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# Kinetic Study of Addition of Some Carboxylic Acids to 1,2-Epoxy-3-phenoxypropane

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## Abstract:

**The kinetics of addition of acetic, acrylic, or methacrylic acids to 1,2-epoxy-3-phenoxypropane (glycidyl phenyl ether) carried out in the presence of chromium(III) ethanoate have been studied. A kinetic model of the reaction has been proposed. The rate constants as well as the activation parameters have been evaluated. The reactivity of the acids in reactions with GPE and 1-chloro-2,3-epoxypropane (epichlorohydrin) without any solvent are compared. The compositions of reaction mixtures have been carefully determined.**

## Introduction

The reactions of carboxylic acids with 1,2-epoxy-3-phenoxypropane and its derivatives were the subject of several kinetic analyses.[1−8] The effects of reagent structure, type of catalyst, and solvent used on the rate and mechanism of reaction were studied. Mostly the effect of basic catalysts was studied since these had been most widely utilized in reactions of carboxylic acids with epoxy compounds. The reaction mechanisms were found to be pretty complex and hard to interpret unambiguously. Consequently, the views on the course of reaction including its order and mechanism differ from author to author, particularly in the case of tertiary amine catalysts.[1−5]

Tanaka et al.[1,2,4] have found that in the presence of tertiary amine, substituted glycidyl phenyl ethers reacted with benzoic acid in xylene, mono-, *o*-dichlorobenzene, or nitrobenzene according to the first order with respect to both reagents and catalyst. The rate of reactions increased with the growing acceptor character of the substituent in either ether or solvent molecules.[1] For the series of aromatic solvents, toluene, chlorobenzene, *o*-dichlorobenzene, nitrobenzene, or benzene-nitrobenzene mixture, the logarithm of the rate constant of the addition of benzoic acid to 1,2-epoxy-3-phenoxypropane catalyzed by pyridine has been found to depend linearly on the solvent dielectric constant.[4] The effect of catalyst structure on the same reaction rate was studied for a series of methyl-substituted pyridine derivatives. An increase in the rate was observed when pyridine was replaced by 3- or 4-methylpyridine, while 2-methylpyridine was a less active catalyst than pyridine.[2] Similar dependence of catalytic activity on the structure of catalyst was observed for methyl derivatives of quinoline.

The kinetics and mechanism of reactions of a series of glycidyl ethers with caproic or capric acids in chlorobenzene were studied by Sorokin et al.[3] The rate and mechanism of addition of carboxylic acid to an epoxy ring were found dependent on the type of catalyst used. The reaction was slow in the absence of catalyst, and its global order was two; one for each substrate. The rate of the same reaction carried out in the presence of sodium or potassium hydroxide was described by a third-order equation: concentrations of both reagents and catalyst all appeared in the first power. A different reaction order was observed for the reaction catalyzed by trihexylamine. In the presence of this catalyst, the addition rate did not depend on acid concentration, but it was found to be proportional to both catalyst and oxirane concentrations. This finding was in contradiction to the result of Tanaka.[1]

Yet another interpretation of kinetic data on the reaction of 1,2-epoxy-3-phenoxypropane with caproic acid was published by Matejka and Dušek.[5] The authors found the first order of the reaction with respect to catalyst and a 0.5 one with respect to both acid and ether concentration.

Despite the different points of view of different authors on the reaction order, they all seemed to agree that a complex of the tertiary amine catalyst with carboxylic acid was formed in the first stage of reaction. This seems quite obvious for the chemical nature of these compounds. As pointed out by Matejka and Dušek,[5] carboxylic acids in contact with amines yield an ammonium salt. Formation of such a salt containing carboxylic anions should result in the same mechanism of reaction as that observed for sodium acetate catalyst.

An obvious change of the catalyst active form takes place also when sodium or potassium hydroxide is used. In this case the neutralization yields the respective carboxylate which becomes the catalyst of the reaction.

The rate of addition taking place in the presence of alkali metal hydroxides or carboxylates as well as tertiary amines should depend on the size of cation in the active form of catalyst. As the radius of the cation increases, the electrostatic attraction between counterions becomes weaker, the nucleophilicity of carboxylate anions increases and hence increases the catalytic activity. Such a relationship was observed for

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the reaction of carboxylic acids with 1,2-epoxypropane[9] or 1-chloro-2,3-epoxypropane.[10] Steric conditions, however, may distort this order. A reduced rate was observed for large cations in the case 2-methylpyridine or 2-methylquinoline.[2]

The differences in the observed reaction order of the addition of carboxylic acids to glycidyl phenyl ethers catalyzed by tertiary amines is probably the result of the equilibrium which is established between the amine and carboxylic acid. The latter strongly depends on the other conditions of the reaction.

The basic catalysts, although quite widely used, have certain disadvantages, the main one being the ability to initiate cationic polymerization of epoxy compounds.[11] In a dilute solution this reaction may be neglected, but in the systems without a solvent, such as in the commercial synthesis of hydroxyalkyl esters, the side polymerization reaction in the alkaline medium may reduce considerably the reaction selectivity.

The chromium(III) catalysts, which are effective in the reactions of carboxylic acids with oxirane, 1,2-epoxypropane, or 1-chloro-2,3-epoxypropane, are free of this disadvantage. They exhibit not only a high selectivity, but are usually more active than basic catalysts.[12−17]

The kinetic relationships observed in the addition of selected carboxylic acids to 1,2-epoxy-3-phenoxypropane in the presence of such a homogeneous chromium(III) catalyst in the system without a solvent are presented in this work.

## Experimental Section

**Materials.** Commercially available acetic, acrylic, and methacrylic acids and 1,2-epoxy-3-phenoxypropane were purified in the standard manner and distilled prior to use. Chromic ethanoate was of p.a. grade and used without further purification.

**Procedures.** The kinetics of addition were studied in purpose designed glass reactors (50 $cm^3$) equipped with a heating jacket, reflux condenser, thermometer, and magnetic stirrer. The content of reactor was brought to desired temperature with an external thermostat. The equimolar ratio of carboxylic acid to epichlorohydrin was used. The concentration of chromium(III) ethanoate was changed in the range 2.0−17.0 mmol·$dm^{-3}$ and temperature from 60 to 90 °C at 10° intervals.

The content of unreacted acid in the samples withdrawn from the reactor at predetermined reaction times was determined by titration. The concentration of 1,2-epoxy-3-phenoxypropane was determined by Jay's method.[18] The final reaction mixtures were carefully analyzed by GLC (HP 5890 chromatograph with an FFAP capillary column, 10 m/0.53 mm/1 $\mu$m).

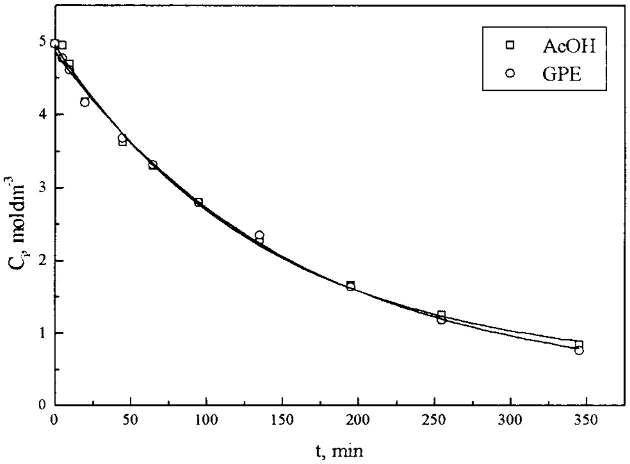

***Figure 1.*** **The concentration of 1,2-epoxy-3-phenoxypropane (GPE) and of acetic acid (AcOH) versus time in the reaction carried out in the presence of chromium(III) ethanoate catalyst (cat); $C_{AcOH,0} \approx C_{GPE,0}$; $C_{cat} = 0.008$ mol·$dm^{-3}$; temperature 70 °C.**

## Results and Discussion

Among the products of reaction in the system containing a carboxylic acid (CA), asymmetric epoxy compound and catalyst one may expect beside the two isomeric esters with alcoholic hydroxy groups also the products of disproportionation of hydroxyesters, subsequent addition of oxirane to hydroxyesters, polymerization of oxirane or its isomerization to ketone or aldehyde, or even esterification of carboxylic acid with the addition product. The extent of either of these reactions depends on the conditions applied and, primarily, on the kind of catalyst used. Among two isomeric hydroxyester products, usually the so-called normal product is formed in excess, i.e., the product of addition to the carbon atom in epoxy ring which has a lower substitution degree.

In our previous papers on the reactions of carboxylic acids with 1-chloro-2,3-epoxypropane carried out in the presence of chromium(III) ethanoate[17,19,20] we have shown that in the systems without a solvent, most of the above-mentioned side reactions involving oxiranes do not take place, or their contribution among products is negligible.

The typical kinetic curves obtained for the reaction of acetic (1), acrylic (2), and methacrylic acid (3) with 1,2-epoxy-3-phenoxypropane in the presence of chromium(III) ethanoate in temperature range 60−90 °C are shown in Figures 1−3.

For all systems, the shape of kinetic curves indicates that the changes of both substrate concentrations are simultaneous. This confirms the small contribution of side reactions in the conditions applied. The same conclusion follows from results of GLC analysis of the crude reaction products. In the crude products of reaction two isomeric esters, 2-hydroxy-3-phenoxypropyl (n-PHPC) and 1-(hydroxymethyl)-

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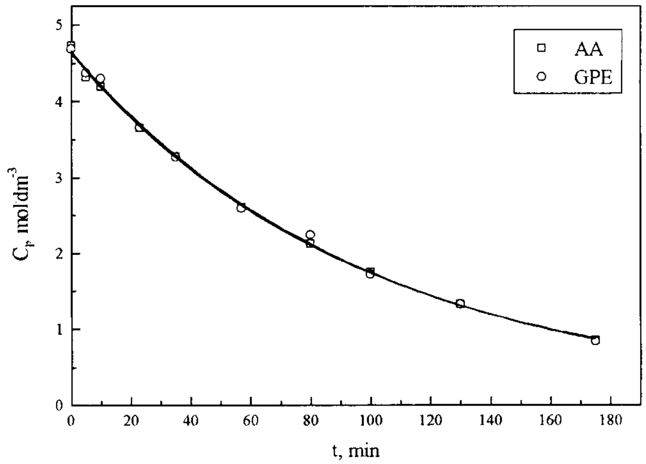


***Figure 2.*** **The concentration of 1,2-epoxy-3-phenoxypropane (GPE) and of acrylic acid (AA) versus time in the reaction carried out in the presence of chromium(III) ethanoate catalyst $C_{AA,0} \approx C_{GPE,0}$; $C_{cat} = 0.008$ mol·dm$^{-3}$; temperature 70 °C.**

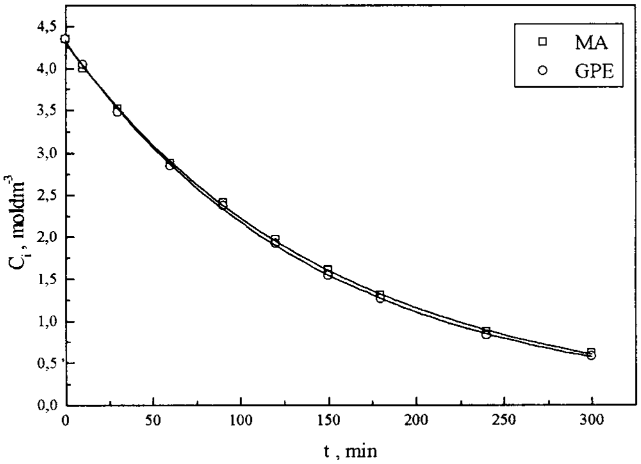
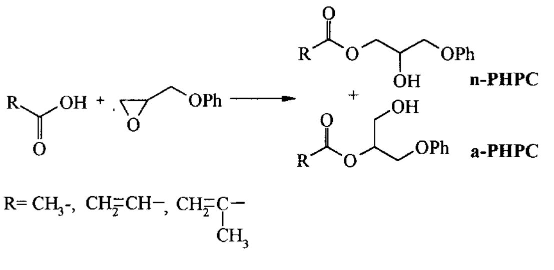


***Figure 3.*** **The concentration of 1,2-epoxy-3-phenoxypropane (GPE) and of methacrylic acid (MA) versus time in the reaction carried out in the presence of chromium(III) ethanoate catalyst; $C_{MA,0} \approx C_{GPE,0}$; $C_{cat} = 0.006$ mol·dm$^{-3}$; temperature 70 °C.**

2-phenoxyethyl carboxylate (a-PHPC), formed by the addition of carboxylic acids to 1,2-epoxy-3-phenoxypropane, dominate:



(1)

As revealed by GLC analysis, the molar fraction of the abnormal isomer in the crude products only slightly depends on temperature; its dependence on the type of carboxylic acid is more pronounced. It increases in the order methacrylic (8.2%), acrylic (8.8%), and acetic acid (12%). The rate curves became straight lines in the semilogarithmic plot (Figures 4 and 5) which means that the reaction is of the first order with respect to substrates.

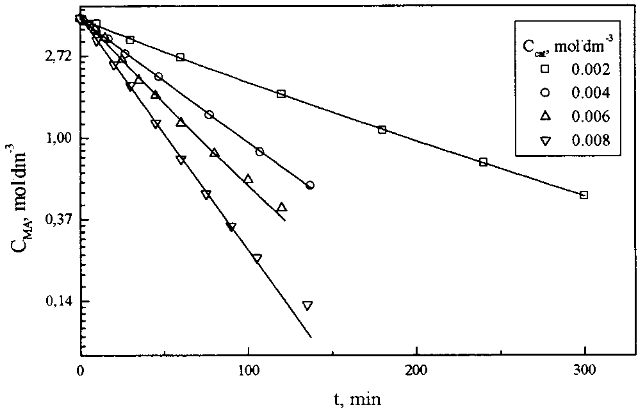


***Figure 4.*** **The effect of catalyst concentration on the time dependence of methacrylic acid (MA) concentration in reaction with 1,2-epoxy-3-phenoxypropane (GPE) carried out in the presence of chromium(III) ethanoate; $C_{MA,0} \approx C_{GPE,0}$; temperature 90 °C.**

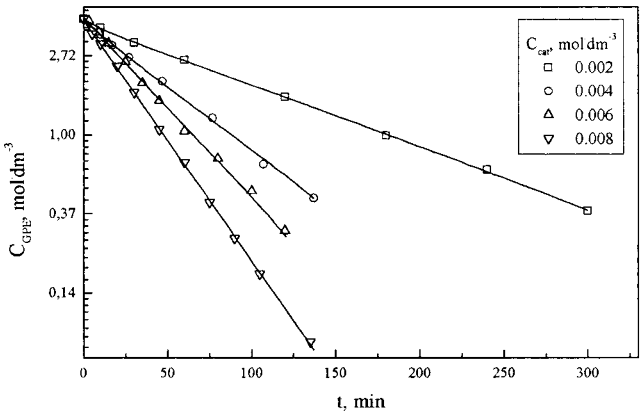


***Figure 5.*** **The effect of catalyst concentration on the time dependence of 1,2-epoxy-3-phenoxypropane (GPE) concentration in reaction with methacrylic acid (MA) carried out in the presence of chromium(III) ethanoate; $C_{MA,0} \approx C_{GPE,0}$; temperature 90 °C.**

The slopes of ln $C_{CA}$ vs time lines depend linearly on the concentration of chromium(III) ethanoate (Figures 6 and 7) which means that all reactions are of the first order with respect to catalyst concentration. The slopes are in fact the effective rate constants of acid addition to the epoxy compound. It follows from their values that acrylic acid reacted with 1,2-epoxy-3-phenoxypropane with the highest rate and acetic acid with the lowest one among acids studied. This order of reaction rates coincide with the order of the acidities of acids in water expressed by their p$K_a$ values.[21] No such consistency was observed for 1-chloro-2,3-epoxypropane which reacted the fastest with methacrylic acid and the slowest with acetic acid.[17,20] The difference, however, between the relative reaction rates of methacrylic and acrylic acids was in both cases pretty small and increased slightly with temperature.

The data presented graphically indicate that in the presence of chromium(III) ethanoate the reaction order of the reaction between carboxylic acids and 1,2-epoxy-3-phenoxypropane is one with respect to catalyst concentration

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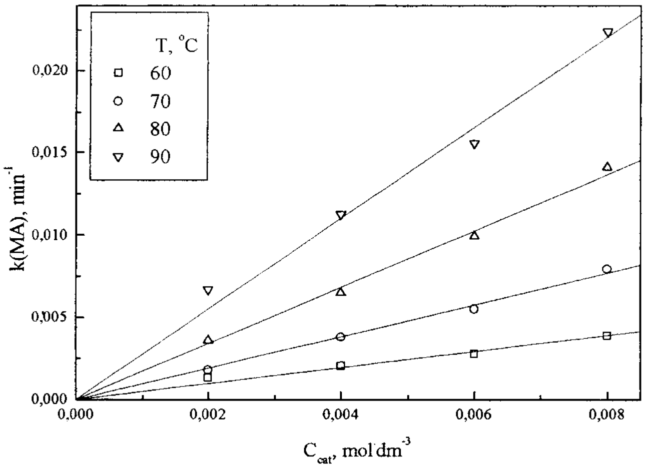

***Figure 6.*** **The effective rate constants ($k$(MA)) of the reactions of methacrylic acid with 1,2-epoxy-3-phenoxypropane carried out in the presence of chromium(III) ethanoate as determined from the correlation ln $C_{MA}$ vs time. $C_{MA}$ and $C_{cat}$ are the methacrylic acid and catalyst concentrations, respectively.**

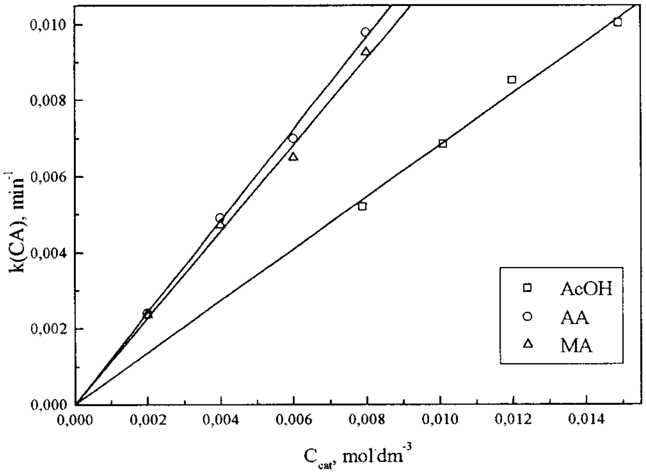

***Figure 7.*** **The dependence of the effective rate constants for reactions of carboxylic acids (CA) with 1,2-epoxy-3-phenoxypropane carried out in the presence of chromium(III) ethanoate at 70 °C as determined from slopes of the plots ln $C_{CA}$ vs time.**

as well as with respect the concentration of one of substrates. Our previous studies on the reaction order in reaction of acetic acid with 1-chloro-2,3-epoxypropane carried out in the presence of the same catalyst revealed the zero-th order with respect to carboxylic acid concentration.[17] The relevant rate equation read:

$$-\frac{dC_{CA}}{dt} = -\frac{dC_{GPE}}{dt} = kC_{cat}C_{GPE} \qquad (2)$$

The rate constants $k$ calculated using eq 2 are shown in Table 1. The relative reactivity ratios $R = k_i/k_{AcOH}$ for the reaction of carboxylic acids with 1,2-epoxy-3-phenoxypropane are also listed. From their values one can see that the reactivity of acrylic and methacrylic acid relative to that of acetic acid reduced 1.2 and 1.5 times, respectively, as temperature increased from 60 to 90 °C. At 60 °C, the unsaturated acids had similar reactivity.

The rate constant $k$ in eq 2 is, in fact, a composed rate constant of formation of two isomeric addition products. If the molar fractions of these products are known, the partial rate constants can be calculated from the equation

$$k_{a-PHPC} = X_{a-PHPC}\,k \qquad (3)$$

$$k_{n-PHPC} = X_{n-PHPC}\,k \qquad (4)$$

where $X_{a-PHPC}$ and $X_{n-PHPC}$ are the molar fractions of products of normal and abnormal substitution, respectively. The partial rate constants calculated by using averaged molar fractions of isomeric hydroxyesters are listed in Table 1. The rate of formation of the abnormal product seems to depend on the structure of carboxylic acid. As follows from the values of $X_{n-PHPC}$ and $X_{a-PHPC}$ the rate of formation of the normal product was the highest among the acids studied. The lowest rate of the normal product formation had acetic acid.

It seems that the steric effects cause the most bulky molecule of methacrylic acid to react harder with the more substituted carbon atom of 1,2-epoxy-3-phenoxypropane than the smaller acrylic acid, despite the higher overall addition rate of the latter.

By using linearized forms of Arrhenius and Eyring equations as well as the temperature dependence of free energy of activation we have calculated the energy, enthalpy, and entropy of activation. The results are listed in Table 2. A clear decrease of values of all these parameters can be observed in the order acetic acid > acrylic acid > meth-

***Table 1.*** **Rate constants of reactions between carboxylic acids and 1,2-epoxy-3-phenoxypropane in the presence of chromium(III) ethanoate**

| acid | temp, °C | $10^2k$, dm$^3$ mol$^{-1}$ s$^{-1}$ | % (a-PHPC) | $10^2k_{a-PHPC}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $10^2k_{n-PHPC}$, dm$^3$ mol$^{-1}$ s$^{-1}$ | $R = k_i/k_{AcOH}$ |
|---|---|---|---|---|---|---|
| acetic | 60 | 0.552 ± 0.030 | 12.13 ± 0.85 | 0.067 | 0.485 | 1.0 |
| | 70 | 1.278 ± 0.020 | | 0.155 | 1.123 | 1.0 |
| | 80 | 2.540 ± 0.107 | | 0.308 | 2.232 | 1.0 |
| | 90 | 5.033 ± 0.213 | | 0.610 | 4.422 | 1.0 |
| acrylic | 60 | 1.075 ± 0.055 | 9.02 ± 1.15 | 0.097 | 0.978 | 1.95 |
| | 70 | 2.217 ± 0.150 | | 0.200 | 2.017 | 1.73 |
| | 80 | 4.080 ± 0.058 | | 0.368 | 3.712 | 1.61 |
| | 90 | 7.798 ± 0.345 | | 0.703 | 7.095 | 1.55 |
| methacrylic | 60 | 1.068 ± 0.022 | 8.19 ± 0.18 | 0.087 | 0.980 | 1.93 |
| | 70 | 1.988 ± 0.045 | | 0.163 | 1.825 | 1.56 |
| | 80 | 3.573 ± 0.073 | | 0.293 | 3.280 | 1.41 |
| | 90 | 6.347 ± 0.117 | | 0.520 | 5.827 | 1.26 |

***Table 2.*** **Activation parameters in reactions of carboxylic acids with 1,2-epoxy-3-phenoxypropane in the presence of chromium(III) ethanoate**

| | acid | | |
|---|---|---|---|
| | acetic | acrylic | methacrylic |
| $E_a$, kJ·mol$^{-1}$ | 73.70 ± 1.55 | 65.39 ± 2.35 | 59.57 ± 0.38 |
| $\Delta H^{\ddagger}$, kJ·mol$^{-1}$ | 70.72 ± 1.55 | 63.07 ± 1.06 | 56.80 ± 0.35 |
| $\Delta S^{\ddagger}$, J·mol$^{-1}$ K$^{-1}$ | −76.61 ± 4.45 | −94.17 ± 3.04 | −113.1 ± 1.00 |

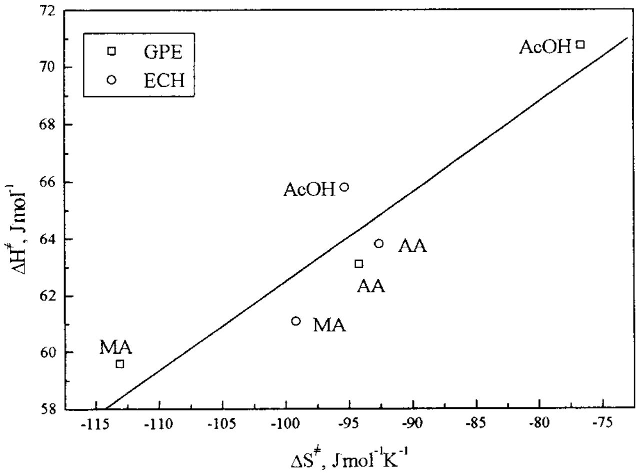

***Figure 8.*** **The isokinetic plot for the reactions of carboxylic acids with 1,2-epoxy-3-phenoxypropane(□) or 1-chloro-2,3-epoxypropane (○) in the presence of chromium(III) ethanoate; AcOH: acetic acid, AA: acrylic acid, MA: methacrylic acid.**

acrylic acid. The order is not consistent with the reactivity order discussed above. The reaction rate which is a function of the activation energy depends on the ratio of activation enthalpy and entropy. Although the addition of acrylic acid to 1,2-epoxy-3-phenoxypropane requires overcoming a slightly higher activation barrier than that of methacrylic acid, the entropy of the first reaction is sufficiently high for the overall rate to be in its favor.

The interrelation between activation energy and entropy (the isokinetic plot) is presented in Figure 8. for both the systems studied in this work and for reactions with 1-chloro-2,3-epoxypropane reported previously.[17,20] The fairly linear relationship indicates that all addition reactions proceed according to the same mechanism. A hypothetical mechanism of the addition taking place in the presence of chromium(III) ethanoate has already been discussed in ref 17.[17] According to this mechanism, the catalyst is solvated when dissolved in a carboxylic acid and the exchange of the ligands takes place in the coordination sphere of chromium(III) atoms. The rate controlling stage is the activation of oxirane molecule by creation of a coordination link between epoxy oxygen and chromium atom which facilitates a quick opening of epoxy ring by the nucleophilic attack of carboxylate ions within the coordination sphere. The active complex immediately splits in the presence of a second carboxylic acid molecule with formation of one of two isomeric hydroxyesters and restitution of the initial form of catalyst. The large difference in the acidity of substrate and products improves the reaction selectivity. It limits the extent of subsequent reactions since the active complex decomposes most easily in the presence of even a small amount of acidic protons. Formation of the normal addition product is also favored by the fact that the addition takes place in the coordination sphere of the catalyst. The steric effects reduce the possibility of the nucleophilic attack on the more substituted carbon atom in epoxy ring. This is evident from the results of the present work.

## Summary

The addition of a carboxylic acid to 1,2-epoxy-3-phenoxypropane carried out in the presence of chromium(III) ethanoate leads to the formation of two isomeric hydroxyesters with the isomer obtained by the addition to the less substituted carbon atom in the epoxy ring formed in large excess. The rate of addition does not depend on the concentration of carboxylic acid. It is proportional to concentrations of 1,2-epoxy-3-phenoxypropane and catalyst. Among the acids studied, the most reactive is acrylic acid, and the least reactive, acetic acid. The amount of the isomer resulting from abnormal addition depends on acid structure and is the lowest for methacrylic acid.

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