Specific Features of the Kinetics of Addition Esterification of Epoxide with the Carboxyl Group

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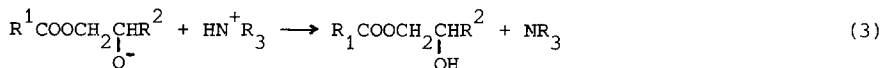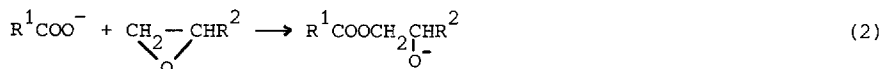Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, CS-162 06 Prague 6, Czechoslovakia

Summary

The kinetics of addition esterification involving epoxide and carboxyl groups in the presence of a tertiary amine was investigated using a model system phenylglycidyl ether - caproic acid. It has been found that the reaction has an induction period. By means of IR spectra it has been proved that the equilibrium formation of catalytically active species (complex acid-amine) is the cause both of nonconstant values of experimentally determined reaction orders and of the occurrence of the induction period. The controversial experimental results reported in the literature are discussed.

Introduction

The reaction between epoxide and carboxylic acid catalyzed with tertiary amine is accompanied by several parallel and consecutive reactions (1-3). The addition esterification is markedly preferred, however, and only after one or both reaction components have been consumed other reactions become operative. Mechanisms based on the ionic course of the reaction or on the formation of a transition complex have been suggested for the addition esterification.

The ionic mechanism according to Shechter (2) assumes that the reaction is initiated by a carboxylate anion arising in the equilibrium interaction between acid and amine.
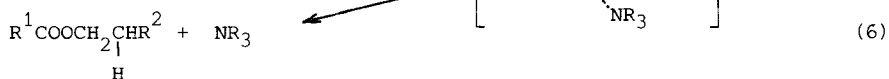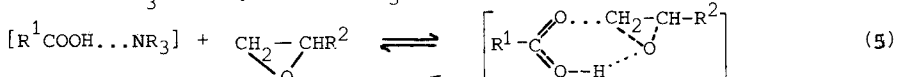
$$R^1COOH + R_3N \rightleftharpoons R^1COO^- + HN^+R_3 \qquad (1)$$

$$R^1COO^- + CH_2 - CHR^2 \longrightarrow R^1COOCH_2CHR^2 \qquad (2)$$
$$\qquad\qquad\qquad \underset{O}{\diagdown\diagup} \qquad\qquad\qquad\qquad \underset{O^-}{|} $$

$$R^1COOCH_2CHR^2 + HN^+R_3 \longrightarrow R_1COOCH_2CHR^2 + NR_3 \qquad (3)$$
$$\qquad \underset{O^-}{|} \qquad\qquad\qquad\qquad\qquad\qquad \underset{OH}{|}$$

This mechanism is used to explain the results obtained by Fiala and Lidařík (4). They determined the reaction orders with respect to the acid and amine as being, respectively, 0.52 and 0.60 in the reaction between glycidyl benzoate and benzoic acid in the presence of benzyldimethylamine. This result is in a comparatively good agreement with the theoretical value 1/2 corresponding to the ionic mechanism: $v = k[E][C]^{1/2}[A]^{1/2}$, where $[E], [C], [A]$, respectively, are the concentrations of epoxide, acid, and amine.

On the contrary, Japanese authors (5,6) found under similar reaction conditions that the reaction is generally of the third order, i.e.

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$v = k[E][C][A]$. When interpreting kinetic results, they suggested a mechanism assuming the formation of a transition ternary complex

$$R^1COOH + R_3N \rightleftharpoons [R^1COOH...NR_3] \qquad (4)$$

$$[R^1COOH...NR_3] + CH_2\!-\!CHR^2 \rightleftharpoons \left[R^1\!-\!C \begin{matrix} O...CH_2\!-\!CH\!-\!R^2 \\ O \\ O\!-\!H \quad NR_3 \end{matrix} \right] \qquad (5)$$

$$R^1COOCH_2CHR^2 + NR_3 \qquad (6)$$
$$H$$

According to Madec (7), two reaction mechanisms participate in the reaction between benzoic acid and phenylglycidyl ether catalyzed with N,N-dimethyldodecylamine: the mechanism of a ternary complex and the mechanism in which the reaction is initiated by an interaction between amine and epoxide. Their combination is used by the authors to explain the experimental reaction order $\kappa = 2.5$ ($v = k[E][A][C]^{1/2}$).

One can trace in the literature not only the nonuniformity of views of the reaction mechanism, but also considerable differences between experimental results obtained by the individual authors investigating the reaction kinetics. This study has been concentrated on an investigation of the kinetics of addition esterification of phenylglycidyl ether with caproic acid catalyzed with tertiary amines. We have tried to demonstrate the possibility of a uniform interpretation of different results reported in the literature.

Experimental

Caproic acid (CA), phenylglycidyl ether (PGE) and tributylamine (TBA) were distilled at reduced pressure. Triethylamine (TEA) was heated with acetic anhydride and redistilled (b.p. 87°C). Purity of the chemicals used was determined by gas chromatography: CA - 99.7%, PGE 99.6%, TEA 99,1%, TBA 98.5% and benzyldimethylamine (BDMA) 99.9%.

The reaction mixture was sealed in ampoules under nitrogen and the reaction temperature was maintained with an accuracy of ± 0.5°C. The reaction took place in a benzene solution with a large excess of PGE in the presence of TBA, TEA or BDMA as the catalyst. The reaction kinetics was evaluated from the consumption of caproic acid determined by potentiometric titration with an alcoholic solution of KOH.

The rate constants and partial reaction orders with respect to the individual components were determined by a differential method using the dependence of the initial rate (v_0) on the initial concentration by means of the relations:

$$v_0 = -d[CA]/dt = k[A]_0^{\alpha}[PGE]_0^{\phi}[CA]_0^{\gamma} \qquad (7)$$

$$\ln v_0 = k' + \gamma \ln[CA]_0, \text{ at const } [A]_0 \text{ and } [PGE]_0$$

$$\ln v_0 = k'' + \alpha \ln[A]_0, \text{ at const } [CA]_0 \text{ and } [PGE]_0$$

$$\ln v_0 = k''' + \phi \ln[PGE]_0, \text{ at const } [CA]_0 \text{ and } [A]_0$$

where [CA], [PGE], [A], $[CA]_0$, $[PGE]_0$ and $[A]_0$ are the instantaneous and initial molar concentrations of CA, PGE and the catalyst, respectively, k is the rate constant, α, ϕ, γ are partial orders with respect to the catalyst, PGE, and CA, respectively.

Results and Discussion

By means of GPC, it was found that in the reaction of phenylglycidyl
ether (PGE) with caproic acid (CA) catalyzed with tertiary amines only ad-
dition esterification takes place under the conditions of kinetic investi-
gation (3), because 1-phenyloxypropanediol-3-caproate is the only product:

$$\text{PhOCH}_2\text{CHCH}_2\underset{O}{\diagdown} + CH_3(CH_2)_4COOH \longrightarrow \text{PhOCH}_2\underset{OH}{\text{CHCH}_2}OCO(CH_2)_4CH_3 \qquad (8)$$
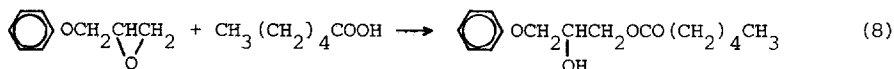
Side reactions become operative to a major extent with an excess of PGE
only after all acid has been consumed. All experiments were performed with
a large excess of epoxide, so that the reaction can be regarded as pseudo-
monomolecular. Under such conditions, the kinetic course of the reaction
characterized by a decrease in the concentration of CA has an induction
period (Fig.1) which is discussed below. After acceleration, the acid is
consumed up to high conversion almost linearly with time, due to the pseudo-
monomolecular character of the reaction and the low reaction order with re-
spect to the acid.
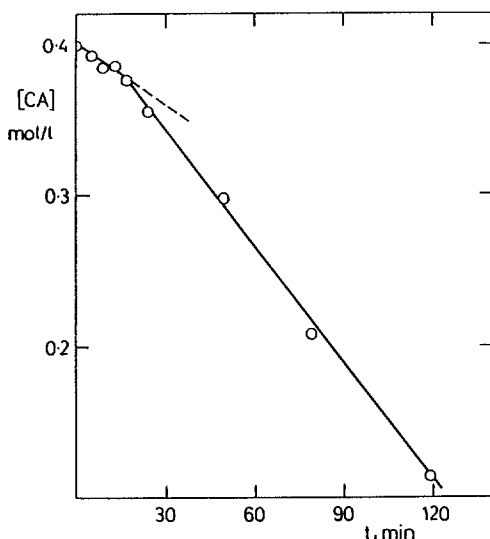
Fig. 1 Time dependence of the
concentration of caproic acid
(CA) in the reaction with phenyl-
glycidyl ether (PGE) catalyzed
with tributylamine (TBA), T =
= 80°C. [CA] = 0.400 mol/l,
[PGE] = 4.87 mol/l, [TBA] = 0.0391
mol/l

Kinetic course of the reaction in the initial stage

Due to its complex course, the kinetics was not evaluated by employing
an integral method using the time dependence of concentration. Instead, the
differential method was used in which the initial rate v_0 and its dependen-
ce on initial composition were determined.

It follows from the dependence of $\ln v_0$ on $\ln [PGE]_0$ that the addition
esterification is first-order with respect to PGE; the orders with respect
to the catalysts used (TBA, TEA, BDMA) and the corresponding rate constants
are given in Table 1. In Fig.2a, it can be seen that the experimentally de-
termined order with respect to the acid, γ, corresponding to the slope of
the $\ln v_0$ vs. $\ln [CA]_0$ dependence at a constant concentration of TBA and
PGE depends on the relative catalyst concentration with respect to the acid.
At $[TBA]_0/[CA]_0 \sim 1$, the dependences are curved, and the orders must be de-
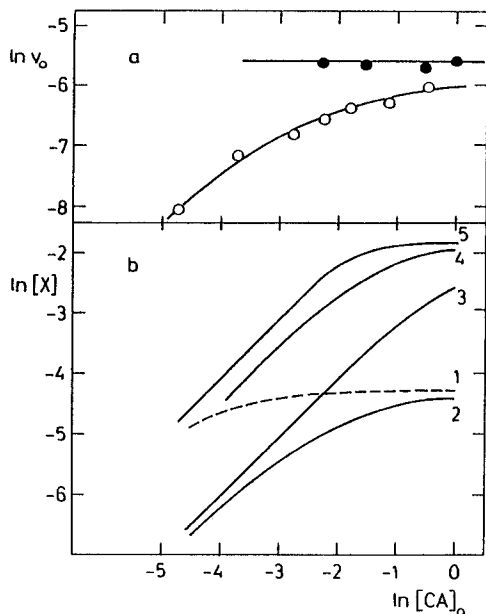
Fig. 2 Effect of the initial concentration of caproic acid on a) the initial rate of the reaction with phenylglycidyl ether (PGE), and b) theoretical values of the equilibrium concentration of catalytically active species X
a) [PGE] = 4.90 mol/1, o [TBA] = = 0.158 mol/1, ● [TBA] = 0.002 mol/1
b) --- 1 ionic mechanism [X = X_i] - concentration of anions $RCOO^-$,
—— complex mechanism [X = X_{com}] concentration of the complex $RCOO^- \ldots H^+NR_3$,
2 $[TBA]_o$ = 0.014 mol/1, K = 10,
3 $[TBA]_o$ = 0.160 mol/1, K = 100,
4 $[TBA]_o$ = 0.160 mol/1, K = 10,
5 $[TBA]_o$ = 0.160 mol/1, K = 1.
K is the equilibrium constant in the formation of the active species

termined locally for a narrow range of the concentration ratio [TBA]/[CA]. The order varies depending on the relative catalyst concentration in the range γ = 0 - 0.55 (cf.Table 2). In order to reach a broad range of relative catalyst concentrations, the concentrations of the acid and TBA at a constant PGE concentration (4.9 mol/1) were varied in the range 0.001-1.5 mol/1, and 0.002-0.180 mol/1, respectively.

Table 1. Rate constants of addition esterification and reaction orders
with respect to catalyst for the reaction in benzene at T = 80°C
(holds for $[A]_o/[CA]_o$ = 0.014 - 0.14; γ = 0).

	TBA	TEA	BDMA
α	0.80	0.85	0.90
$k \cdot 10^3$ [a]	5.0	7.8	

[a] dimension $1^{0.8}mol^{-0.8}min^{-1}$; γ, α reaction orders with respect to acid and catalyst, respectively.

Table 2. Reaction order with respect to caproic acid γ as a function of the
ratio between the catalyst (TBA) and acid (CA) concentrations

[TBA]	0.002	0.014	0.147	0.180
$[TBA]_o/[CA]_o$	0.001-0.010	0.014-0.141	0.12-1.01	0.29-1.50
γ	0	0	0.20-0.45	0.3 - 0.55

The results show that the addition esterification in its initial stage can be described by a kinetic equation

$$v = k[PGE][A]^{\alpha}[CA]^{\gamma} \tag{9}$$

where α and k for the individual catalysts are given in Table 1, γ = 0-0.55 for concentrations $[CA]_o$ = 0.001-1.5 mol/l, $[A]_o$ = 0.002-0.180 mol/l (cf. Table 2).
Activation energy of the reaction is 84 kJ/mol.

In the absence of the catalyst the reaction proceeds without an "induction period" and experimental results correspond to the kinetic equation

$$v = k_1[PGE][CA]^{\gamma_1} \tag{10}$$

At 80°C in benzene we have: γ_1 = 0.9 and $k_1 = 5 \times 10^{-6} \, l^{0.9} mol^{-0.9} min^{-1}$.

The dependence of the order with respect to acid on the relative catalyst concentration is due to the fact that catalytically active species arise by equilibrium interactions between acid and amine. Contrary to the initial concentration sometimes used in the literature (4,8-10) the equilibrium concentrations should appear in the kinetic equations. This simplification may lead to a wrong interpretation of the mechanism. The order calculated using the initial concentrations must depend, in particular, on the ratio of the initial concentrations of amine and acid and on the equilibrium constant of the formation of the active species: $CA + A \rightleftharpoons X_{com}$ for the complex mechanism, or $CA + A \rightleftharpoons X_i^- + X_i^+$ for the ionic mechanism. Fig. 2b shows the calculated dependence of the equilibrium concentration of the active species X on the initial concentration of acid for both mechanisms. The slope of this dependence gives the reaction order with respect to acid γ, because the reaction rate is proportional to the equilibrium concentration $X : v_o \sim k_x[X] \sim k'[CA]_o$. The order (the slope) varies between 0 and unity, depending on the ratio of the amine and acid concentrations and on the equilibrium constant: $\gamma \rightarrow 0$ for a pronounced excess of acid, $\gamma \rightarrow 1$ for an excess of amine, which also fits in with our experimental results. Hence, the considerably different results obtained by various authors (γ = 0 - 1) may, therefore, probably be explained by different experimental conditions (concentrations of the reaction components, factors determining the equilibrium constant - medium, temperature, quality of the catalyst).

Interaction between acid and catalyst

The equilibrium interaction between CA and amines was investigated by means of IR spectroscopy. In benzene solution, CA appears in the form of a dimer wiht the corresponding absorption bands at 1711, 1290 and 950 cm^{-1} (11). The monomer content (band at 1755 cm^{-1}), though negligible in benzene, is much higher in nitrobenzene. In a mixture of CA and TBA in molar ratios 2:1, 1:1 and 1:2, almost no free acid is present; absorption bands appear at 1570 cm^{-1} and 1717 cm^{-1} corresponding to ionic pairs X_2 and X_1 (11). This is also reflected in the formation of absorption bands of the ammonium ion (11) at 1950 and 2500 cm^{-1}.

The equilibrium ratio of salts X_2 and X_1 depends on the concentrations of CA and TBA, on the polarity of the solvent, or on the type of the catalyst. With an excess of CA (2:1), a relatively greater amount of the ionic pair X_2 is formed, and the content of X_1 increases with increasing concentration of TBA. More X_1 is formed in the nitrobenzene solution compared with the solution in benzene, and in CA - BDMA mixtures than in the presence of TBA. The concentration ratio of both ionic pairs was determined from integrated areas of the respective bands.

These results support the assumption that the mechanism of reaction in solution involves the equilibrium formation of an acid dimer and salts X_1, X_2 which then react with the epoxide, giving rise to the respective products:

$$2 \; CA \; \rightleftharpoons \; (CA)_2 \tag{11}$$

$$(CA)_2 + A \; \rightleftharpoons \; X_2 \; \rightleftharpoons \; X_1 + CA \tag{12,13}$$

$$E + X_2 \longrightarrow \; product + X_1 \tag{14}$$

$$E + X_1 \longrightarrow \; product + A \tag{15}$$

This hypothesis allows some experimental findings to be explained, assuming that the X_1 species is more active than X_2. The reaction is faster under conditions where the reaction mixture contains more X_1 species, i.e. in nitrobenzene compared with benzene, and with BDMA used as the catalyst compared with TBA.

Induction period

So far, no unequivocal explanation could be proposed for the mechanism of formation of the induction period. In our experiments the induction period was observed in the reaction of a large excess of epoxide with acid. On the other hand, however, in a paper by Härtel (12) an induction period can be perceived in the reaction between PGE and the carboxyl terminated oligobutadiene also in an equimolar mixture. We found that the relative concentration of the catalyst also affects the existence of the induction period. At a high concentration of tertiary amine with respect to the acid, ($[A] \gtrsim [CA]$), no induction period was detected, similarly to the reaction without catalyst or at a very low absolute concentration of amine. The induction period observed in the literature (12) has not been discussed, or has not been observed at all. The absence of the induction period may be caused by a high rate of the reaction under certain conditions, e.g., at high temperature or at an elevated concentration of the reaction components. Then, the initial phase may be too short and cannot, therefore, be experimentally indicated. The specific experimental conditions used by us, i.e. the large excess of epoxide, should also be born in mind.

When interpreting the induction period, the effect of autocatalysis due to the forming product which contains the OH group may be ruled out, because an addition of sec. butanol does not accelerate the reaction. We believe that the formation of variously active species X_1, X_2 may play a certain role. Under common reaction conditions at $[A]/[CA] < 1$, X_2 is predominantly formed. The more active X_1 is formed in the reaction with epoxide (eq. 14), and the reaction is accelerated. With increasing conversion $[A]/[CA]$ increases, and the equilibrium (eq. 13) is shifted to the right, as has been proved by IR spectra. The larger population of more active X_1 then compensates the anticipated decrease in the rate at a high conversion of the acid.

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