat}(\text{OC}_2\text{H}_4)] = K[(\text{AcO})\text{Cat}(\text{L})][\text{C}_2\text{H}_4\text{O}]/[\text{L}]. \quad (4)$$

Because ligands were in substantial excess in the solution, their total concentration (L) may be considered a constant value equal to the sum of acetic acid and ethylene glycol monoacetate concentrations. If the equilibrium constant of reaction (II) is considered the same for acetic

acid and ethylene glycol monoacetate, the rate law expressed as Eq. (3) takes the following form:

$$w_{\text{cat}} = k'_{\text{cat}}[(\text{AcO})\text{Cat}(\text{L})] \times [\text{C}_2\text{H}_4\text{O}]/[(\text{AcOH}) + [\text{EGMA}]). \quad (5)$$

The closeness of complexation properties of these ligands is confirmed by the closeness of the dipole moments of the SnCl_4 complexes with acetic acid and different alcohols and by the closeness of the parameters of the Drago–Wayland equation for the complexation enthalpies for these ligands [15].

In Eq. (5), $k'_{\text{cat}} = k_{\text{cat}} K$. Because different forms of the catalyst had different catalytic activities, the overall rate of the catalytic reaction was equal to the sum of four terms and, according to the previous equation, had the following form:

$$w_{\text{cat}} = k_{\text{Cat1}}[(\text{Cat1}) + b_{\text{Cat2}}(\text{Cat2}) + b_{\text{Cat3}}(\text{Cat3}) + b_{\text{Cat4}}(\text{Cat4})][\text{C}_2\text{H}_4\text{O}]/[(\text{AcOH}) + [\text{EGMA}]), \quad (6)$$

where k_{Cat1} , k_{Cat2} , k_{Cat3} , and k_{Cat4} are the rate constants of the catalytic reaction involving the corresponding forms of the catalyst; $b_{\text{Cat2}} = k_{\text{Cat2}}/k_{\text{Cat1}}$; $b_{\text{Cat3}} = k_{\text{Cat3}}/k_{\text{Cat1}}$; and $b_{\text{Cat4}} = k_{\text{Cat4}}/k_{\text{Cat1}}$.

Because the noncatalytic addition of ethylene oxide occurred in parallel to the catalytic reaction, the overall rate law had the following form:

$$-\frac{d[EO]}{d\tau} = \left(k_{app,n} + k_{Cat1} \times \frac{[Cat1] + b_{Cat2}[Cat2] + b_{Cat3}[Cat3] + b_{Cat4}[Cat4]}{[AcOH] + [EGMA]} \right) \times [C_2H_4O], \quad (7)$$

where $k_{app,n}$ is the apparent rate constant of the noncatalytic reaction, min^{-1} . The constant $k_{app,n}$ depended on the composition of the reaction mixture in accordance with the equation derived before [11]:

$$k_{app,n} = k_n[AcOH]([AcOH] + b_n[EGMA]), \quad (8)$$

where k_n is the rate constant of the noncatalytic reaction ($\text{l}^2 \text{ mol}^{-2} \text{ min}^{-1}$) in which ethylene oxide was protonated by acetic acid, and b_n is the ratio of the rate constant of the noncatalytic reaction ($\text{l}^2 \text{ mol}^{-2} \text{ min}^{-1}$) in which ethylene oxide was protonated by the reaction products to k_n .

Thus, using Eqs. (1), (7), and (8), we arrived at the following equation for the experimental first-order rate constant:

$$k_{app} = k_n[AcOH]([AcOH] + b_n[EGMA]) + k_{Cat1}([Cat1] + b_{Cat2}[Cat2] + b_{Cat3}[Cat3] + b_{Cat4}[Cat4])/([AcOH] + [EGMA]). \quad (9)$$

$$k_{app} = k_n[AcOH]([AcOH] + b_n[EGMA]) + k_{Cat1}[K_T]_0 \times \frac{[AcOH]^2 + b_{Cat2}K_1[AcOH][EGMA] + b_{Cat3}K_1K_2[EGMA]^2}{([AcOH]^2 + K_1[AcOH][EGMA] + K_1K_2[EGMA]^2)([AcOH] + [EGMA])}. \quad (11)$$

Using this equation, we treated the entire set of experimental k_{app} values by the least-squares method and calculated the activation parameters and the values of constants setting $K_2/K_1 = 1$:

$$\begin{aligned} k_n &= \exp((18 \pm 4) - (10400 \pm 1500)/T), \text{ l}^2 \text{ mol}^{-2} \text{ min}^{-1}; \\ k_{Cat1} &= \exp((23 \pm 1.2) - (8059 \pm 430)/T), \text{ l}^2 \text{ mol}^{-2} \text{ min}^{-1}; \\ b_n &= 0.85 \pm 0.4; \\ K_1 &= 11 \pm 1.8; \\ b_{Cat2} &= 37.6 \pm 2.7; \\ b_{Cat3} &= 2.3 \pm 0.12. \end{aligned}$$

Figure 1 demonstrates the agreement between experimental reaction rate constants and those calculated from Eq. (11) over the entire range of the conditions under study.

The current concentrations of Cat1, Cat2, Cat3, and Cat4 complexes were calculated by solving the set of Eqs. (2).

The least-squares fitting of unknown parameters in Eqs. (9) and (2) that gave the best agreement between calculated and experimental k_{app} values showed that the equilibrium constant K_3 has values several orders of magnitude lower than K_1 and K_2 . This may mean that the equilibrium between the Cat3 and Cat4 forms of the catalyst strongly shifted to the Cat3 form:



This gave us reason to neglect the existence of the catalyst in the form of Cat4 when writing the overall balance over the catalyst. In the case when $[Cat4] = 0$, solving the set of Eqs. (2) gave the following expressions for the current concentrations of different catalytic complexes:

$$\left. \begin{aligned} [Cat1] &= [Cat]_0 N [AcOH] / (K_1 [EGMA]) \\ [Cat2] &= [Cat]_0 N \\ [Cat3] &= [Cat]_0 N K_2 [EGMA] / [AcOH] \end{aligned} \right\}, \quad (10)$$

where $N = (1 + [AcOH]/(K_1[EGMA] + K_2[EGMA]/[AcOH]))^{-1}$.

The substitution of the obtained expressions in Eq. (9) resulted in an equation that related the apparent constant (k_{app}) to the concentrations of acetic acid, ethylene glycol monoacetate, and the catalyst:

The adequacy of the obtained rate law was additionally confirmed by the comparison of the current concentrations of reactants and reaction products calculated by this equation with those experimentally obtained in three runs performed at different temperatures (90, 100, and 110°C) and different initial concentrations of reactants and the catalyst (Fig. 2).

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