

Reactivity of Some Carboxylic Acids in Reactions with Some Epoxides in the Presence Chromium (III) Ethanoate

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Abstract:

Reactivities have been compared of acetic, acrylic, and methacrylic acid in reactions with epichlorohydrin, phenylglycidyl ether, glycidyl acetate, and glycidyl methacrylate carried in the presence of chromium (III) ethanoate. The acid reactivities changed differently with respect to the oxirane series. The effect of solvents on the reactions of acids with epichlorohydrin has also been observed.

Introduction

Reactivity of epoxy compounds is related to the relatively high stress within three-membered rings on one hand and, on the other hand, to polarization of C–O bonds leading to formation of partial charges on carbon and oxygen atoms of magnitudes, depending on the kind of nearest neighbors of epoxy group. Some electrophilic substances (e.g., protonic acids or Lewis acids) may enhance the polarization and hence affect the reactivity of epoxy group by interacting with the electron pair of oxygen atom. The interactions may have hydrogen-bonding, charge-transfer, or donor–acceptor characteristics. Basic compounds (nucleophiles), however, may affect the partially positively charged carbon atoms in epoxy rings, thus facilitating ring-opening and further reactions of epoxy compounds. Consequently, oxiranes undergo many diversified chemical transformations,^{1–4} and reactions involving oxiranes are catalyzed by many compounds, of both acidic and basic character, as well as by acceptor–donor substances.

From practical point of view, addition of carboxylic acids to an epoxy group is an important reaction of oxiranes. One of its applications is the addition of acrylic or methacrylic acid to epoxy compounds, leading to formation of respective hydroxyalkyl esters.⁵

The relative rate of addition of acids to oxiranes has been studied many times in the past.^{6–19} From the published data

it is known that the rate of addition of a carboxylic acid depends on the structure of oxirane. In particular, in the series of reactions of aliphatic and aromatic monoglycidyl ethers with caproic or capric acid in the presence of NaOH, the rate constants of addition were found to increase slightly with increase of the acceptor character of substituents at epoxy rings.⁶ An opposite effect was observed in the system where substituted glycidylamines reacted with acetic, benzoic, 3,5-dinitrobenzoic, or tetrahydrobenzoic acid in chlorobenzene solution in the presence of benzyldiethylamine.^{7,8} One should note that the epoxy ring in glycidylamine is exceptionally reactive. For example, *N*-ethyl-*N*-glycidylamine reacts with benzoic acid in chlorobenzene ca. 100 times faster than phenylglycidyl ether.⁹ Somewhat less reactive, but still much more reactive than glycidyl ethers, are glycidyl esters. For example, glycidyl benzoate reacts with benzoic and hexanoic acid ca. 50–70 times faster than phenylglycidyl ether.⁷ For glycidyl esters of substituted benzoic acids, an increase of addition rate of carboxylic acids was observed with increasing donor character of substituents, as for glycidylamines.

The reactivity studies for series of aliphatic and aromatic carboxylic acids with respect to ethylene oxide in nitrobenzene in the presence of the respective potassium carboxylates that were carried out by Lebedev et al.^{10,11} at the beginning of the 1960s revealed a clear effect of the strength of the acids on addition rate. Separate linear dependences have been found between pK_a 's of acids in water and the logarithms of rate constants of addition for aliphatic and aromatic carboxylic acids. An increase of the reaction rate with the strength of acid was observed also for the reaction of ethylene oxide with acetic acid and its chloro derivatives in the presence of tertiary amines in butanol,¹² for the reaction of ethylene oxide with aromatic carboxylic acids in the presence of pyridine in some protic and aprotic solvents,¹³ or for the addition of a series of aliphatic carboxylic acids to propylene oxide in the presence of CH_3COOK .¹⁴ Mallek et al.,¹³ as Lebedev et al.^{10,11} somewhat earlier, found Brönsted-type relationships in the systems they studied.

The relative rate of addition of carboxylic acids to oxiranes, however, cannot be related to their strength, as can be deduced from the results obtained in the present work.

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- (1) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, 59, 737.
- (2) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, 39(14), 2323.
- (3) Gorzynski Smith, J. *Synthesis* **1984**, 629.
- (4) Jacobsen E. N. *Acc. Chem. Res.* **2000**, 33, 421.
- (5) Bukowska, A.; Bukowski, W.; Galina, H. *Wiad. Chem.* **1997**, 51(3–4), 217.
- (6) Sorokin, M. F.; Gershanova, E. L. *Kinet. Katal.* **1967**, 8(3), 512.
- (7) Klebanov, M. S.; Kiriazev, F. Yu.; Tchervinskij, A. Yu.; Shologon, I. M. *Zh. Org. Khim.* **1984**, 20(11), 2407.
- (8) Klebanov, M. S.; Kiriazev, F. Yu.; Karpov, O. N. *Kinet. Katal.* **1987**, 28(6), 1493.
- (9) Klebanov, M. S.; Kiriazev, F. Yu.; Shologon, I. M. *Kinet. Katal.* **1984**, 25(4), 1004.
- (10) Guskov, K. A.; Lebedev, N. N. *Trudy MChTI (in Russia)* **1963**, 42, 57.
- (11) Lebedev, N. N.; Guskov, K. A. *Kinet. Katal.* **1964**, 5(5), 787.
- (12) Mares, F.; Hettflejš, J.; Bazant, V. *Collect. Czech. Chem. Commun.* **1969**, 34, 3086.

- (13) Malek, J.; Silhavy, P. *Collect. Czech. Chem. Commun.* **1976**, 41, 84.
- (14) Chlebicki, J.; Zwiefka, A. *Tenside Surf. Det.* **1985**, 22(3), 117.
- (15) Bukowska, A.; Bukowski, W.; Mossety-Leszczak, B. *J. Chem. Technol. Biotechnol.* **1999**, 74(12), 1145.
- (16) Jay, R. *Anal. Chim.* **1964**, 36, 667.
- (17) Bukowska, A.; Bukowski, W. *J. Chem. Technol. Biotechnol.* **1996**, 67, 176.
- (18) Bukowska, A.; Bukowski, W. *J. Chem. Technol. Biotechnol.* **1999**, 74, 675.
- (19) Bukowska, A.; Bukowski, W. *Org. Process Res. Dev.* **1999**, 3(6), 432.

Experimental Section

Materials. Commercially available acetic (AcOH), acrylic (AA), methacrylic (MA) acids, epichlorohydrin (ECH), 1,2-epoxy-3-phenoxypropane (GPE), glycidyl methacrylate (GM), glycidyl acetate (GAc), butanol and 2-methoxyethyl ether (diglime) were purified in the standard manner. Chromium (III) ethanoate was of p.a. grade and used without further purification. Glycidyl acetate (GA) was prepared by a method described previously.¹⁵

Procedures. The kinetics of addition of carboxylic acids to oxiranes was studied in a glass reactor (50 cm³) equipped with a heating jacket, reflux condenser, thermometer, and magnetic stirrer. The contents of the reactor were brought to the desired temperature with an external heater. An equimolar ratio of carboxylic acid to epichlorohydrin was used. The temperature of the reaction (80 °C) was controlled using a thermal equilibrium water bath HAAKE C10 (±0.1 °C).

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.¹⁶ The final reaction mixtures were carefully analyzed by GLC (HP 5890 chromatograph with an FFAP capillary column, 10 m/0.53 mm/1 μ m).

The rate constants of addition of carboxylic acids to oxiranes were numerically calculated using the kinetics model proposed in our previous papers.^{17–21}

The relative reactivity of a carboxylic acid or oxirane within a given experimental series was calculated from the equation:

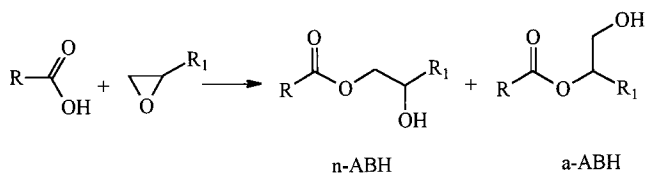
$$R = \frac{k_i}{k_{\text{AcOH or ECH}}} \quad (1)$$

where: k_i is the rate constant of addition of an acid to oxirane (or vice versa), $k_{\text{AcOH or ECH}}$ is the rate constant of addition of acetic acid (or epichlorohydrin, respectively) in a given experimental series.

Results and Discussion

In our earlier works on the kinetics of addition of certain carboxylic acids to oxiranes, such as epichlorohydrin^{17,18} phenylglycidyl ether,¹⁹ or low-molecular weight bisphenol A epoxy resins²⁰ carried out without solvent, chromium (III) ethanoate has been shown to be a very active and selective catalyst in these reactions. In the presence of this catalyst, the main product of addition of an acid to epichlorohydrin or phenylglycidyl ether was the respective hydroxyester with secondary hydroxyl group, that is, the product of the so-called normal addition (*n*-ABH in Scheme 1), and the rate of addition was well described by the first-order equation with respect to both catalyst and oxirane concentrations. The amount of the abnormal product decreased in the order:

Scheme 1^a



^a R = CH₃, CH₂=CH, or CH₂=C(CH₃), R₁ = CH₂Cl, PhOCH₂, CH₃COOCH₂, or CH₂=C(CH₃)COOCH₂.

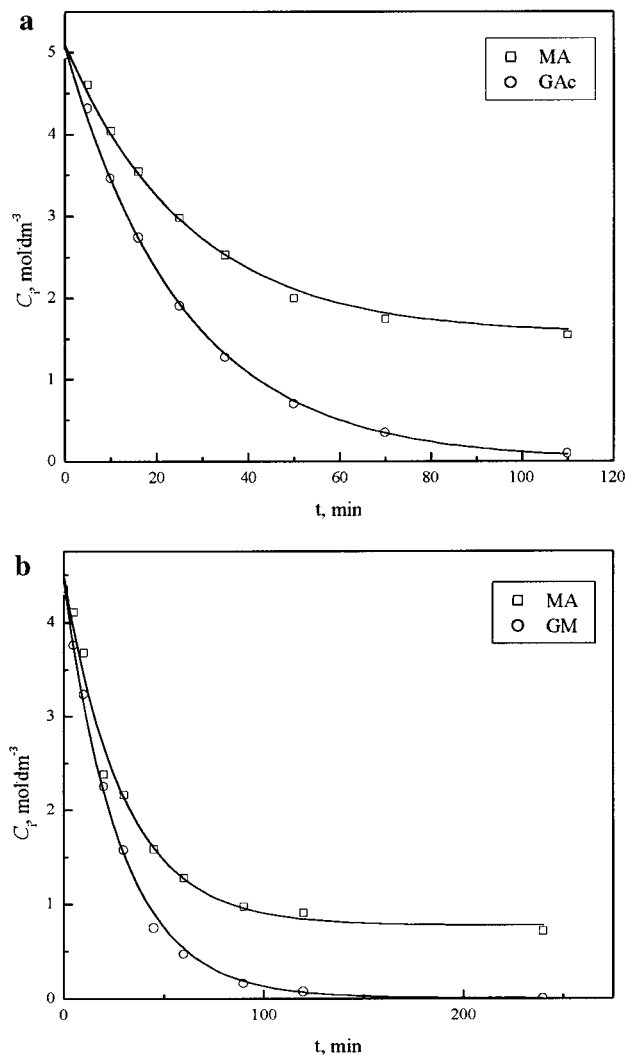


Figure 1. Changes in methacrylic acid (MA) and glycidyl acetate (GAc) concentration vs time during reaction carried out in the presence of (a) chromium (III) ethanoate catalyst; $C_{MA,0} = C_{GAc,0}$; $T = 80^\circ\text{C}$, $C_{cat} = 0.01\text{ mol dm}^{-3}$ and (b) chromium (III) ethanoate catalyst; $C_{MA,0} = C_{GM,0}$; $T = 80^\circ\text{C}$, $C_{cat} = 0.01\text{ mol dm}^{-3}$.

acetic acid > acrylic acid > methacrylic acid and was generally smaller for epichlorohydrin than for phenylglycidyl ether.

A high activity of chromium (III) ethanoate in epoxy ring-opening was also observed in reactions of certain glycidyl esters, namely, glycidyl acetate and methacrylate, with acetic, acrylic, and methacrylic acids. The typical rate curves measured for these systems at 80 °C are presented in Figure 1.

In the case of reactions of glycidyl acetate and methacrylate, the catalytic activity of chromium (III) ethanoate is not accompanied by the selectivity. Consequently, substantial

(20) Bukowska, A.; Bukowski, W.; Galina, H.; Sztycharz, A. *Polimery (Warsaw)* **2000**, 2, 109.

(21) Bukowski, W. *Int. J. Chem. Kinet.* **2000**, 32(6), 378.

(22) Weast, R. C. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, Florida, 1980.

(23) Bukowski, W. *Org. Process Res. Dev.* **2002**, 6, 10.

Table 1. Rate constants and carboxylic acid relative reactivity in addition of acetic, acrylic, or methacrylic acid to phenylglycidyl ether (GPE) or epichlorohydrin (ECH) in the presence of chromium (III) ethanoate, $T = 80\text{ }^{\circ}\text{C}$

acid	GPE		ECH	
	$10^2 k, ^{19}$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	R	$10^2 k,$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	R
acetic	2.54 ± 0.11	1.0	1.51 ± 0.16^a	1.0
acrylic	4.08 ± 0.06	1.61	4.02 ± 0.16^b	2.66
methacrylic	3.57 ± 0.07	1.41	4.55 ± 0.24^b	3.01

^a Reference 17. ^b Reference 18.

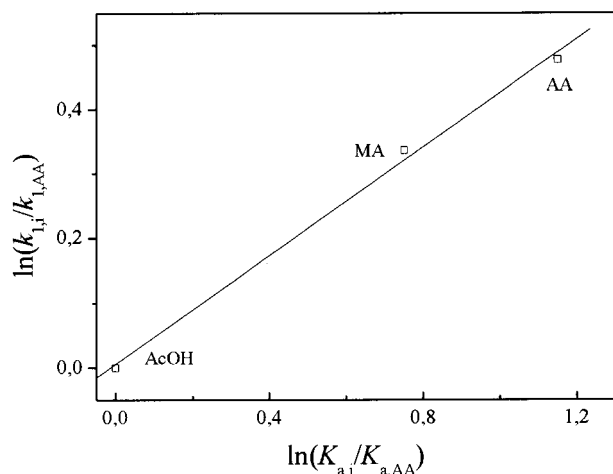


Figure 2. Brønsted-type plot for the reaction of carboxylic acids with epichlorohydrin in the presence of chromium (III) ethanoate.

discrepancies between the changes of acid and oxirane concentrations in reaction time have been observed that were due to subsequent polyaddition of the epoxy compound as found by GLC. Of all acids studied, the contribution from the subsequent reactions was the highest in the case of glycidyl acetate.

Analysis of the rate constants determined for the systems in question has shown that the reactivity of the acids changes from one epoxy compound to another, depending on the structure of the latter. For reactions with phenylglycidyl ether (Table 1) the reactivity of a carboxylic acid relative to that of acetic acid changes in the series $\text{AcOH} < \text{MA} < \text{AA}$, in accord with the strength of the acids in water (the respective ionization constants ($K_a \times 10^5$) are:²² 1.75, 3.72, and 5.53). Similarly as reported for other systems,^{10,13} the rate constants linearly depend on ionization constants in the double logarithmic plot (Figure 2).

A somewhat different reactivity series has been observed for the reactions of epichlorohydrin (Table 1). In the system without a solvent, the reactivity of acids changes in the order $\text{AcOH} < \text{AA} < \text{MA}$. The stronger acrylic acid reacts with epichlorohydrin more slowly than the weaker methacrylic acid, despite the fact that as compared to the reaction with phenylglycidyl ether the former reacts 1.7 times faster than acetic acid.

The relative reactivities of the three acids in reactions with glycidyl acetate and methacrylate are also different (Table 2). For glycidyl acetate the relative reactivity changes in the

Table 2. Rate constants and carboxylic acid relative reactivity in addition of acetic, acrylic, or methacrylic acid to glycidyl acetate (GAc) or glycidyl methacrylate (GM) in the presence of chromium (III) ethanoate, $T = 80\text{ }^{\circ}\text{C}$

acid	GAc		GM	
	$10^2 k,$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	R	$10^2 k,$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	R
acetic	3.12 ± 0.20	1.0	4.78 ± 0.24	1.0
acrylic	6.44 ± 0.26	2.06	8.68 ± 0.31	1.82
methacrylic	4.24 ± 0.10	1.36	4.38 ± 0.16	0.92

Table 3. Rate constants and carboxylic acid relative reactivity in addition of acetic, acrylic, or methacrylic acid to epichlorohydrin in the presence of chromium (III) ethanoate in diglyme or butanol solutions, $T = 80\text{ }^{\circ}\text{C}$, $C_{\text{acid},0} = C_{\text{ECH},0} = 1 \text{ mol} \cdot \text{dm}^{-3}$

acid	diglyme		butanol	
	$10^2 k, ^{23}$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	R	$10^2 k,$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	R
acetic	4.01 ± 0.16	1.0	1.72 ± 0.18^a	1.0
acrylic	4.67 ± 0.10	1.16	2.47 ± 0.08	1.44
methacrylic	2.31 ± 0.07	0.58	3.35 ± 0.12	1.95

^a Reference 21.

order $\text{AcOH} < \text{MA} < \text{AA}$, according to the strength of the acids in water. In this case, the linearity of the plot $\ln k_{a,i}/k_{a,\text{AcOH}}$ versus $\ln K_i/K_{\text{AcOH}}$ ($i = \text{AcOH}, \text{MA}$, or AA) is slightly worse than before, and the correlation coefficient is only 0.966.

A quite different relation has been observed for the system involving glycidyl methacrylate. The relative addition of acids to this compound follows the order $\text{MA} < \text{AcOH} < \text{AA}$. Here, however, a reduction in the reactivity of methacrylic acid is not to "blame". The two other acids, acetic and acrylic acids, react with glycidyl methacrylate at highly increased rate.

The relative reactivity of a carboxylic acid may change upon dilution of the system with an organic solvent. The results obtained for the system of carboxylic acid–epichlorohydrin–3-methoxyethyl ether (diglyme) ($C_{\text{CA}} = C_{\text{ECH}} = 1 \text{ mol} \cdot \text{dm}^{-3}$, Table 3) indicate that in the presence of this aprotic solvent the reactivity order of the acids is $\text{MA} < \text{AcOH} < \text{AA}$, similarly as in the system of carboxylic acid–glycidyl methacrylate (without a solvent) just discussed. Here, however, a substantial decrease of reactivity of methacrylic acid is observed (the rate constant for this acid is much smaller than the rate constants of the reactions of the addition of the same acid to other oxiranes). For acetic acid, on the other hand, an increase of reactivity is observed (cf. Tables 1–3). In diglyme, acetic acid reacts with epichlorohydrin 1.7 times faster than methacrylic acid and only slightly slower than acrylic acid.

In the system where acetic, acrylic, and methacrylic acids reacted with epichlorohydrin in protic solvent, butanol, in the presence of chromium (III) ethanoate, the relative reactivity of the acids does not change as compared with that in the analogous system without the solvent (Table 3). A negative effect of butanol on the reactivity of methacrylic

Table 4. Relative reactivity of epoxides *R* in their reaction with carboxylic acids catalyzed by chromium (III) ethanoate, *T* = 80 °C

epoxy compound	<i>R</i>		
	AcOH	AA	MA
ECH	1.0	1.0	1.0
GPE	1.68	1.01	0.78
GAc	2.07	1.60	0.93
GM	3.17	2.16	0.96

and acrylic is observed with the reactivity of the latter affected slightly more.

A comparison of the rate constants for the reaction of the addition of the individual acids to various epoxy compounds relative to those for addition to epichlorohydrin (Table 4) yields three different orders of relative reactivity. For acetic acid we have ECH < GPE < GAc < GM, for acrylic acid: ECH \approx GPE < GAc < GM, and methacrylic acid: GPE < GAc < GM < ECH. For acetic and acrylic acids the increase of reactivity towards epoxy compounds seems to be consistent with the increase of the acceptor character of the substituent in the epoxy ring. For acetic acid the respective relative rate constants assume the highest magnitudes. Acrylic and methacrylic acids react at the smallest rate with phenylglycidyl ether. In the case of

methacrylic acid, the relative rate constants are the most close to each other; hence, the values are all close to unity.

Perhaps the key factors responsible for the unusually high reactivity of methacrylic acid with epichlorohydrin are the lack of repulsive interactions between π -electrons that occur in reactions of methacrylic acid with other the epoxy compounds studied. Only epichlorohydrin does not contain π -electrons.

Conclusions

The results of the kinetic studies of the addition of carboxylic acids to oxiranes in the presence of chromium (III) ethanoate have shown that the rate of the reaction cannot be correlated with the strength of acids (ionization constant in water) alone. The relative reactivity of an acid is affected also by the nature of oxirane and the type of solvent used.

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