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Kinetic modelling of crosslinking reactions for cycloaliphatic epoxides with hydroxyl- and carboxyl-functionalized acrylic copolymers: 1. pH and temperature effects

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The crosslinking kinetics and reaction mechanism of cycloaliphatic epoxides with both hydroxyl and carboxyl functional groups were studied by using cyclohexene oxide, methanol and acetic acid as model compounds. The reactions of cyclohexene oxide with methanol and acetic acid were performed as a function of pH and temperature. The major products isolated from the reaction system were *trans*-2-acetoxyl cyclohexanol and *trans*-2-methoxyl cyclohexenol. However, none of the corresponding *cis* isomer was observed. The reaction order was determined to be first order in acetic acid and cyclohexene oxide for *trans*-2-acetoxyl cyclohexenol, and first order in methanol, cyclohexene oxide and proton concentration for *trans*-2-methoxyl cyclohexenol. The reaction rate constants, reaction orders, activation energies, activation enthalpies and entropies for the formation of the products in the reactions were determined for the competitive system. Based upon the stereochemistry of the products and the kinetic data, an A-2 type mechanism is proposed for both major products. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: cyclohexene oxide; acrylic polymers; mechanisms)

INTRODUCTION

Epoxy resins are one of the most important and widely used class of binders in the field of surface coatings[1–3]. Their remarkable applications can be attributed to the fact that epoxides can be crosslinked or cured with a variety of functionalized compounds or oligomers that contain hydroxyl, carboxyl, amino and/or amine groups[4]. This versatility has led to a wide range of coating properties with excellent adhesion, strength, toughness and chemical resistance[1–3]. The two primary classes of epoxide that are used for coatings are phenyl glycidyl epoxides and cycloaliphatic epoxides. The diglycidyl ether of bisphenol-A (BPA) has traditionally been the major type of epoxy resin used for industry applications[1–3]. The reaction kinetics and mechanism of epoxides determine the chemical structure, crosslink density, morphology and, ultimately, the performance of the cured products[5–7]. As a result, the reaction kinetics and mechanisms of BPA epoxides with various curing agents, with a special emphasis on amine systems, have been studied extensively[8–11].

Model compound studies are widely used as a means to investigate the curing reactions of phenyl glycidyl ether type epoxy resins with hydroxyl-, carboxyl- or amine-functionalized agents[4–16]. The reaction of the epoxides with hydroxyl and carboxyl groups can be either base- or acid-catalysed[1–3]. The reaction mechanisms are strongly affected by the epoxides and the catalysts[1–4]. Shechter and co-workers[12–14] have studied extensively the reaction kinetics and mechanisms of phenyl glycidyl ether and styrene oxide with a variety of alcohols and carboxylic acids under tertiary amine catalysts. The reaction mechanism was determined to be epoxide-specific. It was found that styrene oxide was more susceptible to attack by acidic reagents, while phenyl glycidyl ether was more susceptible to the attack by basic reagents. It was suggested that the important step in the latter reaction mechanism is the generation of an alkoxyl anion as the active catalytic species. The reaction of phenyl glycidyl ether with tertiary amine(s) results in a ring-opened zwitterionic species which deprotonates a hydroxyl-containing compound to produce the attacking alkoxyl anion species. The reaction rate is first order with respect to the concentration of epoxide and alkoxyl anion.

The relative reactivity of hydroxyl and carboxyl groups towards epoxides has been a great interest of research[1–14]. Shechter and co-workers[12–14] have also studied the reactivity of different alcohols and carboxylic acids towards different epoxide groups such as styrene oxide, phenyl glycidyl ether and benzyl oxide. It was reported that carboxylic acids show higher reactivity than alcohols towards styrene oxide with or without tertiary amines as the catalyst. However, it has also been shown that carboxylic acids exhibit lower reactivity than alcohols towards phenyl glycidyl ethers when tertiary amines are present as catalysts; without catalyst, the reaction is sluggish.

By comparison, the acid-catalysed reactions of epoxides have not been studied as extensively as the base-catalysed reactions[17–20]. A-1 and A-2 are the typical reaction mechanisms for epoxides under acidic conditions. In the A-1 mechanism, the formation of the carbonium ion intermediate is the rate-determining step. In the A-2 mechanism, the nucleophilic attack on the protonated epoxide is the rate-determining step, and the oxirane ring-breaking and new bond formation occur simultaneously[17,18].

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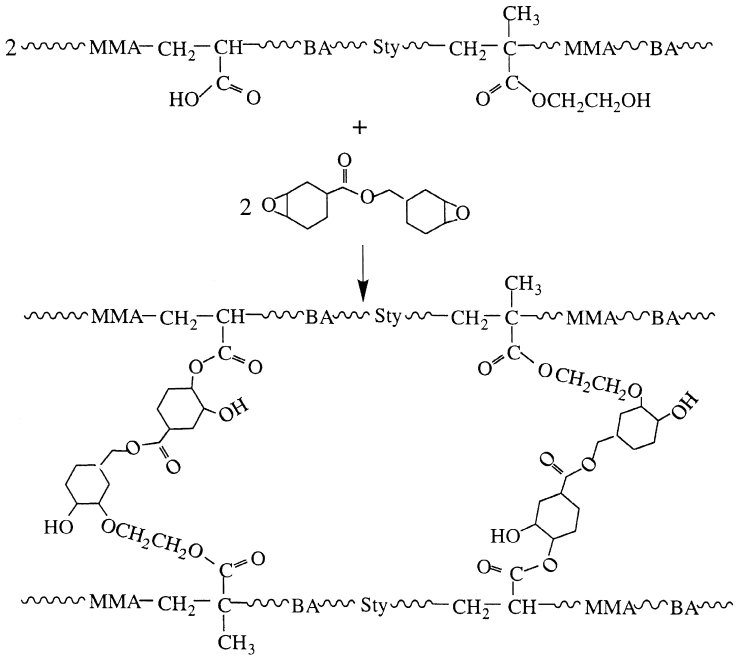


Scheme 1 Proposed crosslinking reaction of cycloaliphatic epoxides with hydroxyl- and carboxyl-functionalized acrylic copolymers

Pritchard and Long[19,20] have studied the mechanism of acid-catalysed hydrolysis of different alkyl-substituted ethylene oxides. Based on the correlation of kinetic data, it was postulated that the reaction pursued an A-1 mechanism. Biggs and co-workers[21–23] studied the mechanism of acid-catalysed alcoholysis of substituted (1,2-epoxyethyl) benzenes. From the correlation of activation entropy and Hammett ρ values, it was suggested that the reactions followed a borderline A-2 mechanism. Therefore, the reaction mechanism of the epoxides with hydroxyl and carboxyl groups were dependent on the epoxides used.

Although there has been an increasing application of cycloaliphatic epoxides in industry[24–27], few kinetic or mechanistic studies have been reported on the relative reactivity of cycloaliphatic epoxides towards different functional groups. Reactions of cyclohexene oxide with alcohols or carboxylic acids were studied separately by using homogeneous[28–33] or heterogeneous catalysts[34–37]. McKusick[28,29] and Cerveny and co-workers[31,32] showed that these reactions gave both *trans* and *cis* ring-opened products, and other byproducts, while using sulfuric acid, boron trifluoride or sodium alkoxide as homogeneous catalyst. Posner *et al*. and Iranpoor and Baltork studied the reactions of cyclohexene oxide with different alcohols and carboxylic acids using alumina[34,35] or Nafion-H[36,37] as heterogeneous catalyst or ceric (IV) ammonium nitrate[33] as a homogeneous catalyst. It was reported that these reactions only gave the *trans* products.

Cycloaliphatic epoxides are presently used in the formulation of cationic ultraviolet-cured coatings[24,25]. Difunctional cycloaliphatic epoxides such as 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate can be cured with polyols (especially ϵ-caprolactone-derived polyols) using a photolytically generated superacid[38]. It was suggested that the reactive species (protonated cations) decay with time and the chain termination occurs through a bimolecular process[39–41]. A substantial amount of post-curing was observed by a living cationic species[42].

In the coatings industry, waterborne coatings are considered one of the efficient vehicles to challenge the VOC (volatile organic compounds) regulations[24,25]. Presently, acrylic water-reducible coatings are typically crosslinked with melamine–formaldehyde (MF) resins which involve an Environmental Protection Agency (EPA) regulated toxic compound, formaldehyde[24,25]. The acrylic binders usually have both hydroxyl and carboxylic functional groups incorporated into the polymer backbone as 2-hydroxyethyl methylacrylate and acrylic acid for the crosslinking and dispersion stability, respectively. Unlike MF resins, which primarily react with hydroxyl groups, cycloaliphatic epoxides have the opportunity to react competitively with both the hydroxyl and carboxyl functional groups to form either ether or ester crosslinks as shown in *Scheme 1*.

To develop cycloaliphatic diepoxides as crosslinkers for waterborne acrylic coatings, the competitive kinetics of the crosslinking reactions needs to be elucidated. Previous work on cycloaliphatic epoxides has not addressed this issue adequately[24,25]. The competitive reactions will afford both ether and ester linkages as crosslinks with the acrylic coatings. Generally, ester linkages show greater photo-oxidative stability, whereas ether linkages exhibit greater resistance to hydrolysis[1–3]. A balance of these properties is essential for coating durability[1–3]. In this study, cyclohexene oxide, methanol and acetic acid were used as the model compounds for cycloaliphatic epoxides, hydroxyl- and carboxyl-functional acrylic polymers, respectively. Products of the reactions of the model compound were identified, and the competitive reactions were performed as a function of pH and temperature. The rate constants, energies of activation and insights into the reaction mechanisms are presented herein.

EXPERIMENTAL

Materials

Cyclohexene oxide ($C_6H_{10}O$, CE) (98%), methanol (CH_3OH, MeOH) (99.9%), acetic acid (CH_3COOH, HOAc) (99.8%), triethylamine [$N(C_2H_5)_3$, TEA] (99.9%) and dichloroethane (ClC_2H_4Cl, DCE) (99.9%) were all

purchased from Aldrich. All of these materials were distilled before use. The *p*-toluene sulfonic acid monohydrate ($CH_3C_6H_4SO_3H{\cdot}H_2O$, 98.5%) and phosphomolybdic acid/ethyl alcohol solution ($MoO_3H_3PO_4$, 20 wt%) were also purchased from Aldrich. The *p*-toluene sulfonic acid monohydrate was dehydrated by a standard method[43]. Ethyl acetate ($CH_3COOC_2H_5$, HPLC grade), hexane (C_6H_{14}, HPLC grade), diethyl ether ($C_2H_5COC_2H_5$, HPLC grade), sodium bicarbonate ($NaHCO_3$, GR), silica gel (Grade 922, 200 mesh) and thin-layer chromatography (t.l.c.) plates (glass-backed silica gel, 60 Å) were all purchased from Curtin Matheson Scientific and used as received.

Instrumentation

A Jeol GSXFT 270 MHz instrument was used to record ^{1}H and ^{13}C nuclear magnetic resonance (n.m.r.) spectra for all compounds. ^{1}H-n.m.r. spectra were obtained in $CDCl_3$ with chemical shifts (δ) referenced to internal tetramethylsilane. ^{13}C-n.m.r. spectra were obtained in $CDCl_3$ with chemical shifts (δ) referenced to $CDCl_3$. A 2020 Galaxy series Fourier transform infra-red (*FT* i.r.) spectrometer was used to record i.r. spectra for all compounds. I.r. spectra were obtained by directly coating the liquid sample onto KBr crystals. An HP 588A spectrometer was used to perform gas chromatography–mass spectrometry (g.c.–m.s.). The mass spectra for the compounds were obtained by 70 eV electron ionization (EI). C/H elemental analysis was performed by Galbraith Laboratories. A 5890 Hewlett Packard series II gas chromatograph with Flame Ionization Detector, FID, and an HP 3396 series II integrator were used to analyse and record quantitative analysis results for the reactions. The separation column used was an intermediate polar capillary column (DB17, 30 m × 0.53 mm i.d., J&W Scientific). The optimum column separation was obtained by using an initial temperature of 50°C for 5 min, and then a ramp rate of 20°C min^{-1} to reach the final temperature. The final temperature was set to 260°C and the final time was 6.5 min in order for all of the components to elute out of the column each time. In addition, helium was used as the carrier gas, and the splitting ratio was set to 1:10. The operation temperature of the detector was set to 250°C and the injection temperature was set to 200°C. The pH value of the reaction solutions was measured directly with a Corning pH Meter 320. The temperature of the reactions was controlled with an MD 20 LAUDA constant-temperature water bath (± 0.1°C).

*Preparation of trans-2-methoxyl cyclohexenol (***I***) and 2-methoxy-2′-hydroxy dicyclohexyl ether* (**II**)

Cyclohexene oxide (0.2 mol, 19.6 g) was added to methanol (0.2 mol, 6.4 g) in dichloroethane (10.0 g, 8.0 ml) and toluene sulfonic acid (1.0×10^{-3} mol, 0.17 g). The mixture was allowed to react for 24 h at 35°C. The mixture was then diluted with diethyl ether (10 ml), and transferred to a separating funnel (125 ml). The mixture was washed with sodium bicarbonate solution (0.1 M, 3 × 10 ml) until a pH of 6.5–7.5. The organic phase was then dried with anhydrous potassium carbonate (4.0 g). The diethyl ether and the residual cyclohexene oxide were removed from the organic phase to afford a crude mixture (21.0 g). A silica gel column (33 mm × 450 mm, 90 g) was used for product isolation. The product mixture (3 g) was diluted with hexane (1 ml). The diluted product mixture was loaded into the column. A mixture of hexane and ethyl acetate (87:13 v/v) was used to elute the two products from the column. The products were detected by use of phosphomolybdic acid as indicator. The first product to elute from the column was the secondary ether product, 2-methoxy-2′-hydroxy dicyclohexyl ether, as a mixture of the two isomers. After the solvents were removed, the product was further purified by micro-distillation (0.31 g, g.c. purity 99.7–99.9%, yield 10.3%). *FT* i.r. (thin film), ν (cm^{-1}): 3443 (OH), 2932, 2862, 1450, 1373 (C–H) and 1095 (C–O–C). ^{1}H-n.m.r. ($CDCl_3$), δ (ppm): 1.08–1.37 (ax, 8H), 1.69 (eq, 4H), 1.85–2.21 (eq, 4H), 3.05–3.25 (ax, 2H), 3.28–3.42 (ax, 2H), 3.41 (CH_3), 3.43 (CH_3), 3.58 (OH) and 5.07 (OH). ^{13}C-n.m.r. ($CDCl_3$), δ (ppm): 23.62, 23.81, 23.91, 24.05, 24.14, 24.31, 24.71, 24.91, 29.38, 30.52, 31.55, 32.19, 32.33, 32.98, 33.27, 72.33, 75.47, 76.60, 77.10, 77.43, 77.6, 81.77, 82.10, 83.97, 84.43 and 96.93. M.s. (EI), *m/z*: 211 ($C_{13}H_{23}O_2^+$), 168 ($C_{12}H_{20}O^+$), 131 ($C_7H_{14}O_2^+$), 113 ($C_7H_{13}O^+$) and 81 ($C_6H_{10}^+$). Elemental analysis for 2-methoxy-2′-hydroxy dicyclohexyl ether: calc. 68.42% (C) and 10.53% (H); found 68.24% (C) and 10.70% (H).

The next product to elute from the column was the primary product, *trans*-2-methoxyl cyclohexenol. After the solvents were removed, the obtained product was further purified by micro-distillation (0.28 g, g.c. purity 99.7–99.9%, yield 9.33%). *FT* i.r. (thin film), ν (cm^{-1}): 3426 (OH), 2934, 2863, 1453, 1192 (C–H) and 1098 (C–O–C). ^{1}H-n.m.r. ($CDCl_3$), δ (ppm): 1.05–1.36 (ax, 4H), 1.65–1.79 (eq, 2H), 1.95–2.05 (eq, 1H), 2.06–2.16 (eq, 1H), 2.93 (ax, 1H), 3.42 (ax, 1H), 3.50 (OH) and 3.42 (OCH_3). ^{13}C-n.m.r. ($CDCl_3$), δ (ppm): 24.06, 24.22, 28.45, 32.18, 56.38, 73.61 and 85.08. M.s. (EI), *m/z*: 130 ($C_7H_{14}O_2^+$), 112 ($C_7H_{13}O^+$), 98 ($C_6H_{10}O^+$) and 71 ($C_4H_7O^+$); Elemental analysis for *trans*-2-methoxyl cyclohexenol: calc. 64.62% (C) and 10.77% (H); found 64.53% (C) and 10.66% (H).

*Preparation of trans-2-acetoxyl cyclohexenol (***III***) and 2-acetoxy-2′-hydroxy dicyclohexyl ether* (**IV**)

Cyclohexene oxide (0.2 mol, 19.6 g) was added to acetic acid (0.2 mol, 12.0 g) in dichloroethane (10.0 g, 8.0 ml). The mixture was allowed to react for 24 h at 35°C, after which the mixture was diluted with diethyl ether (10 ml) and then transferred to a separating funnel (125 ml). The mixture was washed with sodium bicarbonate water solution (0.1 M, 3 × 10 ml) until the pH was 6.5–7.5. The organic phase was dried with anhydrous potassium carbonate (4.0 g). Diethyl ether and residual cyclohexene oxide were removed *in vacuo* to yield a crude product (24.6 g). The product mixture (3 g) was diluted with hexane (1 ml). The diluted product was then loaded onto the same silica column and eluted using the same solvents as previously stated. The products were detected by silica gel t.l.c. with visualization by phosphomolybdic acid/ethyl alcohol solution at 150°C. The first product eluded from the column was one of the two secondary product isomers, 2-acetoxy-2′-hydroxy dicyclohexyl ether. The solvents were removed and the crude product was purified via micro-distillation (0.28 g, g.c. purity 99.5–99.8%, yield 9.1%). *FT* i.r. (thin film), ν (cm^{-1}): 3476 (OH), 2936, 2863, 1451, 1372 (C–H) and 1736 (C=O). ^{1}H-n.m.r. ($CDCl_3$), δ (ppm): 1.20–1.32 (ax, 8H), 1.68 (eq, 4H), 1.96–2.15 (eq, 4H), 3.08–3.16 (ax, 1H), 3.30–3.45 (ax, 1H), 2.08 (CH_3) and 3.18 (OH). ^{13}C-n.m.r. ($CDCl_3$), δ (ppm): 21.39, 23.72, 23.98, 24.57, 30.59, 31.70, 31.86, 32.89, 74.54, 76.65, 80.38, 85.18 and 170.85. M.s. (EI) *m/z*: 196 ($C_{12}H_{21}O_2^+$), 159 ($C_8H_{14}O^+$), 141 ($C_8H_{12}O_2^+$), 98 ($C_6H_{10}O^+$) and 81 ($C_6H_{10}^+$). Elemental analysis for the product: calc. 65.63% (C) and 9.38% (H); found 65.87% (C) and 9.55% (H).

The second product eluted from the column was the other

Table 1 Summary of the competitive reaction compositions as a function of the reactant concentrations and temperatures

Reaction order determination for	Cyclohexene oxide (M)	Methanol (M)	Acetic acid (M)	pH	Temperature (°C)
Cyclohexene oxide	0.5	2.0	2.0	3.5	35
	0.25	2.0	2.0	3.5	35
	0.125	2.0	2.0	3.5	35
Methanol	2.0	0.5	2.0	3.5	35
	2.0	0.25	2.0	3.5	35
	2.0	0.125	2.0	3.5	35
Acetic acid	2.0	2.0	0.5	3.5	35
	2.0	2.0	0.25	3.5	35
	2.0	2.0	0.125	3.5	35
$[H^+]$	2.0	1.0	1.0	4.55-8.88	25, 35, 45

secondary product isomer, 2-acetoxy-2′-hydroxy dicyclohexyl ether. The solvents were removed and the crude product was purified via micro-distillation (0.25 g, g.c. purity 99.5–99.8%, yield 8.2%). *FT*i.r. (thin film), ν (cm^{-1}): 3507 (OH), 2936, 2863, 1451, 1373 (C–H) and 1738 (C=O). ^{1}H-n.m.r. ($CDCl_3$), δ (ppm): 1.10–1.38 (ax, 8H), 1.72 (eq, 4H), 1.95–2.12 (eq, 4H), 3.03–3.13 (ax, 1H), 3.30–3.40 (ax, 2H), 4.65–4.74 (ax, 1H), 2.06 (CH_3) and 2.68 (OH). ^{13}C-n.m.r. ($CDCl_3$), δ (ppm): 21.39, 23.56, 24.04, 24.38, 30.06, 30.25, 30.70, 31.91, 73.35, 74.96, 76.68, 82.36 and 170.59. M.s. (EI) *m/z*: 196 ($C_{12}H_{21}O_2^+$), 159 ($C_8H_{14}O^+$), 141 ($C_8H_{12}O_2^+$), 98 ($C_6H_{10}O^+$) and 81 ($C_6H_{10}^+$). Elemental analysis for the product: calc. 65.63% (C) and 9.38% (H); found 65.55% (C) and 9.62% (H).

The last product to elute from the column was the primary product, *trans*-2-acetoxyl cyclohexenol. The solvents were removed and the product was further purified by micro-distillation (0.38 g, g.c. purity 99.5–99.8%, yield 12.6%). *FT*i.r. (thin film), ν (cm^{-1}): 3447 (OH), 2964, 2941, 1452, 1371 (C–H), 1734 (C=O), 1248, 1078 and 1041 (O–C). ^{1}H-n.m.r. ($CDCl_3$), δ (ppm): 1.22–1.35 (ax, 4H), 1.68–1.78 (eq, 2H), 1.90–2.15 (eq, 2H), 3.56 (ax, 1H), 4.58 (ax, 1H), 2.43 (OH) and 2.12 (CH_3). ^{13}C-n.m.r. ($CDCl_3$), δ (ppm): 21.3, 23.7, 23.8, 30.00, 33.00, 72.3 and 171.4. M.s. (EI) *m/z*: 158 ($C_8H_{14}O_3^+$), 140 ($C_8H_{12}O_2^+$), 115 ($C_6H_{11}O_2^+$), 98 ($C_6H_{10}O^+$) and 70 ($C_4H_7O^+$). Elemental analysis for *trans*-2-acetoxyl cyclohexenol: calc. 60.76% (C) and 8.86% (H); found 60.57% (C) and 8.92% (H).

General procedure for kinetic studies

The competitive reactions as a function of pH were performed at a constant mole ratio of cyclohexene oxide, methanol and acetic acid (2 M, 1.960 g/1 M, 0.320 g/1 M, 0.600 g). The pH of the reaction media was varied from 4.55 to 8.88 solely by the addition of triethylamine. The solvent used in all reactions was dichloroethane. The reactions were carried out at three temperatures (25°C, 35°C and 45°C) to allow construction of an Arrhenius plot. The experimental conditions used to determine the reaction order of each of the reactants are outlined in *Table 1*. The pH was held constant as the molar ratios of the reactants were varied systematically to determine the reaction order of each component.

The appropriate amounts of methanol, acetic acid and triethylamine were added to dichloroethane. The total volume for all of the reactions was 10 ml. The general apparatus for reactions was a 50 ml flask equipped with a magnetic stirrer and septum. After the reaction mixtures had been allowed to come to equilibrium in the constant-temperature water bath (~5 min), the required amount of cyclohexene oxide (at the same temperature as the water bath) was then transferred into the reaction flask with a syringe. In order to reduce any mass loss during reactions or sampling, all of the reactions were performed in closed systems under nitrogen.

Sampling and g.c. analysis

An internal standard method was used to calculate the concentrations of the reactants and products. Cyclohexanol was chosen as an internal standard and the detector response factors were calculated for each of the reactants and products. An aliquot (100 μl) of the reaction mixture was extracted directly with a syringe through the stopper on the reaction flask at the desired time interval. The sample was immediately diluted with 100 μl of 1,2-dichloroethane which contained the internal standard (0.2667 M, 0.0267 mmol). Then, 1 μl of the mixture was immediately injected into the gas chromatograph for quantitative analysis.

Kinetic equations

Typically, the rate of a reaction can be described equivalently by the rate of the disappearance of a reactant or by the rate of the formation of a product[44]. Due to several competitive reactions which occur concomitantly, the reaction rate was derived from the formation of the products. In a reaction of A and B with catalyst C to give product P, the rate equation for the formation of P can generally be expressed as:

$$d[P]/dt = k[A]^n \times [B]^m \times [C]^l \quad (1)$$

$$k = A \exp\left(-E_a/RT\right) \quad (2)$$

$$k = \left(k_B T/h\right) \exp(-\Delta H^{\neq}/RT) \exp(\Delta S^{\neq}/R) \quad (3)$$

where d[P]/d*t* is the reaction rate for the formation of product; [A], [B] and [C] are the concentration of reactants A, B and catalyst C, respectively; *k*, *A*, E_a, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the rate constant, frequency factor, activation energy, activation enthalpy and activation entropy for the formation of product P, respectively; *R*, k_B, *h* are the gas constant, Boltzmann constant and Planck's constant, respectively. The exponents *n*, *m* and *l* in the equation are the reaction orders of compounds A, B and C, respectively. To determine the reaction order *n*, the logarithmic form of equation (1) is used:

$$\log(d[P]/dt) = n \log([A]) + \log\left(k \times [B]^m \times [C]^l\right) \quad (4)$$

As indicated by equation (4), the reaction order *n* with respect to [A] can be obtained from the slope by plotting log(d[P]/d*t*) as a function of log([A]). This requires varying the concentration of reactant A, while keeping the concentrations of B and C in large excess. The other exponents (*m* and *l*) can be obtained in a similar fashion. When the

exponents are known, the observed rate constant can be determined from the initial concentrations of the reactants. In this study, the initial reaction rate was used as d[P]/dt to acquire the data, and it was obtained by using an n quadratic equation to fit the concentration *versus* corresponding reaction time, then taking the derivative of the fitted equation at the reaction time equal to zero. Furthermore, the activation energy, activation enthalpy and activation entropy were given from equations (5) and (6) (rearranged from equations (2) and (3)) by plotting $\ln k$ or $\ln(k/T)$ *versus* $(-1/T)$, respectively.

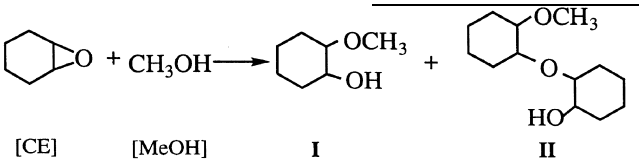
$$\ln k = \ln A - E_a/RT \tag{5}$$

$$\ln(k/T) = \ln(k_B/h) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT \tag{6}$$

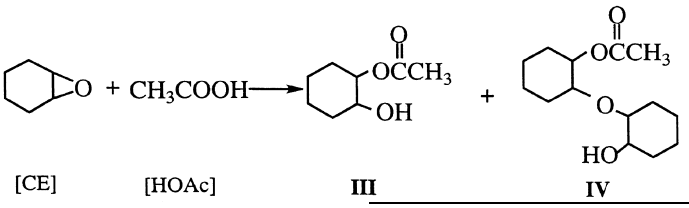
RESULTS AND DISCUSSION

Identification of model compound products

Before the competitive reaction kinetics were investigated, the reaction products had to be isolated and identified. The reaction products from the two component systems of cyclohexene oxide with methanol or acetic acid were isolated and identified individually as depicted in reactions (7) and (8):



(7)



(8)

The products from reactions (7) and (8) were isolated and characterized spectroscopically by means of ^{1}H- and ^{13}C-n.m.r., i.r., m.s. and elemental analysis. Compounds **I** and **III** had been previously reported in the literature[31–35], although by different routes than described in reactions (7) and (8). Compounds **II** and **IV** had not been reported previously. Therefore, in addition to spectroscopic characterization described above, C,H analysis was also performed for **II** and **IV**. The reaction mechanisms for the formation of **II** and **IV** have been reported before[24,25].

For **I**, the ^{1}H-n.m.r. spectrum indicated the presence of CH_3O ($\delta = 3.42$ ppm) and OH ($\delta = 3.50$ ppm) groups in addition to the methylene cycloaliphatic groups, and the proton integration was consistent with the structure of **I** as previously reported[34–46]. The i.r. spectrum also verified the presence of hydroxyl (–OH, 3426 cm^{-1}) and ether groups (C–O–C, 1098 cm^{-1}). The ^{13}C-n.m.r. spectrum showed carbon resonances indicative a methyl ether carbon, cycloaliphatic carbons and a hydroxyl-substituted carbon. The n.m.r. data indicate that **I** has a *trans* stereochemistry. The parent ion and fragment ions obtained from the m.s. data and the C,H analysis were also consistent with the structure of **I**.

The secondary ether product **II** was also isolated from the reaction mixture [see reaction (7)] and was found to be a mixture of isomers. The ^{1}H-n.m.r. spectrum indicated the presence of CH_3O, OH and two sets of $-CH_2O-$ methylene ether protons. The proton integration was consistent with the proposed structure of **II**. The ^{13}C-n.m.r. spectrum showed three C–O carbon resonances corresponding to the methyl ether and two cycloaliphatic methylene units connected to the ring-bridging ether. The ^{13}C spectrum also clearly resolved all of the other carbon resonances expected, including the alcohol carbon resonance. The i.r. spectrum confirmed the presence of both hydroxyl (OH, 3443 cm^{-1}) and ether groups (C–O–C, 1095 cm^{-1}). Unfortunately, the parent ion from the mass spectrum could not be obtained. However, the ion fragments and fragment pattern, and C,H analysis results, were consistent with the proposed structure.

The ^{1}H-n.m.r. spectrum of the primary ester product **III** showed cycloaliphatic methylene proton resonances, acetyl methyl protons CH_3CO ($\delta = 2.12$ ppm) and a hydroxyl proton at $\delta = 2.43$ ppm. The proton integration vale was consistent with the proposed structure. The ^{1}H-n.m.r. spectrum revealed that **III** was also the *trans* isomer; there was no *cis* isomer detected in the product. The ^{13}C-n.m.r. spectrum exhibited six cycloaliphatic carbon peaks as well as an ester carbon resonance ($CH_3\underline{C}O_2-$) and an acetyl methyl carbon resonance ($\underline{C}H_3CO_2-$). The i.r. spectrum confirmed the presence of a carbonyl group (C=O, 1734 cm^{-1}), an ester group (C–O–C, 1248, 1078 and 1041 cm^{-1}) and a hydroxyl group (OH, 3447 cm^{-1}). The parent ion ($m/z = 157$) and overall ion fragmentation pattern, as well as the C,H analysis, were all consistent with the structure of **III**.

Similar to the secondary ether product, the secondary ester product **IV** was found to consist of two isomers. The overall structure was deduced from i.r., m.s., ^{1}H- and ^{13}C-n.m.r. data, and C,H analysis. The ^{1}H-n.m.r. spectrum showed acetyl protons CH_3CO, hydroxyl protons, and cycloaliphatic protons. The ^{13}C-n.m.r. spectrum provided evidence for cycloaliphatic carbons, an ester carbon ($CH_3\underline{C}O_2-$), an acetyl methyl carbon ($\underline{C}H_3CO_2-$), a hydroxyl carbon and two ring-bridging ether carbons ($\underline{C}$–O–$\underline{C}$). The i.r. data confirmed the presence of an ester carbonyl, a hydroxyl group and ether groups. As in the case of the secondary ether product, a parent m.s. ion could not be obtained for **IV**. However, the ion fragments, ion pattern and C,H analysis were all consistent with the proposed structure of **IV**.

Competitive reactions

In the competitive reaction study, the primary products and secondary products were isolated from the reaction

Table 2 Summary of the kinetic data for the formation of products **I** and **III**

Product	*Trans*-2-methoxyl cyclohexenol	*Trans*-2-acetoxyl cyclohexenol
Rate equation	$dC_I/dt = k_{obs,I}[CE][MeOH][HOAc]/\sqrt{[B]}$	$dC_{III}/dt = k_{obs,III}[CE][HOAc]$
pH range	4.6–8.9	4.6–8.9
Observed rate constant (k_{obs})		
45°C	$1.5 \pm 0.7 \times 10^{-5}$ ($l^2\ mol^{-2}\ min^{-1}$)	$1.8 \pm 0.8 \times 10^{-4}$ ($l\ mol^{-1}\ min^{-1}$)
35°C	$6.9 \pm 0.6 \times 10^{-5}$ ($l^2\ mol^{-2}\ min^{-1}$)	$10.0 \pm 0.6 \times 10^{-5}$ ($l\ mol^{-1}\ min^{-1}$)
25°C	$2.5 \pm 0.8 \times 10^{-5}$ ($l^2\ mol^{-2}\ min^{-1}$)	$4.0 \pm 0.6 \times 10^{-5}$ ($l\ mol^{-1}\ min^{-1}$)
E_a (kJ mol^{-1})	71.0 ± 8.3	59.4 ± 6.2
$\Delta H^{\neq}$ (kJ mol^{-1})	68.5 ± 6.4	56.9 ± 5.7
$\Delta S^{\neq}$ (kJ mol^{-1} K^{-1})	$-12.2 \pm 1.3 \times 10^{-2}$	$-13.8 \pm 1.1 \times 10^{-2}$

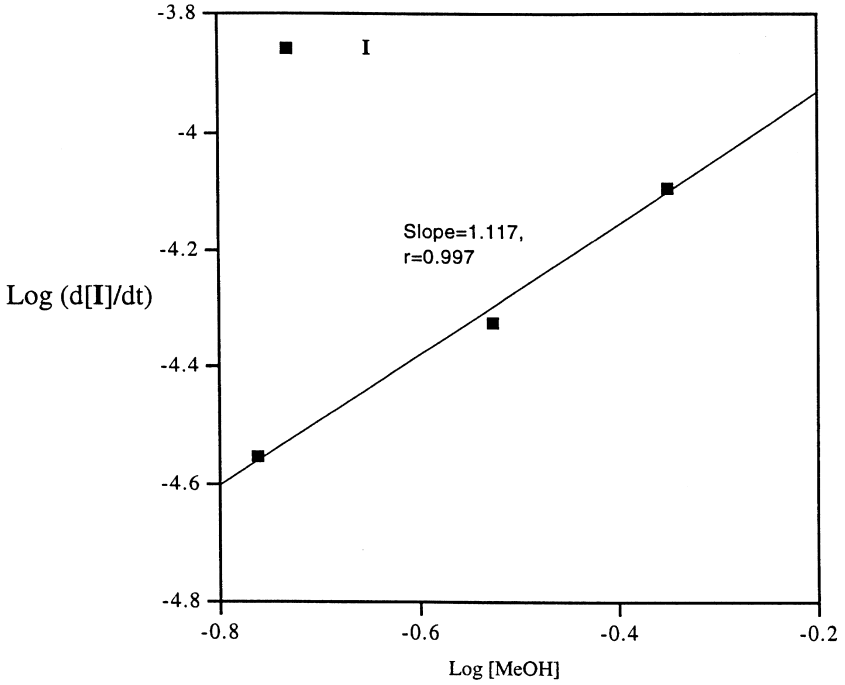
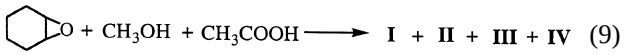
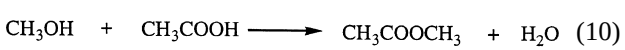


Figure 1 Initial formation rate of product **I** as a function of concentration of methanol at pH 3.5 and 35°C

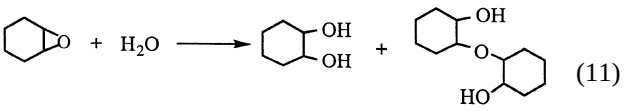
mixtures as depicted in reaction (9). The consumption of the reactants was monitored simultaneously with the formation of the products via g.c.



(9)



(10)



(11)

Reactions (10) and (11) were significant only when the acidity of the reaction system was high (pH < 2). As monitored by g.c., the maximum concentrations of methyl acetate and hydrolysis products from the cycloaliphatic epoxide were about 10^{-3} mol l^{-1} in the pH range of this study. The acetic acid/triethylamine buffer system does not catalyse either hydrolysis of the epoxide or esterification of the acetic acid at 25, 35 or 45°C. Therefore, the reactions shown in reactions (10) and (11), as compared with the formation of the products **I**, **II**, **III** and **IV**, are negligible.

Determination of reaction orders

The reaction order for each of the reactants was determined using the molar concentrations outlined in *Table 1*. *Figures 1 and 2* depict the reaction orders of the nucleophiles (methanol and acetic acid) for the formation of the ether and ester products **I** and **III**. The slope of 1.12 suggests that the reaction order for methanol is one, and the correlation factor of 0.997 indicates that a good fit was obtained of the data. The formation of the primary ester product **III** has a first-order dependence with respect to acetic acid (1.09) with a correlation factor of 0.991. *Figure 3* shows the reaction orders of cyclohexene oxide for both the ether and the ester products, **I** and **III**, respectively. The results indicate that the rate expression for the formation of both the ether and the ester product were first order with respect to cyclohexene oxide. Similarly, the reaction orders with respect to proton concentrations ($[H^+]$) for **I** and **III** were also obtained. First order and zero order of the formation rate of **I** and **III**, respectively, were shown to be dependent on the proton concentration. From the reaction order of each of the reactants, the observed rate expressions for the formation of primary ether and ester products **I** and **III** can be represented in equations (12) and (13), respectively:

$$d[\mathbf{I}]/dt = k_{obs,I}[CE][MeOH][HOAc]/([B])^{1/2} \quad (12)$$

$$d[\mathbf{III}]/dt = k_{obs,III}[CE][HOAc] \quad (13)$$

where $k_{obs,I}$ and $k_{obs,III}$ are the overall rate constants for the formation of **I** and **III**.

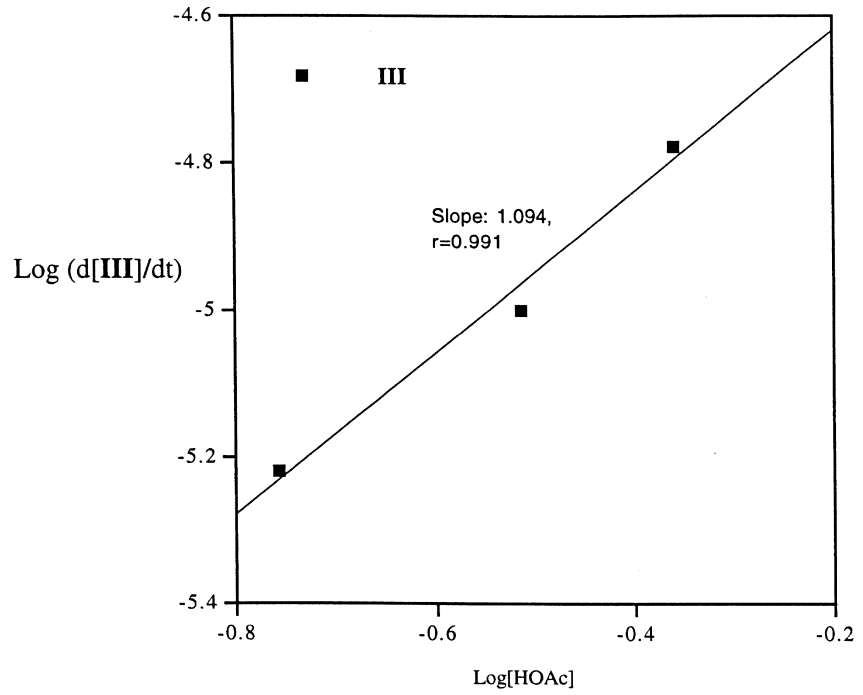


Figure 2 Initial formation rate of product **III** as a function of concentration of acetic acid at pH 3.5 and 35°C

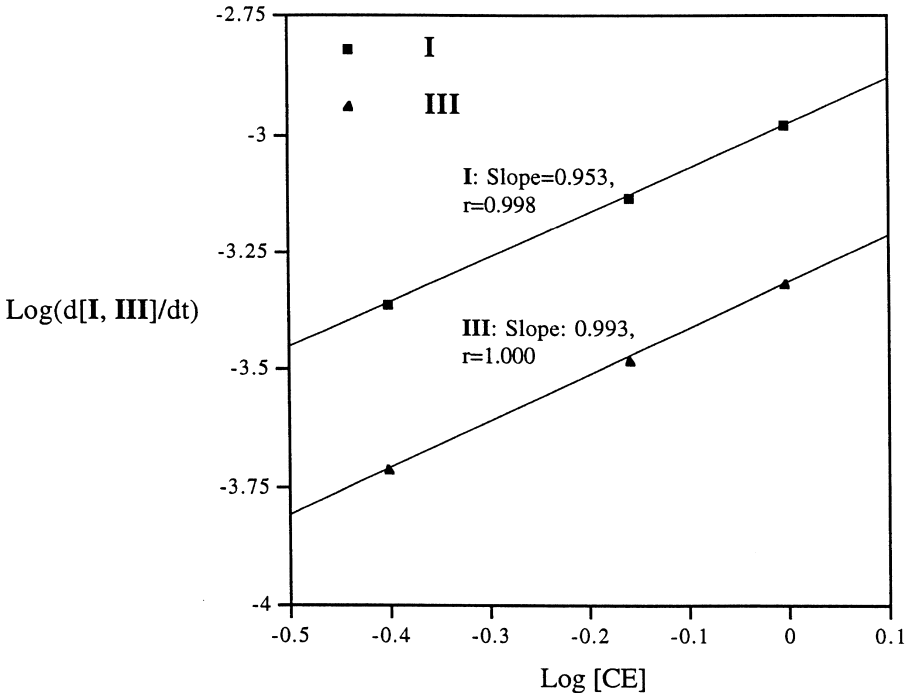


Figure 3 Initial formation rates of products **I** and **III** as a function of concentration of cyclohexene oxide at pH 3.5 and 35°C

After the reaction orders were determined, the rate constants were calculated for a pH range of 4.55 to 8.88. The energies of activation, activation enthalpies and activation entropies were calculated for the experimental conditions outlined in *Table 1* at 25, 35 and 45°C. A summary of the kinetic parameters is shown in *Table 2*.

pH effects on the reactivity of cyclohexene oxide and formation of products **I** *and* **III**

The disappearance of cyclohexene oxide as a function of pH is shown in *Figure 4*. The consumption rate of cyclohexene oxide with methanol and acetic acid increased as the pH was decreased. Therefore, the reactivity of cyclohexene oxide in the competitive reaction [reaction (9)] was greater when the pH was lower. As a result, the triethylamine did not appear directly to accelerate and participate in the formation of the products **I** and **III**. This appears to be in contrast with the accelerating effects of the tertiary amines normally used for the phenyl glycidyl ether type of epoxides[4–14]. Furthermore, this suggests that the reactions of cyclohexene oxide with methanol and acetic acid are acid-catalysed.

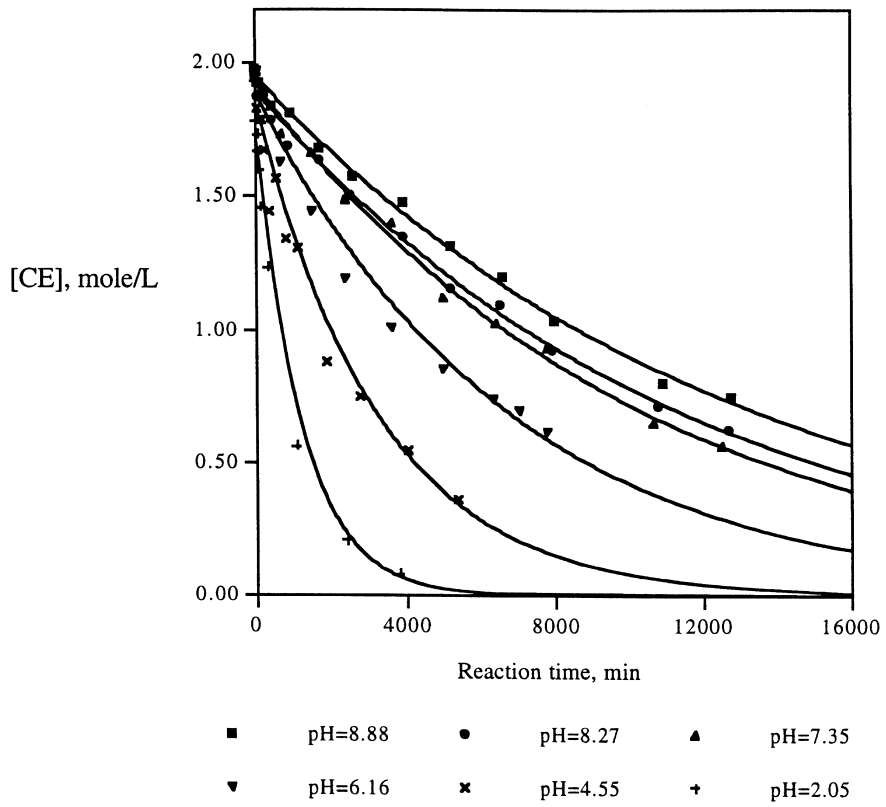


Figure 4 Disappearance of cyclohexene oxide as a function of pH at 35°C: ■, at pH 8.88; ●, at pH 8.27; ▲, at pH 7.35; ▼, at pH 6.16; ×, at pH 4.55; +, at pH 2.05

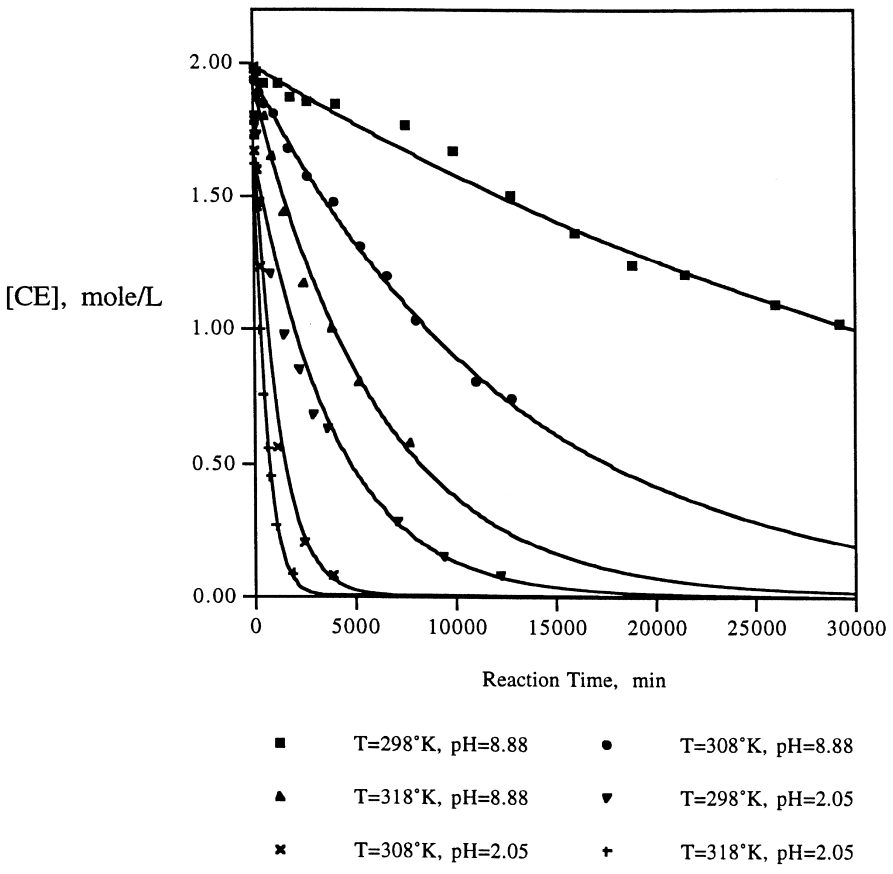


Figure 5 Disappearance of cyclohexene oxide as a function of temperature at pH 2.05 and 8.88: ■, at $T = 298$ K and pH 8.88; ●, at $T = 308$ K and pH 8.88; ▲, at $T = 318$ K and pH 8.88; ▼, at $T = 298$ K and pH 2.05; ×, at $T = 308$ K and pH 2.05; +, at $T = 318$ K and pH 2.05

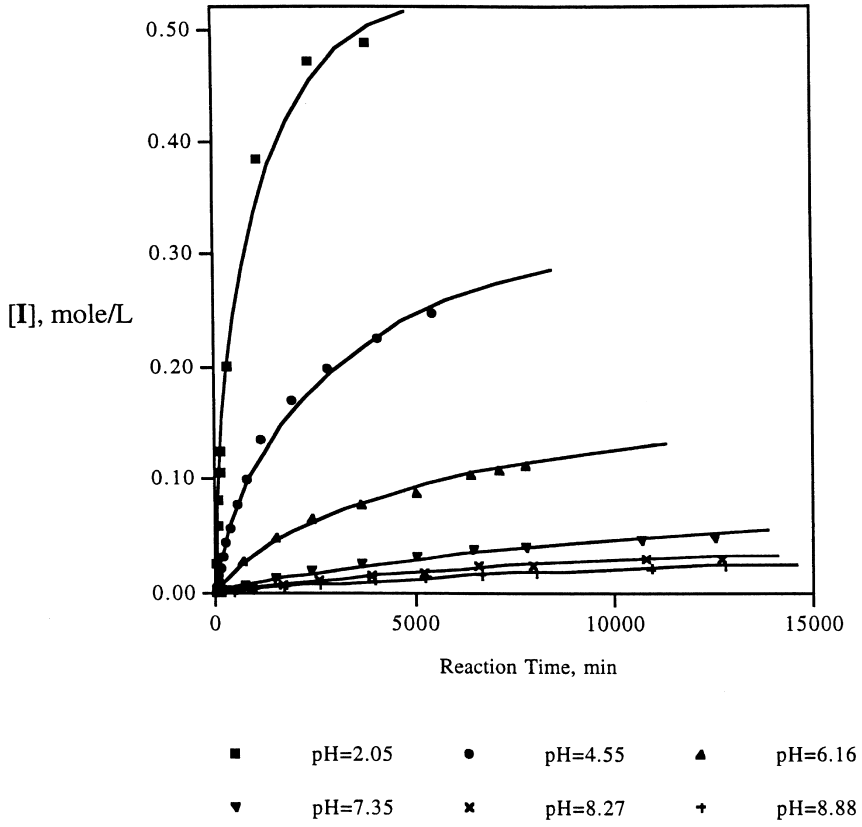


Figure 6 Formation of *trans*-2-methoxyl cyclohexenol as a function of pH at 35°C: ■, at pH 2.05; ●, at pH 4.55; ▲, at pH 6.16; ▼, at pH 7.35; × , at pH 8.27; + , at pH 8.88

Figure 5 illustrates the consumption of cyclohexene oxide as a function of temperature at two different pHs. The consumption of cyclohexene oxide as a function of time was accelerated as the reaction temperature was increased. It was also evident that the increased temperature effect on the consumption of cyclohexene oxide was more pronounced at the higher pH than that at the lower pH. Concomitantly, the formation rates of these products **I** and **III** were also strongly dependent on the pH. *Figures 8 and 9* (shown below) depict the observed increase in the concentrations of products **I** and **III** as a function of decreasing pH at 35°C. From these data, it can be further suggested that the formation of these products appeared to be acid-catalysed. Furthermore, by comparing the results in *Figures 6 and 7*, the concentration of product **III** was generally observed to be greater than the concentration of product **I** at the same pH over the time. This result suggests that the carboxyl group is more reactive than methanol towards cyclohexene oxide. This probably can be attributed to the fact that the acetate anion is a better nucleophile than methanol due to the negative charge[44]. Moreover, this result is consistent with the study of Shechter and co-workers[12–14] on the reactivity of different alcohols and carboxylic acids towards styrene oxide and benzyl oxide.

Proposed mechanism(s) for the formation of **I** *and* **III**

The formation rates of *trans*-2-methoxyl cyclohexenol and *trans*-2-acetoxyl cyclohexenol have been shown to be dependent on the pH and the respective nucleophiles [reaction (9)]. As a consequence, it can be suggested that the overall mechanism must include a protonation step of cyclohexene oxide and a bimolecular attack step. From the control experiments, it was shown that the triethylamine functioned only as a base to adjust and control pH of the reactions [see equation (14)] and did not participate as a catalyst, in contrast to the previously reported glycidyl epoxy systems[4–14]. Since the molar concentration of triethylamine in all of the reactions was less than the acetic acid concentration, it can be assumed that the reaction of triethylamine with acetic acid [see equation (14)] leads to neutralization and complete consumption of the triethylamine with the formation of an associated ion pair, triethylamine–acetate, in dichloroethane. This can be attributed to the relatively strong acidity and basicity of acetic acid and triethylamine, respectively[4,18,44]. Thus, the pH of the reaction system can be understood from the equilibria indicated by equations (15) and (17):

$$\mathrm{HOAc} + \mathrm{NR_3} \rightarrow \mathrm{OA\bar{c}\,\overset{+}{H}\,NR_3} \qquad (14)$$

$$([\mathrm{HOAc}] + [\mathrm{B}] \rightarrow [\mathrm{OAc^-\,HB^+}])$$

$$\mathrm{OA\bar{c}\,\overset{+}{H}\,NR_3} \overset{K_d}{\rightleftharpoons} \mathrm{OA\bar{c}} + \mathrm{\overset{+}{H}\,NR_3} \qquad (15)$$

$$([\mathrm{OAc^-\,HB^+}] \rightleftharpoons [\mathrm{OAc^-}] + [\mathrm{HB^+}])$$

$$K_d = \frac{[\mathrm{OAc^-}][\mathrm{HB^+}]}{[\mathrm{OAc^-\,HB^+}]} \qquad (16)$$

$$\mathrm{HOAc} \overset{K_a}{\rightleftharpoons} \mathrm{H^+} + \mathrm{OA\bar{c}} \qquad (17)$$

$$([\mathrm{HOAc}] \rightleftharpoons [\mathrm{H^+}] + [\mathrm{OAc^-}])$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{OAc^-}]}{[\mathrm{HOAc}]} \qquad (18)$$

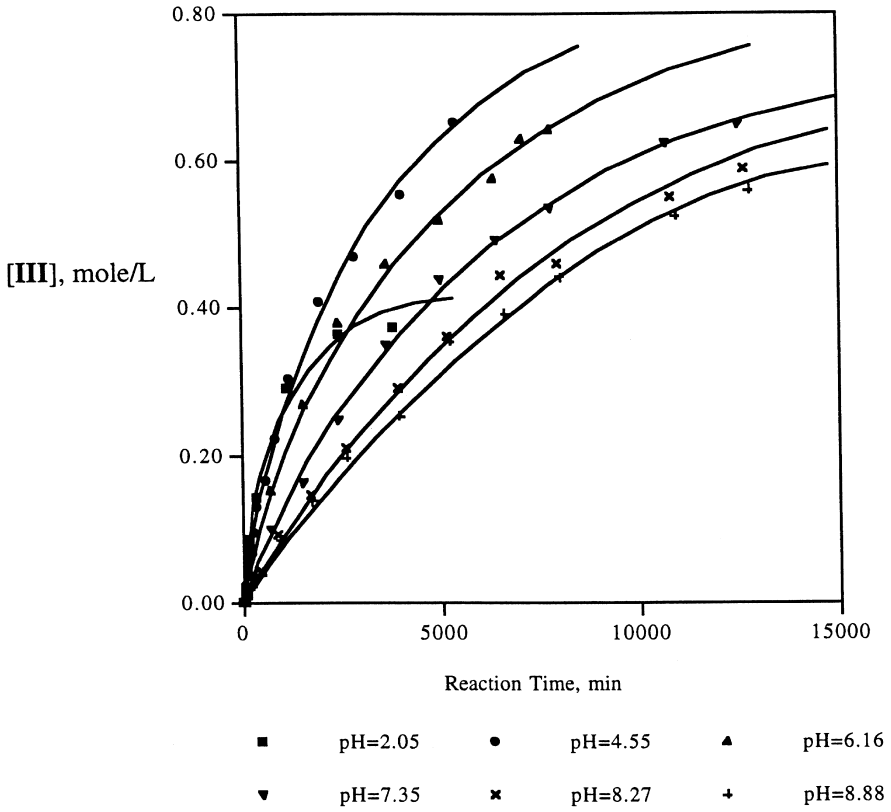


Figure 7 Formation of *trans*-2-acetoxyl cyclohexenol as a function of pH at 35°C: ■, at pH 2.05; ●, at pH 4.55; ▲, at pH 6.16; ▼, at pH 7.35; ×, at pH 8.27; +, at pH 8.88

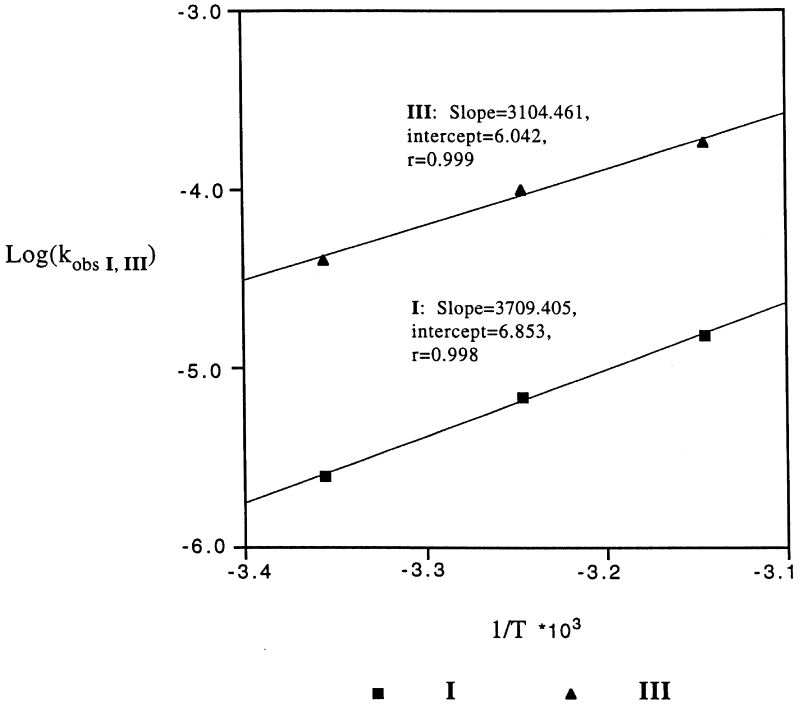


Figure 8 Observed reaction constants of *trans*-2-methoxyl cyclohexenol and *trans*-2-acetoxyl cyclohexenol as a function of reaction temperature: ■, product **I**; ▲, product **III**

In addition, it was also assumed that the acetate anion was mainly provided by partial dissociation [equation (15)] of the associated ion pair triethylamine–acetate in dichloroethane, and that the concentration of the acetate anion, from the equilibrium shown by equation (17), was negligible and can be ignored[44,47]. Therefore, the concentration of H^+ can be considered to be determined by the following

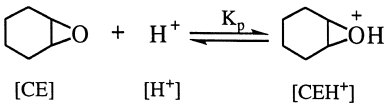
equation:

$$[H^+] = \frac{K_a[HOAc]}{[OAc^-]} = \frac{K_a[HOAc]}{\sqrt{K_a[B]}} \quad (19)$$

Obviously, the dissociation equilibria shown by equations (15) and (17) can be much more complicated due to presence of several possible species, such as solvated ions, solvent-separated ion pairs, and contact ion pairs or ionic aggregates, in non-aqueous solvents[44,47]. However, the relative concentration of each of the species can be strongly affected by the polarity of the solvent used[48,49]. Madec reported that carboxylic acids in solvents of low dielectric constant (< 10) were mainly present as molecular or ionic aggregates[49]. Ritchie summarized that acidic or basic non-aqueous solutions free of ion pairs or other ionic aggregates require solvents with dielectric constants greater than 30[47]. Thus, it is reasonable to assume the presence of solvated H^+ in the competitive reactions due to the increased solvent polarity by addition of methanol[44,47]. However, the question regarding the solvated H^+ will need to be studied further.

Protonation of cyclohexene oxide can generally be treated as a fast equilibrium as shown in reaction (20)[21–23]. The protonated cyclohexene oxide can possibly proceed to a ring-opened carbocation as indicated in reaction (21). From the experimental observation previously discussed, only the *trans* products were observed [see reaction (9)]. This suggests that a ring-opened cyclohexene oxide was not the reaction pathway resulting in the formation of the major products **I** and **III**. A carbocation as shown in reaction (22) would have resulted in formation of both the *cis* and *trans* isomers. Therefore, it is reasonable to assume that the protonated species [CEH^+] and not the ring-opened carbocation leads to the product formation, as depicted by the nucleophilic attack in reaction (23).

Furthermore, in the competitive reaction system, the protonated species [CEH^+] can be then competitively attacked by a variety of nucleophiles including methanol, acetic acid, acetate anion or cyclohexene oxide involved in the competitive reaction system. Because of its stronger acidity, acetic acid is a much weaker nucleophile than the acetate anion[44,47]. Cyclohexene oxide is also a much weaker nucleophile than both methanol and acetate anion, owing to its bulkiness, evident from the control experiments. Consequently, methanol and acetate anion are suggested as the major nucleophiles for the products **I** and **III** in the competitive reaction system [see reactions (24) and (25)].



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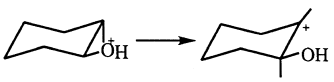

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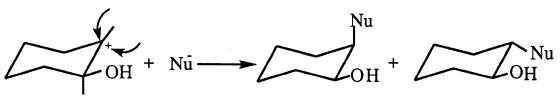

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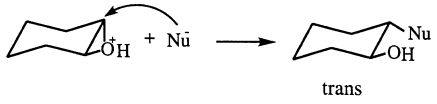
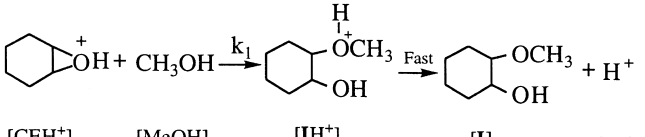


(23)

The competitive nucleophilic attack of methanol on [CEH^+] is shown by reaction (24). It was further assumed that dissociation of the protonated species [$\mathbf{I}H^+$] [see reaction (24)] into the final product, *trans*-2-methoxyl cyclohexenol (**I**), is a fast step in the reactions. In a competing nucleophilic reaction, the acetate anion attacks the protonated cyclohexene oxide (CEH^+) to form *trans*-2-acetoxyl cyclohexenol (**III**) as indicated in reaction (25).



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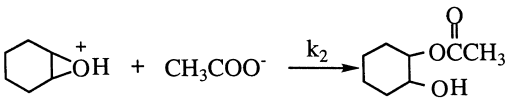

(25)

According to the mechanisms proposed above and the assumption of fast equilibrium for the protonation of cyclohexene oxide applied for reaction (20), the rate expressions for the formation of *trans*-2-methoxyl cyclohexenol (**I**) and *trans*-2-acetoxyl cyclohexenol (**III**) can be derived and expressed as equations (26) and (27), respectively:

$$\frac{d[\mathbf{I}]}{dt} = \frac{K_p K_a k_1 [CE][MeOH][HOAc]}{\sqrt{K_d}\sqrt{[B]}} = k_{obs,I}\frac{[CE][MeOH][HOAc]}{\sqrt{[B]}} \quad (26)$$

$$\frac{d[\mathbf{III}]}{dt} = K_p K_a k_2 [CE][HOAc] = k_{obs,III}[CE][HOAc] \quad (27)$$

From equation (26) (see above), the formation rate of *trans*-2-methoxyl cyclohexenol is first-order dependent on the concentrations of cyclohexene oxide, methanol and protons. From equation (27) (see above), the formation rate of *trans*-2-acetoxyl cyclohexenol is first order with respect to the concentrations of cyclohexene oxide and acetic acid. These results are consistent with the experimentally determined reaction orders for the corresponding components discussed and the rate equations [equations (12) and (13)] proposed previously.

Kinetic parameters

The important kinetic parameters are the rate constant, activation energy, activation enthalpy and activation entropy. The observed rate constants at 35°C for the formation of products **I** and **III** were obtained from the intercepts of the plots in *Figures 4 and 5*. The observed rate constants at the other temperatures, 25°C and 45°C, were also obtained in the same way. The activation energies, activation enthalpies and activation entropies for the formation of the products were obtained from the corresponding observed rate constants at the three different temperatures as shown in *Figures 8 and 9*. The results obtained for products **I** and **III** are shown in *Table 2*. The rate constants for the formation of *trans*-2-acetoxyl cyclohexenol are greater than those for the formation of *trans*-2-methoxyl cyclohexenol at the pH range of 4.55 to 8.88. The corresponding activation energies and enthalpies, however, are much lower as expected[44]. These results are consistent with the greater reactivity of the acetate anion than methanol towards cyclohexene oxide, as discussed previously, within the pH range of the reactions. The

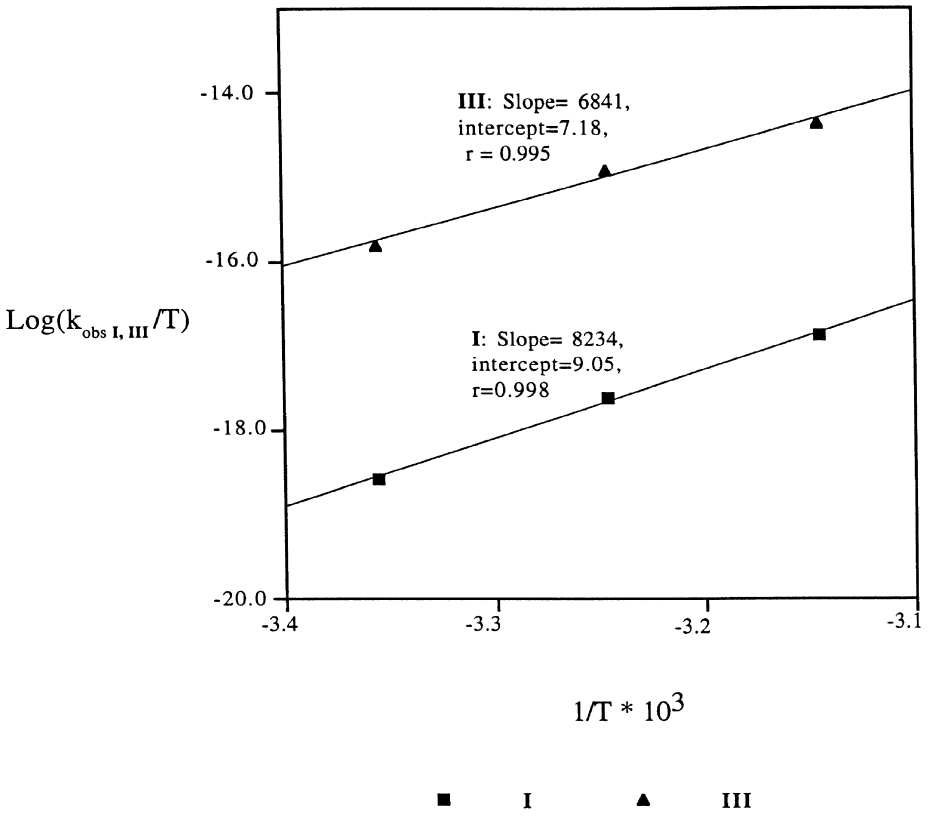

Figure 9 Temperature-reduced observed rate constants as a function of 1/*T*: ■, product **I**; ▲, product **III**

activation energy and activation entropy of a reaction are a function of the specific reaction, mechanism and the reaction conditions[44], and as a consequence can be used to elucidate the type of mechanism(s) involved within a specific chemical reaction[4,21–23].

The average activation energy (71.0 kJ mol^{-1}) for the formation of **I** appears to be higher than the activation energy (56.8–63.7 kJ mol^{-1}) for acid-catalysed alcoholysis of a phenyl glycidyl ether type of epoxide[21–23]. The average activation energy (59.4 kJ mol^{-1}) for the formation of **III** is lower than the activation energy for the reaction of phenyl glycidyl ether with benzoic acid catalysed by either pyridine (71.48–86.11 kJ mol^{-1})[15,16] or Dimethylbenzylamine (86.4 kJ mol^{-1})[50]. In comparison with phenyl glycidyl ether type of epoxides, the cycloaliphatic epoxide is more reactive towards the carboxyl group than the hydroxyl group under the acid-catalysed condition. However, the phenyl glycidyl ether type of epoxides are more reactive towards the hydroxyl group than the carboxylic acid groups, even under base-catalysed conditions. In addition, the negative activation entropies for the formation of the products can be understood in terms of the proposed limiting bimolecular attacking steps [see equations (14) and (15)]. Negative activation entropies have been shown for a bimolecular nucleophilic reaction where the bond breaking and the bond formation require a corresponding spatial restriction of the molecules involved in the rate-determining step[15,16]. These results are consistent with the proposed mechanisms for formation of the products as previously reported[19–23].

The primary objective of this study was to understand the competitive reaction kinetics of cycloaliphatic epoxides with hydroxyl and carboxyl groups. Ultimately, these data should be useful for designing cycloaliphatic epoxide crosslinkable acrylic coatings. As evident from the kinetic data, the crosslinking reactions of cycloaliphatic epoxides with hydroxyl and carboxyl functional groups are acid-catalysed. In contrast to the glycidyl epoxides, tertiary amines have been shown to be inhibiting agents for cycloaliphatic epoxides within the pH range of this study. For coatings applications, the selectivity of the crosslinking reactions is also important. In our study, we have shown that the chemical structure of the crosslinks is pH-dependent. As a result, the overall properties of the coatings can be optimized by selecting the pH which affords the necessary hydrolytic and/or photolytic stability needed for a specific usage[24,25].

CONCLUSION

Cyclohexene oxide, methanol and acetic acid were used as model compounds to elucidate the competitive crosslinking reaction kinetics and mechanisms of cycloaliphatic epoxides with hydroxyl and carboxyl functional groups. The reaction gave two major products: *trans*-2-methoxyl cyclohexenol and *trans*-2-acetoxyl cyclohexenol. Only the *trans* isomers were observed for both the primary ether and ester products. The competitive reaction for the formation of **I** and **III** was shown to be acid-catalysed, and triethylamine was shown to function only as a spectator cation over the entire pH range of this study. In terms of relative reactivity, acetic acid had a greater reactivity than methanol towards cyclohexene oxide. These results are in contrast with the previously reported reaction chemistry for glycidyl epoxide[11–20]. The energies of activation (E_a) and the rate constants (k_{obs}) of the competitive reactions also reflected this same trend. The formation rate of ether product **I** was observed to have a first-order dependence on cyclohexene oxide, methanol and proton concentration. The formation

rate of ester product **III** was found to be first order with respect to the concentrations of cyclohexene oxide and acetic acid. On the basis of the stereochemistry of the products, the negative entropic energy of activation and the observed reaction orders, an A-2 mechanism was postulated for the formation of both **I** and **III**.

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