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Acidolysis of epichlorohydrin by acetic acid in the presence of tetraethylammonium bromide

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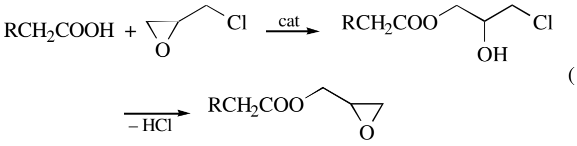
The effects of acid and catalyst concentrations and temperature on the rate of oxirane ring opening in the reaction of epichlorohydrin with acetic acid in the presence of tetraethylammonium bromide were studied.

Carboxylic acids and their hydroxyalkyl and glycidyl esters are used in the manufacture of various polyepoxy materials.[1–3]

The monomers of carboxylic acid–based epoxy resins are obtained by the acidolysis of 1-chloro-2,3-epoxypropane (epichlorohydrin) followed by the dehydrochlorination of the chlorohydrine ester:[1,3]



(1)

This reaction was studied in an excess of carboxylic acid[4,5] or in chlorobenzene,[4] nitrobenzene,[5] acetic acid[1] and epichlorohydrin[3] at 70–120 °C.[1,3–5] Metal acetates[1,4,6] and ammonium salts or amines[1,3] were employed as catalysts. The efficiency of catalysis is 10–100, and it reaches 325 only for chromium acetate.[6] Catalysis by metal acetates was carried out at 90-120 °C.[1,4–6] The use of tetraalkylammonium salts[3] allows one to lower the reaction temperature. To study the kinetic aspects of reaction (1), we chose the interaction between acetic acid and epichlorohydrin in solution. Tetraethylammonium bromide was used as a catalyst.

The reaction was of pseudo-first order with respect to 1-chloro-2,3-epoxypropane, and it was monitored by measuring a decrease in the acetic acid concentration, which was determined by potentiometric acid–base titration. A low concentration of acetic acid (~0.2 mol dm^{-3}) in epichlorohydrin was used to prevent the formation of acid–acid associates.

Epichlorohydrin[7] was dried with sodium sulfate and twice distilled; the fraction with bp 116–116.5 °C was collected. Acetic acid[8] was refluxed with potassium permanganate and distilled with collecting a fraction with bp 118–118.5 °C. Tetraethylammonium bromide[3,7] was purified by triple crystallization from a benzene–ethanol mixture (3:2 by volume) and dried in a vacuum desiccator at 60–70 °C.

The determination of the kinetic order of reaction with respect to acetic acid in an excess of epichlorohydrin in the presence of tetraethylammonium bromide as a catalyst was an important part of this study. Note that the acidolysis of epichlorohydrin in chlorobenzene[4] and nitrobenzene[5] in the presence of metal acetates is of first order with respect to acetic acid.[4] However, the reaction of epichlorohydrin with 4-methyl-1,4-tetrahydrophthalic acid in the presence of ammonium salts[3] is of zero order with respect to the acid. We performed experiments with different initial acetic acid concentrations in a large excess of epichlorohydrin at a constant catalyst concentration (m = 0.005 M) at 60 °C to determine the kinetic order of the reaction. The plot of acid concentration *vs.* time is linear (Figure 1); this is typical of a zero-order reaction. The initial rate method[9] also gave a zero kinetic order of the reaction with respect to acetic acid. Therefore, the experimental data were treated using the equation:

$$k_{\mathrm{exp}} = a - (a - x)/bt, \qquad (2)$$

where k_{exp} is the apparent rate constant (s^{-1}); a and $(a - x)$ are the initial and current concentrations of acetic acid, respectively (mol dm^{-3}); b is the concentration of epichlorohydrin (mol dm^{-3}) and t is time (s).

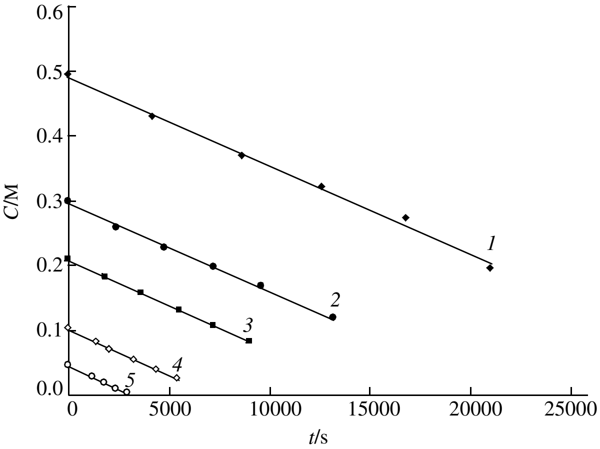


Figure 1 The influence of acetic acid concentration on the rate of the reaction of epichlorohydrin acidolysis in the presence of tetraethylammonium bromide at 333 K: (*1*) 0.495 M; (*2*) 0.299 M; (*3*) 0.211 M; (*4*) 0.101 M; (*5*) 0.045 M.

Table 1 The rate constants (k_{calc} and k_{exp}) of the reaction of acetic acid with epichlorohydrin (b = 12.06–12.37 M) in the presence of tetraethylammonium bromide (m = 0.005 M), 333 K.

a/M	Maximum conversion of the acid (%)	$k_{\mathrm{calc}}/10^{-6}$ s^{-1}	$k_{\mathrm{exp}}/10^{-6}$ s^{-1}
0.495	60.6	1.14±0.04	1.20±0.02
0.299	60.3	1.09±0.03	1.21±0.02
0.211	60.2	1.15±0.03	1.23±0.01
0.101	75.3	1.13±0.03	1.23±0.02
0.045	97.8	1.18±0.02	1.22±0.01
k_{mean}		1.14±0.01	1.22±0.00

The rate coefficients remained constant up to very high conversions of acetic acid, confirming the zero order of reaction with respect to the acid. The rate constants calculated by equation (2), k_{exp}, and those estimated by the least-squares method, k_{calc}, are invariable to within the experimental error (Table 1).

The catalyst concentration (m) was varied in the range 0.005–0.00125 M at 60 °C to determine the kinetic order of the reaction with respect to catalyst. The experimental data were treated by the equation $k = k_0 + k_{\mathrm{K}}m$ (k_0 and k_{K} are non-catalytic and catalytic rate constants) to give an excellent correlation coefficient (Table 2, Figure 2), indicating the first order with

Table 2 The rate constants (k_{calc} and k_{exp}) of the reaction of acetic acid (a = 0.196 M) with epichlorohydrin (b = 12.56 M) at different concentrations of the catalyst (tetraethylammonium bromide), 333 K.

m/M	$k_{\mathrm{calc}}/10^{-6}$ s^{-1}	$k_{\kappa}/10^{-4}$	$k_{\mathrm{exp}}/10^{-6}$ s^{-1}	$k_{\kappa}/10^{-4}$	r
0.00500	1.06±0.02	2.15±0.06	1.15±0.02	2.33±0.06	0.999
0.00375	0.794±0.020		0.828±0.020		0.999
0.00250	0.546±0.008		0.563±0.008		0.999
0.00125	0.247±0.005		0.266±0.005		0.999

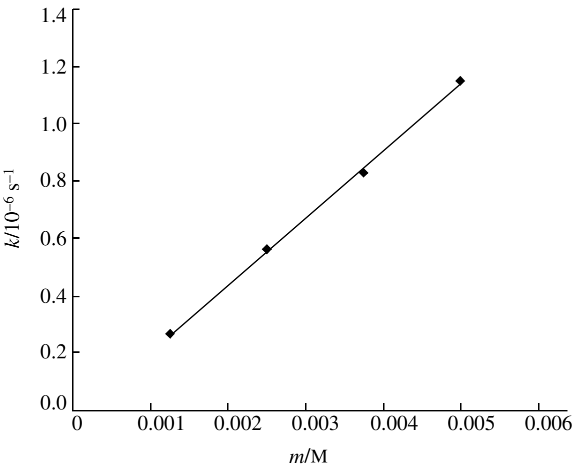


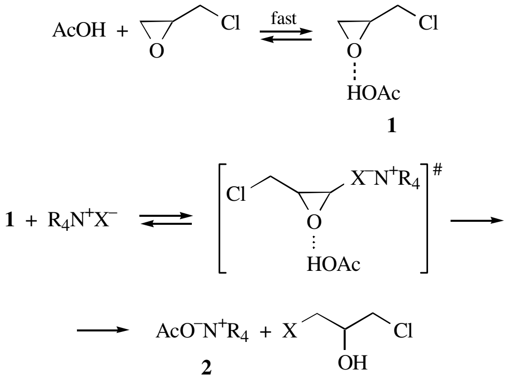
Figure 2 Dependence of the rate constant of the reaction of acetic acid with epichlorohydrin at 333 K on catalyst concentration.

respect to catalyst.

The straight line of k *vs.* m was extrapolated almost to zero, showing that the non-catalytic reaction is very slow. The efficiency of catalysis by the quaternary ammonium salt is high: $k_K/k_0 \sim 1\times10^4$, and the reaction completed within 50 min at 70 °C.

The rate constants calculated by equation (2) (Table 3) gave a linear function ($r = 0.999$, $SD = 6\%$) in the $\ln k$–$1/T$ coordinates, indicating the invariance of the reaction mechanism in the specified temperature range. The temperature coefficient γ is 2.56. The activation parameters were calculated according to the equations $\Delta H^{\#} = E_a - nRT$ and $\Delta S^{\#} = R[\ln A - \ln(k_B/h) + n]$ (k_B is the Boltzmann constant, h is the Planck constant and n is the molecularity of the reaction) for a bimolecular process[10] (Table 3).

The experimental activation energy (E_a) is comparable to that for the reactions of acetic acid with epichlorohydrin in the presence of potassium acetate[6] ($E_a = 77.4$ kJ mol^{-1}) and 4-methyl-1,4-tetrahydrophthalic acid with epichlorohydrin in the presence of tetraethylammonium chloride[3] ($E_a = 58.6$ kJ mol^{-1}). Thus, the experimental activation energy in the presence of a basic catalyst strongly depends on the basicity ($p\mathrm{K}_a^{\mathrm{H_2O}}$ for acetate is 4.70[11] or –6.30 for bromide[11]). Thus, the true catalyst of acidolysis is an ammonium salt,[3] which is formed by the interaction of tetraethylammonium bromide with acetic acid



Carboxylate **2** reacts with epichlorohydrin in a slow step:

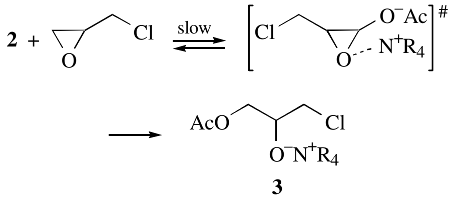
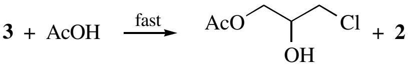


Table 3 Activation parameters of the reaction of acetic acid (a = 0.198 M) with epichlorohydrin (b = 12.55 M) in the presence of the catalyst tetraethylammonium bromide (m = 0.005 M).

T/K	k_{exp}/ 10^{-7} s^{-1}	E_a/kJ mol^{-1}	A/s^{-1}	$\Delta H^{\#}$/ kJ mol^{-1}	$-\Delta S^{\#}$/ J mol^{-1} K^{-1}	$\Delta G^{\#}$/ kJ mol^{-1}
303	0.728±0.019	76.7±1.5	2.5×10^8	71.7	144.8	116
313	1.88±0.05			71.5	145.1	117
323	5.16±0.16			71.3	145.4	118
333	12.1±0.4			71.2	145.6	120
345	28.8±0.8[a]			71.0	145.9	121

[a] $a = 0.159$ mol dm^{-3}.

In view of a significant difference in the acidities of AcOH ($p\mathrm{K}_a$ 4.75[11]) and 1-chloro-3-acetopropan-2-ol ($p\mathrm{K}_a$ 13.5[12]), ammonium salt **3** reacts rapidly with acetic acid with formation of chlorohydrine ester and regeneration of true catalyst **2**:



Zero order with respect to the acid is possible if the acid is consumed in the fast step, which is equivalent to the proposed catalysis mechanism.

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