The Solvent Effects in the Reactions of Carboxylic Acids with Oxiranes.
1. Kinetics of the Reaction of Acetic Acid with Epichlorohydrin in Butan-1-ol

WIKTOR BUKOWSKI

Faculty of Chemistry, Rzeszów University of Technology, 35-959 Rzeszów, Poland

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ABSTRACT: Kinetics of the reaction of acetic acid with epichlorohydrin in the presence of chromium(III) acetate in butan-1-ol solution have been studied. The partial reaction orders with respect to reagents were found. The reactions were of first-order with respect to both epichlorohydrin and catalyst and zeroth order with respect to acetic acid. A kinetic model for the overall process has been proposed. The reaction constants have been calculated along with the activation parameters. The effect of dilution on the rate of addition is discussed. In the equimolar mixture of acetic acid and epichlorohydrin the apparent rate constant of the addition k_1 initially decreases to increase again at the concentration of butan-1-ol exceeding 3 M. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 378–387, 2000

INTRODUCTION

The course of reaction of carboxylic acids with oxiranes significantly depends on the properties of solvent used [1–9]. The solvent may affect both the rate and mechanism of reaction. The solvent effect is also different for different reagents and products and depends on its polarity and donor-acceptor properties. Lebiedev et al. [1] were the first to report on the relationship between solvent polarity and the rate of addition of carboxylic acids to oxiranes. While studying the reaction of chloroacetic acid with ethylene oxide in several organic solvents, they observed an increase of the rate constant with increasing solvent polarity for the reaction carried out both without catalyst or with a catalytic amount of potassium hydroxide added. The rate of the catalysed reaction increased somewhat more than that of the uncatalysed one. The same authors pointed at the negative effect of water on the rate of reaction between acetic acid and ethylene oxide in the presence sodium acetate.

Correspondence to: W. Bukowski (wbuk@prz.rzeszow.pl)

An attempt to express this effect quantitatively was presented by Tanaka and Takeuchi [2], who used dielectric constant as the measure of solvent polarity. In the double-logarithmic plot, they obtained linear relationships between the rate constant k and the solvent dielectric constant for the reaction of phenylglycidyl ether with benzoic acid in the presence of pyridine, all dissolved in an aromatic solvent (toluene, chlorobenzene, *o*-dichlorobenzene, nitrobenzene, *o*-nitrotoluene, xylenes, and mixtures of the above).

The effect of electron-donor properties of solvents in the reaction in question was studied by Klebanov [3]. He obtained a linear relationship between log k and donor and acceptor numbers of solvents in the reaction of benzoic acid with selected oxiranes in nitrobenzene, dimethylacetamide, and hexamethylphosphoamide. The correlations of this type as well as those obtained by Tanaka and Takeuchi [2] are valid only for a limited number of solvents. A more extensive study on this problem is under way [4].

Much more complicated relationships between the rate constants and solvent concentrations were described by Dumitriu and Oprea [5]. They have found that for the reaction between acrylic acid and epichlorohydrin in N,N-dimethylformamide (DMF), the rate constants k_1 and k_2 characteristic for the two autocatalytic reactions (catalyzed by the substrate and product, respectively) initially increased with DMF concentration and then rapidly decreased to rise again at the high solvent concentration.

Other reported observations [3,10] suggest a solvent may influence the mechanism of reactions between carboxylic acids and oxiranes. N,N-Dimethylacetamide, N,N,N′,N′,N″,N″-hexamethylphosphoamide, N,N-dimethylformamide, and dimethylsulphoxide may serve as examples. The s-shaped kinetic curves observed for these solvents are not just the result of the autocatalytic effect of addition products as claimed previously [5,11,12], but reflect more complicated reaction mechanisms. It has been shown [3,10] that the reason might be a catalytic effect of the side products formed in the reaction of epoxy groups with the solvent. The ion pairs of the onium type thus formed and containing acetic anions are effective addition catalysts.

The complexity of these reactions and the lack of general theories describing these processes leave open questions to explore. This article is the first of the series dealing with the effect of the environment on the kinetics and selectivity of the addition of carboxylic acids to oxiranes carried in the presence of chromium(III) compounds. The results obtained for the reaction of acetic acid with epichlorohydrin in the solution in a selected protic solvent—butan-1-ol.

EXPERIMENTAL

Materials

Acetic acid (CH_3COOH, AA) (glacial, 99.99%) and epichlorohydrin (C_3H_5ClO, ECH) were purchased from Aldrich and were purified by using standard methods [13]. Butan-1-ol ($C_4H_{10}O$, BuOH) (99.5%) was purchased from Chempur. Chromium(III) acetate ($(CH_3COO)_3Cr$, cat) (grade p.a.) was purchased from Sverdlovskij Khimicheskij Zavod. Solvent and catalyst were used without further purification. Acetone (CH_3COCH_3) (99% and 99.9% GC grade), chloroform (CH_3Cl) (98.5%), acetic anhydride ($C_4H_6O_3$) (99%), sodium hydroxide (NaOH) (0.1 M standard solution), and bromthymol blue ($C_{27}H_{28}Br_2O_5S$) (indicator) were purchased from POCH. Glycidyl acetate was prepared following the procedure of a previous paper [14]. Perchloric acid ($HClO_4$) (60 wt%), crystal violet (indicator), and 1,3-dichloro-2-hydroxypropane ($C_4H_6Cl_2O$) (98%) were purchased from Merck. Tetraethylammonium bromide ($(C_2H_5)_4NBr$) was a product from Fluka.

Instrumentation

A 5890 Hewlett Packard series II gas chromatograph with Flame Ionization Detector, FID, and a HP 3394 integrator were used to analyze reaction mixtures. The separation column used was a polar capillary column (FFAP, 10 m × 0.53 mm i.d., Hewlett Packard). The optimum column separation was obtained by using an initial temperature of 50°C and heating rate 30°C min^{-1} up to 130°C. In this temperature the column was kept for 6 min, and then the temperature was raised to 220°C. This final temperature level was maintained for 6 min in order to elute all components out of the column. Helium was used as the carried gas and the spitting ratio was set to 1:10. The operation temperature of the detector and injector were set to 220°C.

The temperature of the reaction was controlled using a thermal equilibrium water bath HAAKE C10 (± 0.1°C).

General Procedure for the Kinetics Measurements

The kinetics of addition was studied in the purpose designed glass reactors (50 cm^3) equipped with a temperature control system. The equimolar ratio of acetic acid to epichlorohydrin was used or the concentration of one of the reagents was changed while that of the other was kept constant. The total mass for each reaction mixture was 30 g. The concentration of chromium(III) acetate was in the range 2.5–17.5.10^{-3} M. The temperature was 60, 70, 80, or 90°C. Butan-1-ol concentration was adjusted to obtain round molar ratios of reagents (1 : 1, 2 : 2, etc). The experimental data concerning temperature and catalyst concentration are summarized in Table I. Other experimental data are moved to Tables IV and V.

The concentration of unreacted acid and epichlorohydrin were determined by dissolving 0.1–1g samples withdrawn from reaction mixtures in 10 cm^3 acetone. They were titrated with 0.1 M NaOH aqueous solution in the presence of bromthymol blue us indicator. The concentration of epichlorohydrin was determined by dissolving similar samples in 10 ml of chloroform. 10 cm^3 of 25 wt% tetraethylammonium bromide solution in glacial acetic acid was then added and the solution titrated with 0.1 M $HClO_4$ solution in glacial acetic acid in the presence of crystal violet as indicator [15].

GLC Analysis

The final reaction mixtures were analyzed by GLC. Byproducts were identified by comparing their retention times with those of known species: commercial glycidyl acetate, commercial 1,2-dichloro-2-hydroxypropane, isomeric products of addition of acetic acid to epichlorohydrin compounds prepared and isolated in separate experiments [16], glycerin diacetate (prepared in the reaction of acetic acid with glycidyl acetate in the presence of chromium(III) acetate), and butyl-3-chloro-2-hydroxypropyl ether (prepared in the reaction of excess BuOH with epichlorohydrin in the presence of chromium(III) acetate).

The external standard method was used to calculate concentrations of components. A 0.015 g sample of reaction mixture was dissolved in 5 ml of acetone. Then, 0.1 μl of the solution was injected into the gas chromatograph for analysis.

RESULTS AND DISCUSSION

In our previous papers, the reactions of some carboxylic acids with epichlorohydrin [16–18] or 1,2-epoxy-3-phenoxypropane ether [19] carried out in the presence of chromium(III) acetate homogeneous catalyst were described. The reactions were carried out without any solvent. The addition was found to be a relatively highly selective and regioselective reaction. Both selectivity and regioselectivity were much better than for the same reactions carried out in the presence basic catalysts, such as alkali metal acetates [20].

The rate of addition was well described by an equation of the first-order with respect to both chromium(III) acetate and epoxy compound and of the zeroth order with respect to acetic acid concentration. The zeroth reaction order with respect to acetic acid follows from the coordination mechanism of the addition carried out in the presence of chromium(III) acetate. The rate-limiting step is the reaction of the chromium(III)–acetic acid complex with epichlorohydrin. Sorokin et al. [21] observed the same reaction order with respect to acetic acid for the reaction of the acid

Table I The Experimental Conditions Used in the Kinetic Investigations of the System Acetic Acid-Epichlorohydrin-Chromium(III) Acetate-Butan-1-ol

Temperature, K	$[AA]_0$ (M)	$[ECH]_0$ (M)	$[BuOH]_0$ (M)	[cat] (M)
333.2	1.002	0.998	8.968	0.010
333.2	0.998	0.999	8.962	0.013
333.2	1.001	1.002	8.948	0.015
333.2	1.003	1.002	8.939	0.018
343.2	0.999	1.011	8.801	0.010
343.2	0.994	0.996	8.807	0.015
343.2	1.004	1.002	8.800	0.013
343.2	1.046	0.993	8.761	0.018
353.2	0.997	1.000	8.624	0.010
353.2	0.997	1.000	8.616	0.013
353.2	0.997	0.999	8.609	0.015
353.2	1.000	1.000	8.637	0.005
363.2	0.999	1.000	8.569	0.008
363.2	1.001	1.001	8.575	0.005
363.2	1.000	0.999	8.563	0.010
363.2	1.000	1.002	8.551	0.013

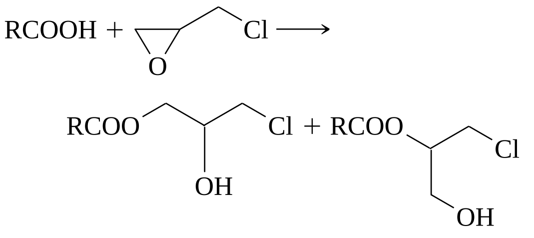
with oxiranes in the presence of ternary amines. However, they explained this observation in terms of formation of a cyclic intermediate state.

Usually one or two molecules of acetic acid take part in the addition to oxiranes. They act as a nucleophilic reagent and/or as a component activating oxirane molecule by forming hydrogen bond. Hence, the reaction order with respect to acid in the addition to oxiranes, carried out with acidic or basic catalysts, is 1 or 2 [22]. In some cases, variable orders were encountered in dependence of stoichiometry [23].

While trying to unravel the role of the homogeneous chromium catalyst, we extended our study to the systems containing solvents, both protic and aprotic. The system: acetic acid–epichlorohydrin–chromium(III) acetate–butan-1-ol was evaluated with respect to reagent concentrations, reaction order, the effect of temperature, and degree of dilution.

Interpretation of the Primary Kinetic Curves

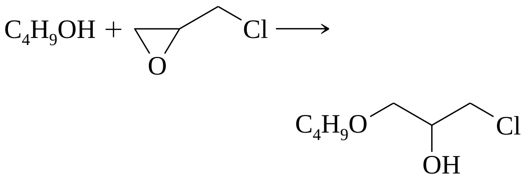
In the reaction system consisting of acetic acid (AA), epichlorohydrin (ECH), butan-1-ol, and chromium(III) acetate, the main reaction leads to two isomeric esters:



(1)

n-ABH a-ABH

One cannot exclude the reactions of epichlorohydrin with hydroxy groups of the solvent and with those of the products, mainly of *n*-ABH:



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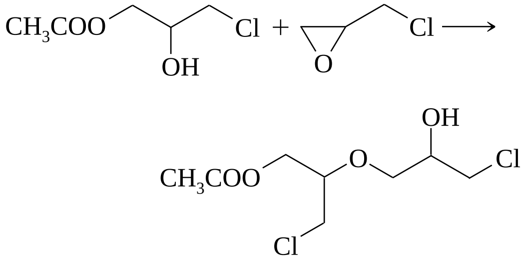
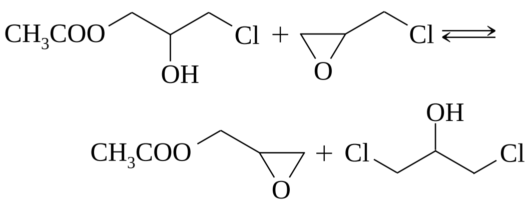


(3)

The subsequent-parallel reaction between *a*-ABH and ECH is less likely since the concentration of the abnormal product is substantially smaller than that of *n*-ABH. No traces, however, of AA-butan-1-ol ester have been detected in the reaction products.

Furthermore, the following side reactions are also possible:



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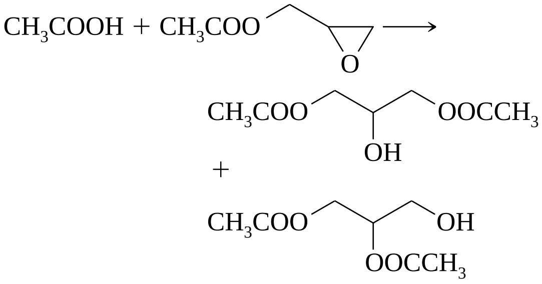

(5)

Some traces of 1,3-dichloro-2-hydroxypropane and glycerin diacetate were indeed detected among reaction products.

In a series of complementary experiments, the possibilities of other reactions in the system were excluded by GLC analysis of individual systems: (mixture of 3-chloro-2-hydroxypropyl acetate and 1-(chloromethyl)-2-hydroksyethyl acetate) + epichlorohydrin, glycidyl acetate + acetic acid, butan-1-ol + epichlorohydrin and butan-1-ol + acetic acid all in the presence of catalytic amount of chromium(III) acetate. The systems were kept in the typical reaction conditions.

By GLC analysis we have found that epichlorohydrin, beside the main reaction (1), was consumed by reactions (2–4). Acetic acid, on the other hand, took part in the side reaction (5) only to a negligible extent. Nevertheless, the excess in the rate of epichlorohydrin consumption over that of acetic acid could not be justified by the amount of side products identified. Some amount of epichlorohydrin was probably consumed in homopolymerization of the epoxy ring. An indirect evidence for this conclusion is that even in the system where ABH or butan-1-ol is present in a large excess, the chromatographically determined amount of products obtained in the presence of chromium(III) acetate

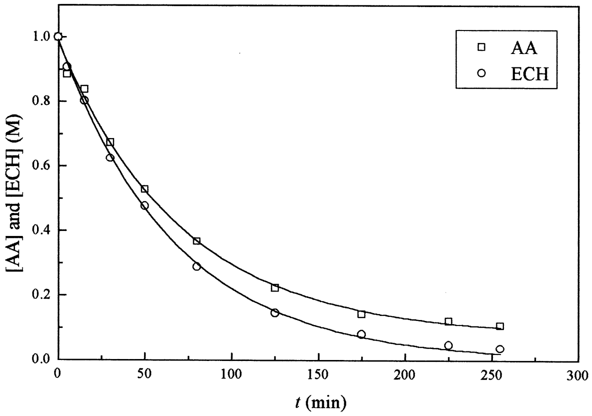

Figure 1 The change of acetic acid (AA) and epiclorohydrin (ECH) concentration during the reaction carried out in the presence of chromium(III) acetate in butan-1-ol, $[AA]_0 = [ECH]_0 \cong 1$ M; [cat] = 0.0125 M; temperature 353.2 K.

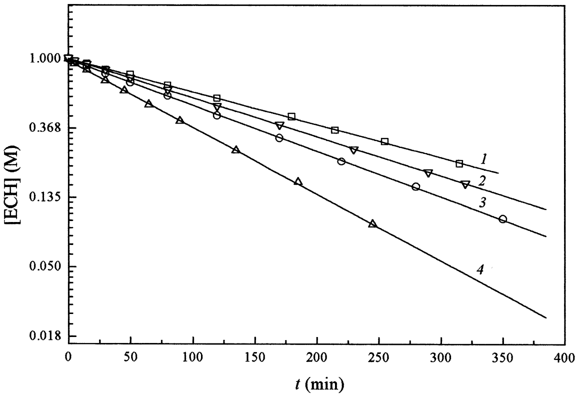

Figure 3 The effect of catalyst concentration on the change of epichlorohydrin concentration during its reaction with acetic acid carried out in the presence of chromium(III) acetate in butan-1-ol; $[AA]_0 \cong [ECH]_0 \cong 1$ M; temperature 343.2 K; [cat]: 1–0.01, 2–0.0125, 3–0.015, 4–0.0175 M.

was always smaller than that calculated from epichlorohydrin consumption.

The results confirm the high selectivity of chromium catalyst in addition of acetic acid to epichlorohydrin. It limits the extent of competing addition of alcohol hydroxyl groups to epoxy rings much more effectively than do acidic or basic catalysts, for which the reactivity of a hydroxyl group in alcohol is not much different than that in carboxylic group.

The difference becomes particularly small in the presence of acidic catalysts, as follows from the study by Soucek et al. [24–29] of the system cyclohexene oxide–acetic acid–methanol.

The typical curves illustrating the change of AA and ECH concentrations in the series of experiments at the equimolar substrate ratio with $[AA]_0 \cong [ECH]_0 \cong 1$ M are shown in Figure 1. The shapes of these curves indicate a somewhat faster consumption of ECH compared to that of AA. This is related to the subsequent reactions in which the former takes part.

In the logarithmic scale, the primary kinetic curves obtained for the series of experiments with $[AA]_0 \cong [ECH]_0 \cong 1$ M become straight lines (Figs. 2 and 3). This indicates that the reaction is of the first-order with respect to the substrates. The slopes of the lines linearly correlate with the catalyst concentration (Figs. 4 and 5), which means that the reaction is monomolecular with respect to chromium(III) ions both for the main reaction exemplified by the change of AA concentration and for the global conversion of epichlorohydrin. The lines start at the origin of the coordinate system; hence the effect of noncatalytic reactions is negligible at the range of temperature studied.

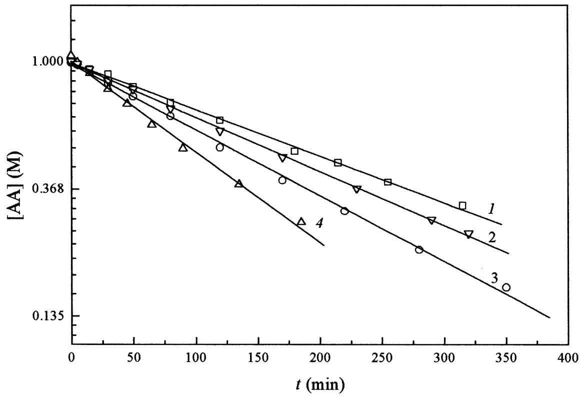

Figure 2 The effect of catalyst concentration on the change of acetic acid concentration during its reaction with epichlorohydrin carried out in the presence of chromium(III) acetate in butan-1-ol; $[AA]_0 \cong [ECH]_0 \approx 1$ M; temperature 343.2 K; [cat]: 1–0.01, 2–0.0125, 3–0.015, 4–0.0175 M.

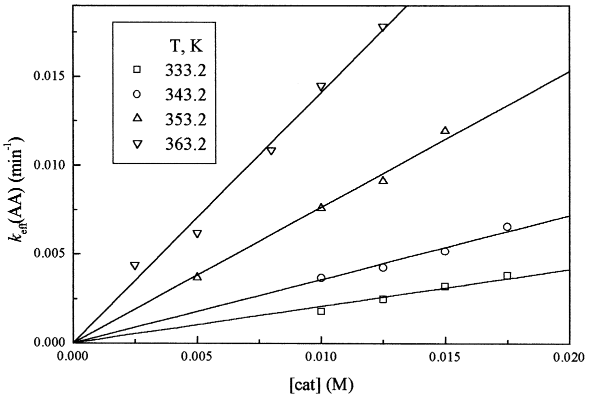

Figure 4 The effective rate constant determined from acetic acid concentration as a function of catalyst concentration.

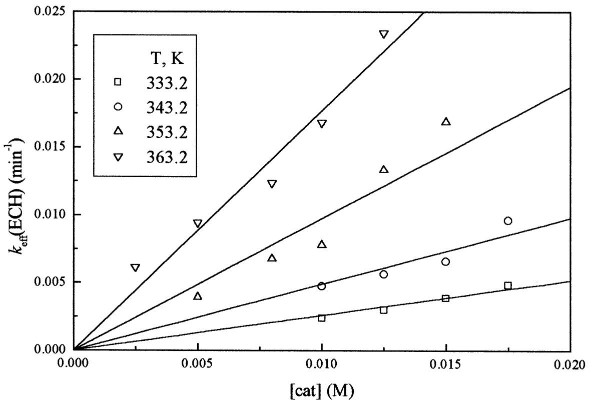

Figure 5 The effective rate constant determined from epichlorohydrin concentration variations as a function of catalyst concentration.

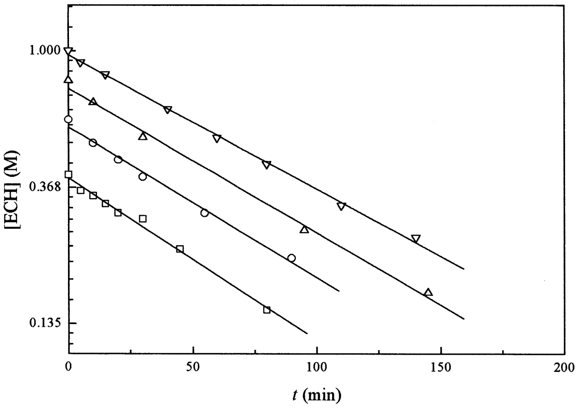

Figure 7 The variation of epichlorohydrin concentration during its reaction with acetic acid carried out in the presence of chromium(III) acetate in butan-1-ol; $[AA]_0 = 1.0$ M; temperature 353.2 K; [cat] = 0.01 M.

Additional information on the reaction order with respect to substrates provides the series of experiments with varying concentrations of one of the substrates (Figs. 6 and 7). Under conditions required by the isolation method of reaction order evaluation, a linear dependence of AA concentration on time was obtained at the large excess of epichlorohydrin (Fig. 6). This indicates the zeroth order or the reaction relative to acetic acid.

The linearization of the primary kinetic curves by plotting them in the semilogarithmic system (Fig. 7) proves the first-order of the reaction with respect to epichlorohydrin. The lines in Figure 7 are practically parallel, which additionally confirms the independence of reaction rate on AA concentration.

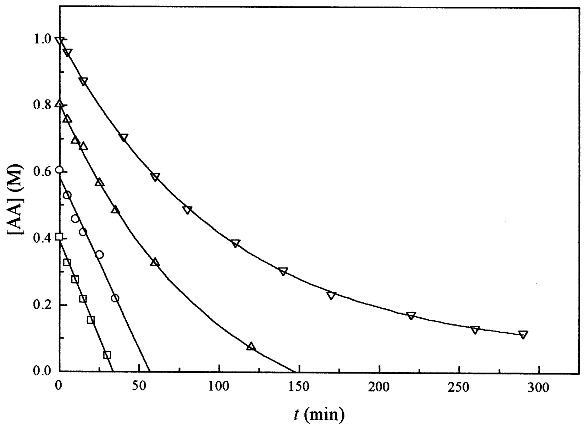

Figure 6 The variation of acetic acid concentration during its reaction with epichlorohydrin carried out in the presence of chromium(III) acetate in butan-1-ol; $[ECH]_0 = 1$ M; temperature 353.2 K; [cat] = 0.01 M.

Mechanism and Kinetics of Reaction

The graphical relationships obtained for the reaction of acetic acid with epichlorohydrin in the presence of chromium(III) acetate carried out in butan-1-ol are similar to those observed for the analogous reaction carried out without any solvents. Introduction of a protic solvent, butan-1-ol, to the system acetic acid–epichlorohydrin–chromium(III) acetate does not alter the reaction orders. In both cases, the rate of addition is determined by an interaction of the solvated form of catalyst with ECH. The following attack of carboxylate ion does not affect the overall rate. The reaction taking place in the coordination sphere of chromium(III) ions directs the addition towards the normal isomer. The amount of *a*-ABH formed in the series of experiments with $[AA]_0 \cong [ECH]_0 \cong 1$ M is 5.5–10.7 mol-% and increased with increasing temperature. According to the same mechanism—i.e., in the coordination sphere of chromium ions—but much slower, the subsequent reaction of epichlorohydrin with hydroxy groups of the solvent and with those of chlorohydroxypropyl esters takes place.

It was found that in the system acetic acid–epichlorohydrin–chromium(III) acetate the following rate equations hold [17]:

$$-\frac{d[AA]}{dt} = k_1[cat][ECH] \quad (6)$$

$$-\frac{d[ECH]}{dt} = k_1[cat][ECH] + k_2[cat][ECH] \quad (7)$$

where k_1 is the rate constant of addition of acetic acid to epichlorohydrin and k_2 is the overall rate constant of all side reactions involving epichlorohydrin. The

Table II The Rate Constants of the Reaction of Acetic Acid with Epichlorohydrin Carried Out in the Presence of Chromium(III) Acetate in Butan-1-ol at $[AA]_0 \cong [ECH]_0 \cong 1$ M

10^2[cat], (M)	T (K)	10^2k_1 ($\mathrm{dm^3mol^{-1}s^{-1}}$)	10^3k_2 ($\mathrm{dm^3mol^{-1}s^{-1}}$)	10^2k_1 without Solvent [15] ($\mathrm{dm^3mol^{-1}s^{-1}}$)
1.00–1.75	333.2	0.37 ± 0.04	0.43 ± 0.03	0.36
1.00–1.75	343.2	0.78 ± 0.11	0.98 ± 0.07	0.72
0.50–1.50	353.2	1.72 ± 0.18	1.55 ± 0.22	1.50
0.25–1.25	363.2	3.40 ± 0.04	3.85 ± 0.78	2.74

same rate equations seem to hold also in the presence of butan-1-ol. The rate constants calculated for the series with $[AA]_0 \cong [ECH]_0 \cong 1$ M are presented in Table II.

At low temperature (60°) the values of k_1 obtained in the presence of butan-1-ol are very similar to those in the system without a solvent (cf. Table II). The difference becomes more significant at elevated temperature. This different temperature characteristic for the two systems leads to different values of activation energy, enthalpy, and entropy of the reaction (Table III).

The addition of acetic acid to epichlorohydrin in the presence of chromium(III) acetate has a slightly higher activation energy (enthalpy) in butan-1-ol solution than in the system without solvent. Furthermore, the solvent affects the reaction kinetics by increasing the activation entropy of the addition. The reason seems to be interactions between the solvent with substrates.

One should notice that the small extent of the subsequent reactions makes the accuracy of k_2 determination pretty poor. The ratio of k_2 to k_1 at different temperatures remains roughly constant, suggesting that the share of side reactions is independent of temperature.

The Effect of Environment

As mentioned in the introduction, the kinetics of addition of carboxylic acids to oxiranes depends on the reaction environment. The differences presented above in activation parameters of the reactions carried out with or without solvent may serve as evidence. The values of rate constant k_1 depend on the molar ratio of reagents, as shown in Table IV. Analogous dependence was observed before for the reaction of acetic acid with epichlorohydrin without a solvent and catalyzed with chromium(III) [17] or sodium [20] acetate.

The series of experiments at different concentrations of butan-1-ol revealed that k_1 constant changed with the dilution of reaction system (Table V).

The dependence of the apparent rate constant k_1 on the concentration of butan-1-ol is shown in Figure 8. The plot splits into two straight lines of roughly opposite slopes. At low solvent concentration, below ca. 3 M, the rate constant decreases with dilution of the system. At the concentration ca. 3 M, the rate constant k_1 starts to rise with concentration. These difficult-to-interpret changes in the values of the apparent rate constant k_1 are definitely higher than the error of their determination.

Two straight lines can approximate the butan-1-ol concentration dependence of k_1:

line *a* ($[BuOH]_0 < 3$ M)

$$k = (1.50 \pm 0.10) \cdot 10^{-2} - (1.94 \pm 0.04) \cdot 10^{-3}[BuOH]_0 \qquad (8)$$

line *b* (($[BuOH]_0 > 3$ M

$$k_1 = (6.40 \pm 0.68) \cdot 10^{-3} + (9.81) \pm 1.04) \cdot 10^{-4}[BuOH]_0 \qquad (9)$$

Table III The Activation Parameters for the Reaction of Acetic Acid with Epichlorohydrin in the Presence of Chromium(III) Acetate

Activation Parameters	In Butan-1-ol at $[AA]_0 \cong [ECH]_0 \cong 1$ M	Without Solvent [17]
E_a, $\mathrm{kJ \cdot mol^{-1}}$	74.78 ± 1.58	68.64 ± 1.50
$\Delta H^{\neq}$, $\mathrm{kJ \cdot mol^{-1}}$	72.25 ± 0.96	65.81 ± 1.53
$\Delta S^{\neq}$, $\mathrm{J \cdot mol^{-1}K^{-1}}$	−75.68 ± 2.77	−93.33 ± 4.28

Table IV The Values of Rate Constants for the Reaction of Acetic Acid with Epichlorohydrin in the Presence of Chromium(III) Acetate in Butan-1-ol at 353.2 K for the Series of Experiments with Varying Substrate Concentration, [cat] = 0.01 M

$[AA]_0$ (M)	$[ECH]_0$ (M)	$[BuOH]_0$ (M)	$10^2 k_1$ ($dm^3 mol^{-1} s^{-1}$)
0.997	1.000	8.624	1.51 ± 0.03
0.404	1.004	8.998	2.42 ± 0.06
0.605	0.999	8.868	2.38 ± 0.09
0.801	0.999	8.731	2.03 ± 0.08
0.998	0.402	9.182	1.72 ± 0.08
1.003	0.602	8.985	1.78 ± 0.07
0.998	0.800	8.802	1.72 ± 0.06

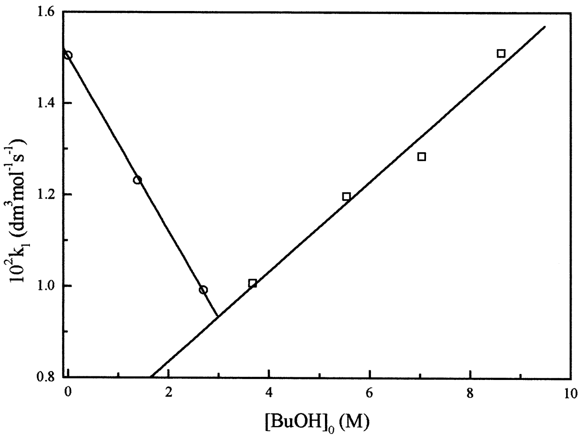

Figure 8 The dependence of rate constant on butan-1-ol concentration; $[AA]_0 = [ECH]_0$, [cat] = 0.01 M; temperature 353.2 K.

The complexity of interactions in the reaction system does not allow equations (8) and (9) to be related to any particular physicochemical parameter usually considered in kinetic studies, such as dielectric constant or the acceptor or donor number. It is possible that butan-1-ol directly affects the donor-acceptor interactions in the system. It is known that chromium(III) ions, the hard acids, form complexes with compounds containing oxygen. Both reagents and the solvent contain oxygen. The acid and alcohol, however, solvate Cr^{3+} ions better than epichlorohydrin. The coordination of the latter with chromium(III) ions is a slow process, and hence it is the rate-limiting step determining the reaction order. Most of the catalysts in the reacting system are either in the form solvated by acid or alcohol or in the form of mixed complexes. The ability of these two forms to activate the epoxy group is not necessarily the same, hence the different values of the effective rate constant k_1 and the dependence on acid and/or solvent concentration. A change of ECH concentration should affect the value of k_1 less significantly. The values of k_1 presented in Tables III and IV seem to confirm these remarks. At a practically constant butan-1-ol, constant ECH, and variable AA concentrations, one observes a marked increase of k_1 constant as AA concentration decreases from the stoichiometric value. The effect of ECH concentration is much less pronounced. A decrease in butan-1-ol and simultaneous increase of reagent concentrations result in an initial drop in the k_1 value, which reaches minimum at $[BuOH]_0 = 2.98$ M (cross section of lines *a* and *b*) and then starts to linearly increase.

The chromatographic analysis of the postreaction mixtures revealed the effect of butan-1-ol concentration on the yield of (1-chloromethyl)-2-hydroxyethyl acetate (*a*-ABH), the product of abnormal addition of AA to ECH (Table VI, Fig. 9). With a decrease of solvent content (increase of substrate concentration), the content of *a*-ABH drops down to reach a minimum at $[BuOH]_0$ ca. 3.6 M and then rises again. Unfortunately, this does not correlate with the system without a solvent. In the undiluted system, the amount of *a*-

Table V The Values of Rate Constants for the Reaction of Acetic Acid with Epichlorohydrin in the Presence of Chromium(III) Acetate in Butan-1-ol at 353.2 K for the Series of Experiments with Varying Butan-1-ol Concentration, [cat] = 0.01 M

$[AA]_0$ (M)	$[ECH]_0$ (M)	$[BuOH]_0$ (M)	$k_1 \cdot 10^2$ ($dm^3 mol^{-1} s^{-1}$)	$k_2 10^2$ ($dm^3 mol^{-1} s^{-1}$)
0.997	1.000	8.62	1.51 ± 0.03	0.11 ± 0.02
2.037	1.994	7.03	1.28 ± 0.04	0.21 ± 0.02
3.002	2.998	5.54	1.20 ± 0.02	0.13 ± 0.02
4.000	4.002	3.67	1.01 ± 0.01	0.13 ± 0.02
5.011	4.997	2.69	0.99 ± 0.03	0.10 ± 0.03
5.997	5.999	1.38	1.23 ± 0.03	0.01 ± 0.03
	Without solvent [17]		1.52 ± 0.02	0.07 ± 0.02

Table VI The Molar Fraction of 1-(Chloromethyl)-2-Hydroxyethyl Acetate at Different Reaction Temperature

$[AA]_0 : [ECH]_0$	Temperature, (K)	10^2[cat], (M)	*a*-ABH, (%-mol)
1 : 1	333.2	1.00–1.75	5.55 ± 0.32
1 : 1	343.2	1.00–1.75	8.87 ± 0.91
1 : 1	353.2	0.50–1.50	9.61 ± 0.80
1 : 1	363.2	0.25–1.25	10.73 ± 0.58
2 : 2	353.2	1.00	8.55
3 : 3	353.2	1.00	7.67
4 : 4	353.2	1.00	7.52
5 : 5	353.2	1.00	8.11
6 : 6	353.2	1.00	8.68
Without solvent [16]	353.2	0.81–1.50	8.2 ± 0.1

ABH is still smaller than that at butan-1-ol concentration of 1.48 M.

The molar fraction of the abnormal addition product depends on temperature as well. It increases when temperature rises (Table VI). The higher energy supplied with the substrates favors crossing the barrier of formation of the abnormal isomer. Its yield becomes higher at higher temperature.

CONCLUSIONS

The present study confirmed that the addition of acetic acid to epichlorohydrin carried out in the presence of chromium(III) acetate in butan-1-ol as a selected protic solvent is a bimolecular reaction. It is a first-order reaction with respect to both catalyst and oxirane and of zeroth order with respect to acid, similar to the analogous system without solvent. Furthermore, the rate constant, activation parameters, as well as the regioselectivity of the reaction depend on both the molar ratio of reagents and the degree of dilution of the system.

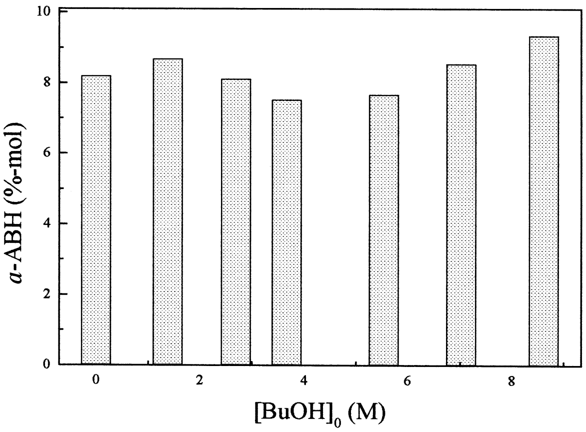

Figure 9 The content of *a*-ABH in the product versus butan-1-ol concentration; $[AA]_0 \cong [ECH]_0$, [cat] = 0.01 mol.dm^{-3}; temperature 353.2 K.

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