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Articles

The Effect of Diglyme on the Kinetics of Chromium(III) Ethanoate-Catalyzed Reactions of Carboxylic Acids with Epichlorohydrin

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Abstract:

The kinetics of reaction between acetic, acrylic, or methacrylic acid and epichlorohydrin in diglyme solution are studied with chromium(III) ethanoate as catalyst. The reaction has been found to be of first-order with respect to both epichlorohydrin and catalyst and zeroth order with respect to acid. Relative reactivities of the acids in reaction with epichlorohydrin and regioselectivity of the addition in diglyme are compared with those for the systems without solvent.

Introdution

The reactions of carboxylic acids with oxiranes yield products of commercial importance. Specifically, hydroxyalkyl acrylates and methacrylates are monomers widely used in production of various polymers, including coatings for metals, leather, paper, and wood.[1] Products of addition of carboxylic acids to epichlohydrin are raw materials in the synthesis of glycidyl esters then used as epoxy resins themselves or as reactive solvents for the bisphenol A or novolac-based epoxy resins.[2,3] Glycidyl (meth)acrylate readily polymerizes or copolymerizes, and it is often used as a modifier of physical or chemical properties of engineering or commodity polymers. They are also used in manufacturing of reactive polymers.[4−6] Adducts of unsaturated carboxylic acid to commercial epoxy resins, the so-called vinyl-ester resins, exhibit an enhanced chemical resistance when cured in the same way as the less chemically stable classical unsaturated polyester resins.[7−11] Hence, the adducts are used for manufacturing laminates or other products reinforced with glass fibres.[12]

These examples of practical importance of the products of addition of carboxylic acids to epoxy compounds are one of the reasons why the addition reaction is still a subject of both basic and application studies.[13−19]

We have found in our previous studies that the addition of carboxylic acids to oxiranes is effectively catalysed by chromium(III) ethanoate.[20−24] The catalyst strongly differentiates between the abilities of hydroxyl groups of an acid and alcohol to react with oxiranes. Hence, in the presence of $Cr(AcO)_3$, the substituted derivatives of ethylene oxide, such as epichlorohydrin, react with acids with high selectivity and regioselectivity.

Catalytic activity of chromium ions is closely related to the presence of *d* orbitals. These orbitals make them susceptible to action from any electron donors. The presence of a donor substance may, due to donor−acceptor interactions, lead to changes in the catalytic activity. Specifically, while studying the reaction of acetic acid with epichlorohydrin, we have found that gradual dilution of the system with a protic solvent, butanol, initially reduced the rate of addition, but as the dilution increased, the rate constant of the reaction increased again.[24] Substantial dilution of the system with butanol did not affect the regioselectivity of reaction; however, side reactions involving epichlorohydrin intensified, and up to 10% of the oxirane was wasted in side reactions.

As found in this work, no such a negative effect is observed for the system dissolved in 2-methoxyethyl ether (diglyme). Nonetheless, this aprotic solvent, dispossessed of any functional groups capable of reacting with epoxy groups

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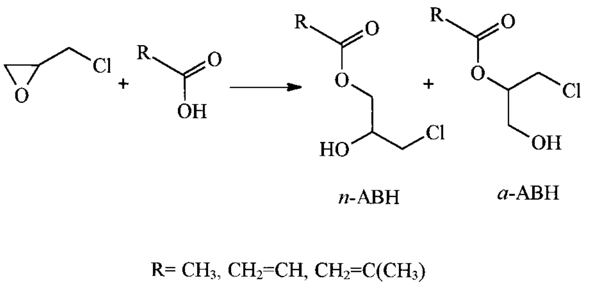
Scheme 1



and bearing three donor centers, substantially modifies the catalytic activity of chromium(III) ions and the regioselectivity of addition.

Experimental Section

Materials. Commercially available acetic (AcOH), acrylic (AA), methacrylic (MA) acids, epichlorohydryn (ECH), and 2-methoxyethyl ether (diglyme) were purified in the standard manner and distilled prior to use. Chromium(III) ethanoate was of p.a. grade and used without further purification.

Procedures. The kinetics of addition of carboxylic acids to epichlorohydrin were studied in a glass reactor (50 cm^3) equipped with heating jacket, reflux condenser, thermometer, and magnetic stirrer. The content of reactor was brought to the desired temperature with external heater. The concentration of reagents was changed in the range 0.4−1.0 $mol{\cdot}dm^{-3}$, concentration of chromium(III) ethanoate in the range 1.2−17.0 $mmol{\cdot}dm^{-3}$, and temperature from 60 to 90 °C in intervals of 10°.

The content of unreacted acid in the samples withdrawn from the reactor at predetermined reaction times was determined by titration. The concentration of epichlorohydrin was determined by Jay's method.[25] The final reaction mixtures were carefully analyzed by GLC (HP 5890 chromatograph with an FFAP capillary column, 10 m × 0.53 mm × 1 μm).

Results and Discussion

Kinetics study of reactions between acetic, acrylic, or methacrylic acid and epichlorohydrin were carried out in the presence of chromium(III) ethanoate catalyst and in diglyme solutions. For acetic acid, the molar ratios of reagents as well as their total concentrations in diglyme were changed. The reactions with acrylic or methacrylic acid were carried out at the equimolar conditions with diglyme amount adjusted to obtain reagent concentrations equal to 1 $mol{\cdot}dm^{-3}$.

GLC analysis of the addition products revealed the presence of two isomeric esters (Scheme 1) with a significant excess of the 3-chloro-2-hydroxypropyl carboxylate (*n*-ABH), the product of addition of carboxylic ion to the less substituted carbon atom of oxirane ring. Beside the two main esters, no more than traces of other compounds were found among the products.

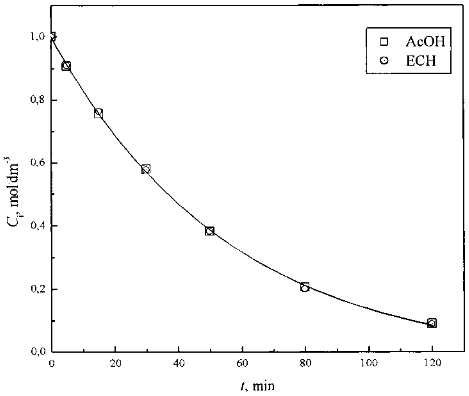


Figure 1. **The change of acetic acid (AcOH) and epichlorohydrin (ECH) concentrations during the reaction carried out in the presence of chromium(III) ethanoate in diglyme, $C_{0,AcOH} = C_{0,ECH} = 1\ mol{\cdot}dm^{-3}$; $C_{cat} = 0.0175\ mol{\cdot}dm^{-3}$; temperature 80 °C.**

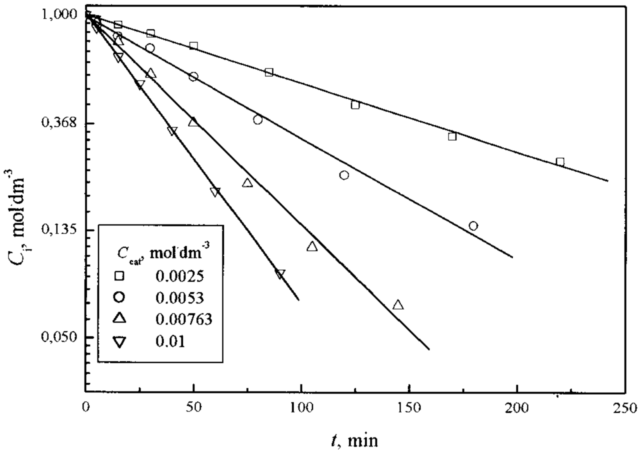


Figure 2. **The effect of catalyst concentration on the change of reagent concentrations during the reaction of acetic acid with epichlorohydrin carried out in the presence of chromium(III) ethanoate in diglyme; $C_{0,AcOH} = C_{0,ECH} = 1\ mol{\cdot}dm^{-3}$; temperature 90 °C.**

The typical plot illustrating the changes of reagent concentrations with time of addition is presented in Figure 1 for the reaction of acetic acid with epichlorohydrin (ECH) at initial concentrations of reagents $C_{0,AcOH} = C_{0,ECH} = 1$ $mol{\cdot}dm^{-3}$. The similar rates of consumption of both reagents (the same shapes of curves) are evidence of a high selectivity of reaction.

In semilogarithmic plot (Figure 2), the rate curves linearize, thus indicating a first-order reaction with respect to substrates. The slopes of the lines in Figure 2 nicely correlate with the catalyst concentration, yielding again a linear plot (Figure 3). Thus, the addition is monomolecular with respect to catalyst concentration.

More information on the partial reaction order for each substrate was obtained in experiments carried out with an excess of one of the reagents. The linear dependence of acetic acid concentration on reaction time at the relatively small 2.5-fold excess of epichlorohydrin (Figure 4) indicates the zeroth reaction order with respect to the acid. On the other hand, the exponential character of the curves obtained at the acid excess (Figure 5) proves a first-order reaction with respect to epichlorohydrin.

The rate curves obtained for the reaction of acetic acid with epichlorohydrin carried out in diglyme solution in the

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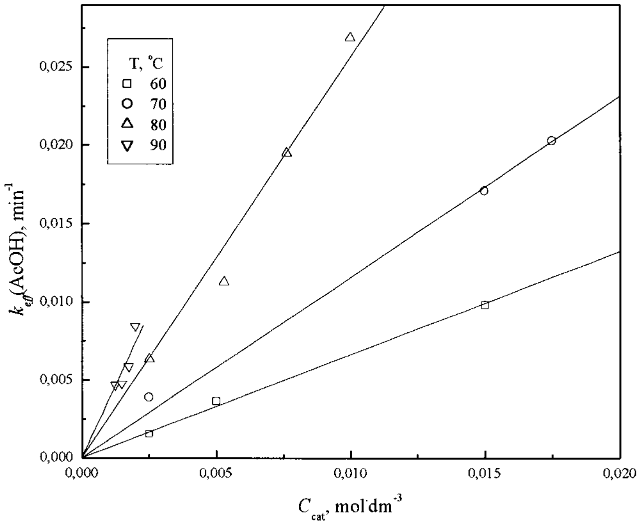

Figure 3. **The effective rate constant of the reaction of acetic acid with epichlorohydrin vs catalyst concentration; $C_{0,AcOH} = C_{0,ECH} = 1$ mol·dm^{-3}.**

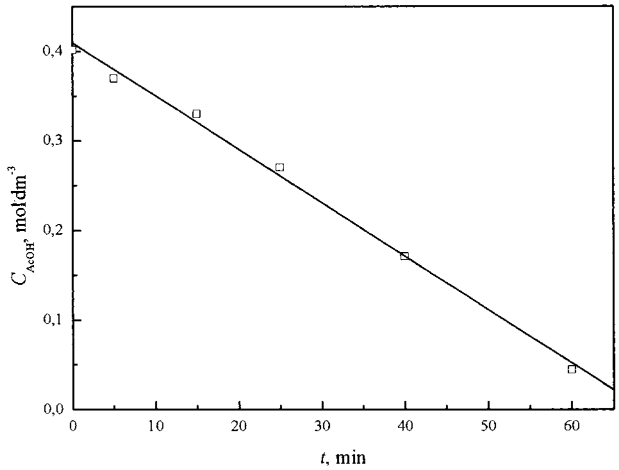

Figure 4. **The change of acetic acid concentration during its reaction with an excess of epichlorohydrin carried out in the presence of chromium(III) ethanoate in diglyme; $C_{0,ECH} = 1$ mol·dm^{-3}; $C_{cat} = 0.005$ mol·dm^{-3}; temperature 80 °C.**

presence of chromium(III) ethanoate catalyst are very similar to those obtained for the same reaction carried out without any solvent[20] or carried out in butanol.[24] The strong electron-donor character of diglyme (donor number DN ≈ 24)[26] does not seem to influence the reaction orders in the system.

Among the acids studied, the most reactive with respect to epichlorohydrin in diglyme solution is acrylic acid, while methacrylic acid is the least reactive one (Figure 6). This order is different than that found in the analogous reactions carried out without any solvent, where the most reactive was methacrylic acid and acetic acid was the least reactive one.[21]

The high selectivity of addition of acetic, acrylic, and methacrylic acids to epichlorohydrin justifies the following form of rate equation (subscripts CA and cat stand for carboxylic acid and catalyst, respectively):

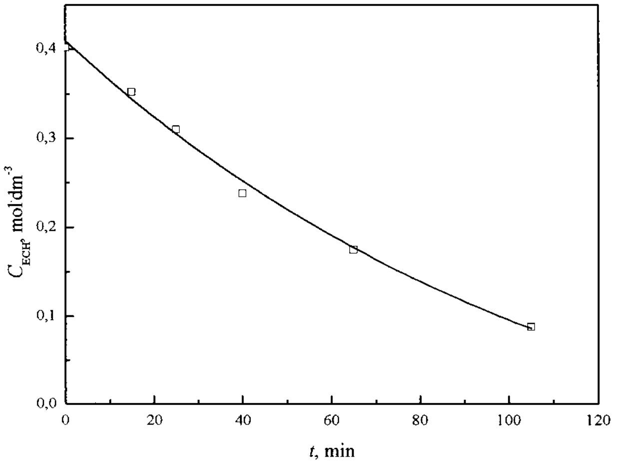

Figure 5. **The change of epichlorohydrin concentration during its reaction with an excess of acetic acid carried out in the presence of chromium(III) ethanoate in diglyme; $C_{0,AcOH} = 1$ mol·dm^{-3}; $C_{cat} = 0.005$ mol·dm^{-3}; temperature 80 °C.**

$$-\frac{dC_{CA}}{dt} = -\frac{dC_{ECH}}{dt} = kC_{cat}C_{ECH}$$

The rate constants k calculated for this model at different reaction conditions are listed in Table 1. A comparison of the values in Table 1 with the rate constants evaluated for the analogous reaction carried out without solvent leads to the conclusion that dilution of the system with diglyme results in an increase of the rate constant by a factor of 2.2−2.9 for acetic acid[20] and by 1.1−1.4 for acrylic acid[21] in the temperature range studied. On the other hand, the presence of diglyme reduces the reaction rate of methacrylic acid addition to epichlorohydrin by a factor of 2 as compared with that of the undiluted system.[21]

This raises the question as to the reason behind the effect of diglyme on reaction rate. We believe that diglyme, having three ether oxygen atoms, may play a role of a tridendate ligand of the catalyst. Dissolution of catalyst in diglyme should be accompanied by formation of the complex (Scheme 2).

Introduction of diglyme to the system carboxylic acid−epichlorohydrin−chromium(III) ethanoate leads to reorganization of the system, due to reduction of concentration of carboxylic groups and the abundance of electron-donor oxygen atoms. A reduction in the concentration of hydroxyl groups diminishes the probability of formation of cyclic hydrogen bonding between pairs of carboxylic acid molecules that moderates acid reactivity. On the other hand, hydrogen bonds may appear between the carboxyl OH groups and oxygen atoms of the solvent. These bonds may more or less activate the acid, depending on its strength. This, however, does not explain the negative effect of diglyme on the addition of methacrylic acid to epichlorohydrin and the highest increase of activity of the weakest acetic acid.

As follows from kinetics data, the rate of addition of an acid to epichlorohydrin is controlled by the interactions between catalyst and oxirane molecules and does not depend on the carboxylic acid concentration. The different effects of diglyme on the rates of reactions suggest an influence of the structure of the carboxylic acids. The reason for the

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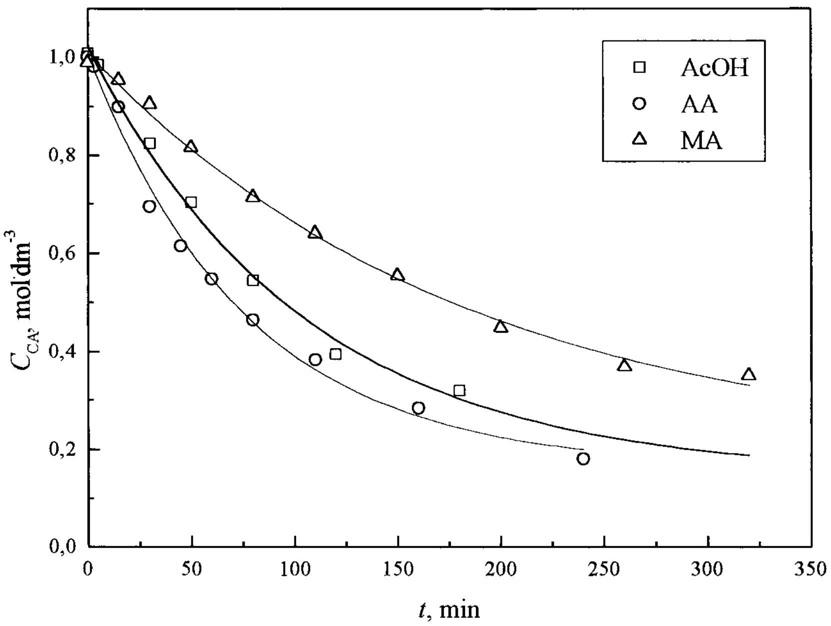


Figure 6. **The change of carboxylic acids (CA) concentration during the reaction of acetic, acrylic and methacrylic acids with epichlorohydrin carried out in the presence of chromium(III) ethanoate in diglyme, $C_{0,CA} = C_{0,ECH} = 1$ mol·dm^{-3}; $C_{cat} = 0.002$ mol·dm^{-3}; temperature 90 °C.**

Table 1. **Rate constants of the reaction of acetic (AcOH), acrylic (AA), and methacrylic (MA) acids with epichlorohydrin (ECH) carried out in the presence of chromium(III) ethanoate (cat) in diglyme solution at $C_{0,CA} = C_{0,ECH} = 1$ mol·dm^{-3}**

	AcOH		AA		MA	
T, °C	$10^2 C_{cat}$, mol·dm^{-3}	$10^2 k$, dm^3 mol^{-1} s^{-1}	$10^2 C_{cat}$, mol·dm^{-3}	$10^2 k$, dm^3 mol^{-1} s^{-1}	$10^2 C_{cat}$, mol·dm^{-3}	$10^2 k$, dm^3 mol^{-1} s^{-1}
60	0.25−1.76	1.06 ± 0.08	0.6−0.8	1.38 ± 0.08	0.7−1.0	0.64 ± 0.03
70	0.25−1.75	2.32 ± 0.53	0.8	2.52 ± 0.43	0.8−1.2	1.10 ± 0.03
80	0.25−1.00	4.01 ± 0.16	0.4	4.67 ± 0.10	0.2−0.6	2.31 ± 0.07
90	0.12−0.20	6. 09 ± 0.40	0.2−0.4	8.20 ± 0.12	0.2−0.8	3.84 ± 0.12

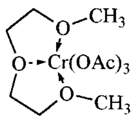
Table 2. **Activation parameters for the reaction of acetic, acrylic, and methacrylic acids with epichlorohydrin in the presence of chromium(III) ethanoate in diglyme solution at $C_{0,CA} = C_{0,ECH} = 1$ mol·dm^{-3} and without solvent**

activation parameters	AcOH		AA		MA	
	in diglyme	without solvent[20]	in diglyme	without solvent[21]	in diglyme	without solvent[21]
E_a, kJ·mol^{-1}	46.4 ± 2.44	68.6 ± 1.5	60.0 ± 0.6	66.8 ± 2.1	61.6 ± 3.2	61.9 ± 1.2
$\Delta H^{\ddagger}$, kJ·mol^{-1}	55.34 ± 4.9	65.8 ± 1.5	57.1 ± 0.6	63.8 ± 0.8	58.5 ± 3.3	61.1 ± 0.8
$\Delta S^{\ddagger}$, J·mol^{-1} K^{-1}	−116.9 ± 14.0	−93.3 ± 4.3	−110.1 ± 1.8	−92.6 ± 2.2	−112.5 ± 9.4	−99.2 ± 2.3

activity reduction in the addition of methacrylic acid to epichlorohydrin in diglyme solution might be interactions between electron pairs of oxygen atoms of the solvent and π electrons of C=C double bond of methacrylic ions in chromium ion coordination sphere. These kinds of interactions, enhanced by a steric effect of the acid branched structure, might limit contacts between reagents sufficiently effectively to reduce the addition rate as compared to those for the system without any solvent. The combined effects of electronic and steric causes might also explain why for the less branched acrylic acid the negative and positive effects of diglyme presence compensate each other. In the case of this acid the rate constants of the reactions carried out without solvent and in diglyme have similar magnitudes.

The activation parameters of the reactions studied are presented in Table 2. They have been calculated from the rate constants measured at four temperatures from Arrhenius plots and using Eyring equations.

Scheme 2



As can be seen from Table 2, the values of activation energy, enthalpy, and entropy of addition of acetic acid to epichlorohydrin in diglyme are substantially smaller as compared to the values measured in the system without solvent. The decrease in values of activation parameters is significantly smaller in the case of acrylic acid. For methacrylic acid, the activation energy and enthalpy are similar to those in no solvent system. The smaller value of entropy component, however, seems to point at the importance of the effect of entropic factor on addition rate.

Besides the high selectivity of addition of carboxylic acids to epichlorohydrin catalyzed by chromium(III) ethanoate, the

Table 3. **Molar fraction of abnormal products (*a*-ABH) in the reaction of acetic, acrylic, and methacrylic acids with epichlorohydrin in the presence of chromium(III) ethanoate in diglyme solution at 80 °C**

	a-ABH, mol %	
acids	in diglyme	without solvent[27]
AcOH	3.9	8.1
AA	2.3	7.1
MA	3.0	3.9

presence of diglyme improves the regioselectivity of addition as compared to that for the system without any solvent. The fractions of *a*-ABH isomer present in the products of reactions carried out at 80 °C both in diglyme solution and in nonsolvent system are compared in Table 3. The presence of diglyme in the active complex favors, for steric reasons, the addition of carboxyl group to the less substituted carbon atom of oxiranes ring.

Conclusions

The study has shown that in the presence of diglyme, the addition of acetic, acrylic, or methacrylic acid to epichlorohydrin catalysed with chromium(III) ethanoate is a bimolecular reaction. It is a first-order reaction with respect to catalyst and oxiranes concentrations and zeroth order with respect to acid.

In diglyme solution, the regioselectivity of addition of carboxylic acids to epichlorohydrin is enhanced as compared with that in nonsolvent system.

The presence of diglyme modifies the relative reactivity carboxylic acids in their reactions with epichlorohydrin.

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