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Influence of the reactivity of amine hydrogens and the evaporation of monomers on the cure kinetics of epoxy–amine: kinetic questions

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The mechanism of cure (pregel) of a highly purified diglycidylether of bisphenol A (DGEBA, 99.6% molecular weight = 340 g mol^{-1}) with 1,3-bis(aminomethyl)-cyclohexane (1,3 BAC) was studied. A kinetic model was developed which considered the different reactivities of the amine hydrogens involved in the process. The possibility of simultaneous evaporation of the starting monomers and its influence on the rate of reaction is also taken into account. The rate constants of the elementary process and the general mechanism were determined. The ratio of the elemental rate constants, R (secondary amine to primary amine), is obtained directly from a simple equation, its value being $< 1/2$, decreasing with temperature. Our results show that the noncatalytic path is more important than the catalytic one up to 20% of the reaction. Differential scanning calorimetry (d.s.c.) and gas chromatography–mass spectrometry (g.c.–m.s.) were used for epoxy and amine quantification respectively. G.c–m.s. proved a very powerful technique for quantification of the amine. © 1997 Elsevier Science Ltd.

(Keywords: reactivity ratio; purified system; evaporation)

INTRODUCTION

Many kinetic studies of the mechanism of epoxy–amine reactions have been published[1–9], including excellent revisions of such an interesting and attractive field[10–13]. However, to our knowledge, there is no equation which allows the direct determination of R (ratio of elemental rate constants, secondary amine to primary amine), deduced from a model which simultaneously considers catalytic and noncatalytic paths.

On the other hand, we have observed that, depending on thermal conditions, vapour pressure of monomers and reactivity of the epoxy–amine mixture, partial evaporation of monomers can be very important and can have an adverse influence in both senses: blistering (e.g. laminates) and cure kinetics behaviour. Such a parameter is also included in our kinetic study. From our point of view there are still many contradictory findings and unsolved questions in all technical literature related to the cure of epoxy resins. Among them we can cite:

- Is it important to distinguish the different reactivities of the rate constants primary–secondary amine/secondary–tertiary amine?
- Are the ratios of these constants temperature and/or conversion dependent?
- Are the values given in the technical literature really activation energies and pre-exponential factors?
- Does monomer evaporation influence the rate of reaction?
- Can a hot technique (such as gas chromatography) be used in order to separate and quantify monomers in a reactive mixture?

The most important reasons for choosing highly pure DGEBA/1,3 BAC are: (i) to obtain reproducible results, avoiding the specification variations of a commercial product; (ii) to study the kinetic behaviour of a cycloaliphatic amine which is a mixture of isomers, as probably many, if not all, amines contain one or more saturated rings of six carbon atoms; and (iii) to observe the kinetic behaviour of a practically impurity-free epoxy–amine system.

EXPERIMENTAL

Materials

Highly pure diglycidyl ether of bisphenol A (DGEBA) was used. It was supplied by Gairesa (Spain) and its purity was determined by h.p.l.c. (99.6%)[14–17] and wet analysis (epoxy equivalent 170.01 g equiv^{-1}). This product is a solid white crystalline powder (melting point 44.8°C, heat of fusion, $\Delta H_f \simeq 85\,\mathrm{J\,g^{-1}}$ (28.9 kJ mol^{-1}). In *Figure 1*, d.s.c. analysis shows a very well defined peak.

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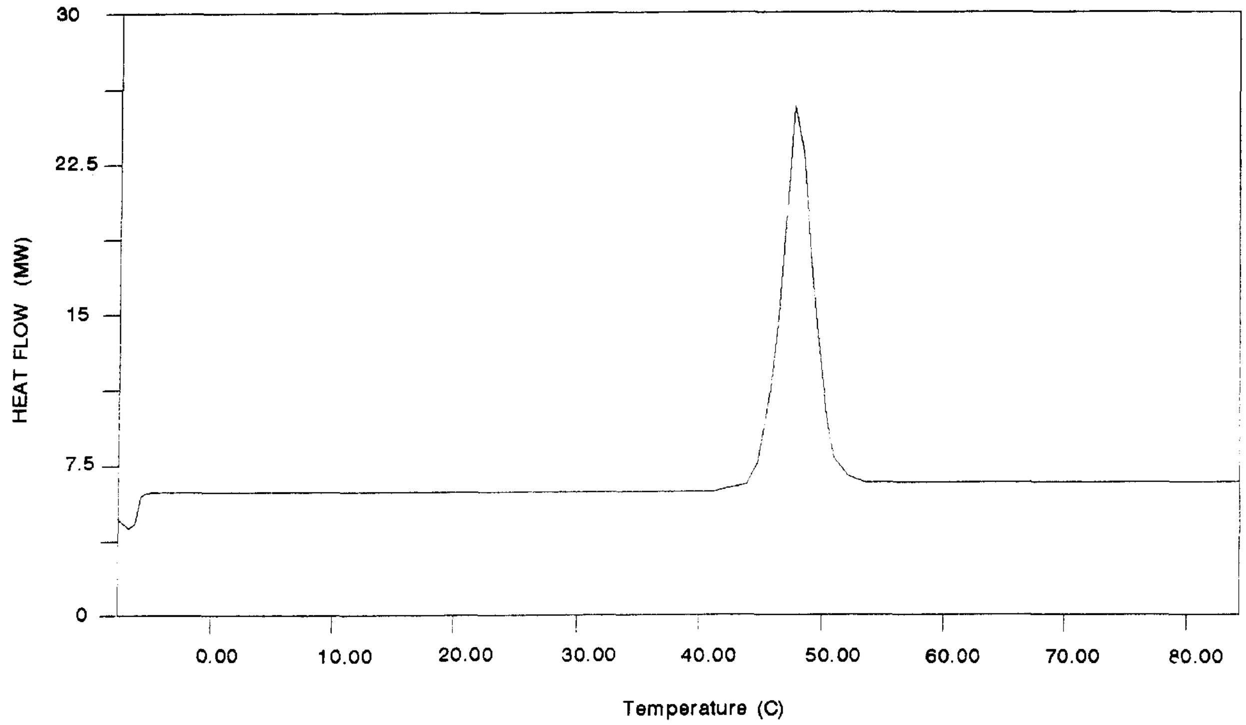


Figure 1 D.s.c. melting endotherm of DGEBA (purity $\simeq 99.6\%$)

The amine used was 1,3-bis(aminomethyl)-cyclohexane (1,3 BAC, Aldrich Co.) with 99% purity. This purity was tested by gas chromatography and wet analysis, finding that this product is a mixture of *cis–trans* isomers (approximately 76/24%). The details of chromatographic study will be given later.

Sample preparation

Stoichiometric amounts of DGEBA/1,3BAC were used. The resin was previously melted and both weighing and mixing took place in an N_2 atmosphere with silica gel as desiccant.

Techniques

Differential scanning calorimetry analysis was conducted with a Perkin-Elmer DSC-7 coupled to a 7700 professional computer with isothermal and dynamic software. As the load sample temperature was 0°C a cryogenic device was necessary. More details about calibration procedure and thermal conditions can be found elsewhere[18,19].

Dynamic experiments were carried out to obtain the maximum value of enthalpy of reaction (ΔH_0), at $10\,\mathrm{K\,min^{-1}}$, as reference to evaluate the extent of reaction (α) from isothermal experiments. It is important to point out that the value of enthalpy of reaction, $\Delta H = 560\,\mathrm{J\,g^{-1}} \simeq 115\,\mathrm{kJ\,eq^{-1}}$, is one of the highest values found in the references for bisphenol A epoxy resin/amines[13].

$$\alpha = 1 - \frac{(\Delta H)_{T,t}}{\Delta H_0}$$

where $\Delta H_{T,t}$ = enthalpy of reaction at T (isothermal temperature) and t (time).

Isothermal runs were carried out at 50, 60, 80 and 90°C, and performed as follows. For each test, samples contained in open aluminium pans were placed in the d.s.c. at 0°C until the d.s.c. signal was completely stable. Samples were then heated at $100\,\mathrm{K\,min^{-1}}$. After recording the first run at the selected temperature, a second 'blank' was carried out to minimize transient interference in the first seconds of the isothermal reaction and later subtracted from the first run through the computer. The weight of samples was $5.5 \pm 0.2\,\mathrm{mg}$.

Gas chromatography–mass analysis was conducted with an Autosystem gas chromatograph, Perkin-Elmer, equipped with a 60 m non-polar capillary colum (i.d. = 0.22 mm) coupled with a Q-Mass 910 spectrometer through a heating transfer line, also Perkin-Elmer. Chromatographic conditions were found to be critical in order to avoid any previous reaction in the injection block and/or in the column. Optimum results (without prereaction) were found for the following conditions: injection block temperature 220°C; initial oven temperature 50°C; final oven temperature 200°C; heating rate (thermal ramp) $7^\circ\mathrm{C\,min^{-1}}$; helium flow $0.8\,\mathrm{ml\,min^{-1}}$; pressure $22\,\mathrm{lb\,in^{-2}}$; transfer line temperature 220°C. The injection block was equipped with a split liner (i.e. = 4 mm) packed with 15 mm of glass wool, split ratio 1/12.

Approximately $5.5 \pm 0.2\,\mathrm{mg}$ of the reactive mixtures contained in open aluminium pans were placed in the d.s.c. holder at 0°C (which was also used as a thermal controller) and programmed exactly as described before for d.s.c. measurements. At the established temperatures the samples were taken out of the d.s.c. at different, previously programmed times. The samples were dissolved in 2.5 ml of methanol carrying 80 ppm of limonene (internal standard) in an ultrasonic bath. 1 μl of the solution was injected into the chromatograph. In order to quantify the amine a calibration line was performed. Solutions in methanol containing 80 ppm of limonene with different 1,3 BAC concentrations (410, 320, 209, 124 and 82 ppm) were used for this purpose. The reactivities of the isomers are not necessarily the same, so the quantification was established by summing both areas. The calibration line was done by plotting the ratio of areas (amine-*cis* + amine-*trans*/limonene) against the ratio of concentrations ([1.3 BAC]/[limonene]).

Figure 2 shows a typical g.c.–mass chromatogram (for 124 ppm of 1,3 BAC) where both isomers and their respective mass spectra can be observed. The quantification, as stated, was carried out within the limits of retention times. The noise included between the two peaks is completely negligible. We found more reproducible results from TIC (total ion chromatogram) than from the maximum intensity peaks ($m/z = 30$ and 108 for *cis* and *trans* respectively). Both peaks were identified by the NIST library.

Figures 3 and *4* show the experimental results of the evolution of the reaction between the epoxy resin and the amine at the two limit temperatures (50 and 90°C). It is important to point out that, in order to obtain reproducible results, all chromatographic experiments were repeated four or five times and calibration lines were accepted only when the relative standard deviations were less than 4%. To be sure that no previous reaction in the injection block occurred, a blank (reactive mixture dissolved in methanol with 80 ppm of limonene) was injected between experiments for each selected temperature.

Thermogravimetry analysis was conducted with a

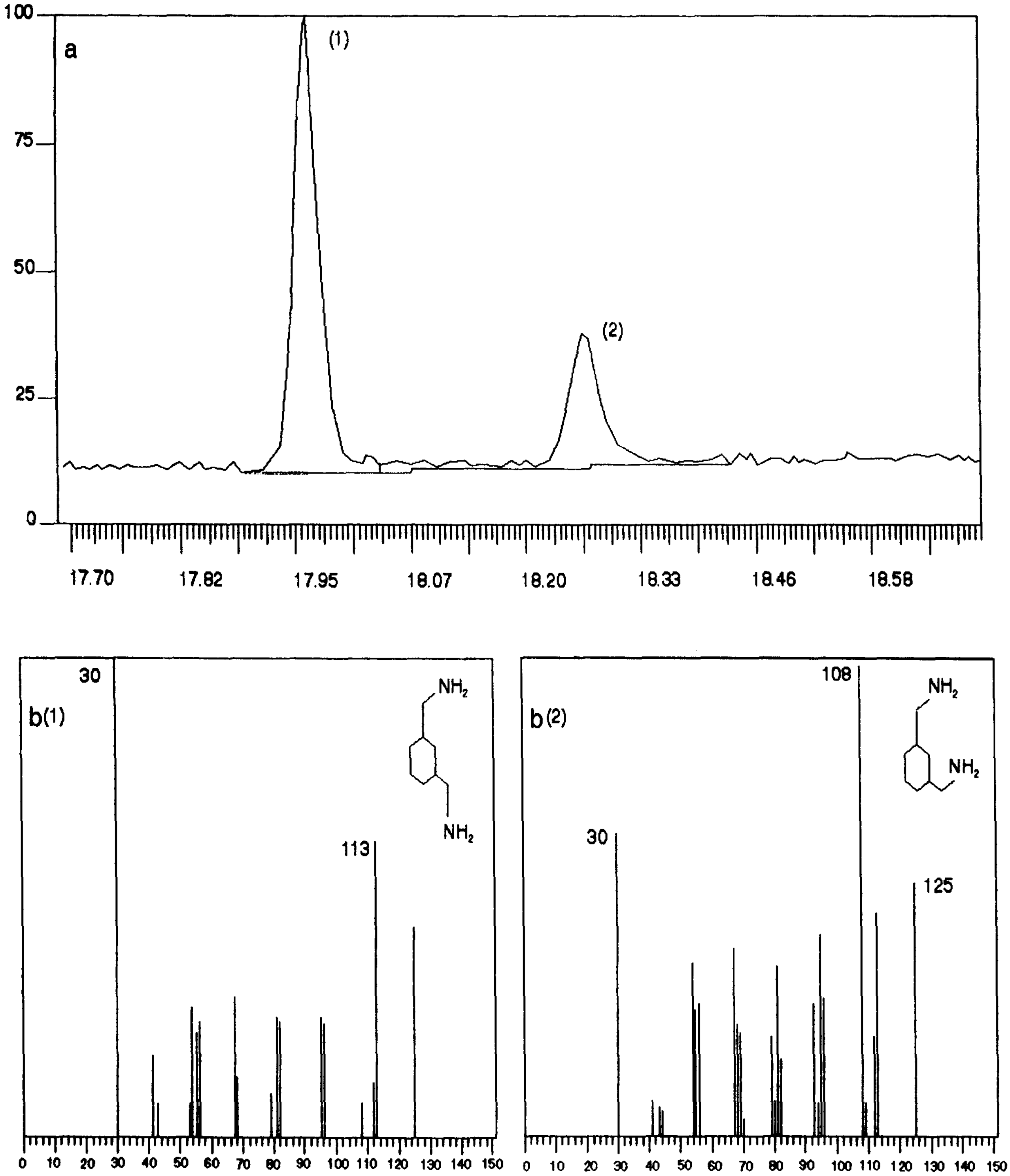


Figure 2 G.c.–mass chromatogram peaks of 124 ppm of 1,3 BAC: a(1), *cis*-1,3 BAC; a(2), *trans*-1,3 BAC; b, mass spectra *cis–trans*, respectively

Perkin-Elmer TGA-7 coupled to a PC-IBM-386 computer, with isothermal and dynamic software. The calibration was done following the TGA-7 procedure manual, using high purity elements for the determination of Curie temperatures (Alumel and perkalloy).

About 5.5 ± 0.2 mg of the reactive mixture was placed at room temperature on the thermobalance pan, and the experiments were programmed with the isothermal software for each chosen temperature. In order to avoid any previous evaporation the mixture was cooled to 10–12°C, and was weighed when equilibrium was reached just before the start of the runs, which were programmed to increase the temperature at different rates between 60 and 80 K min^{-1} (depending on the test temperature). The runs were stopped when a negligible loss of weight signal was detected; the cure has then significantly taken place.

RESULTS AND DISCUSSION

Model

As stated, we consider in our model that the epoxy–amine reaction can follow two different but simultaneous paths; uncatalysed and catalysed (autocatalysed). Horie's model[20] has already considered both possibilities, but it assumes the equal reactivity of all amine hydrogens. Our model is developed taking into account that:

(1) the impurities present in the epoxy resin and/or amine are not necessarily the catalysts of the epoxy–amine reaction;
(2) not necessarily all amine hydrogens have the same reactivities;
(3) the partial evaporation of monomers influences the rate of reaction.

where A_1, A_2, A_3, E and CAT represent primary, secondary and tertiary amines, epoxy and catalyst respectively.

This model does not consider either homopolymerization or etherification reactions. The first one occurs only in the presence of Lewis acid or base type catalyst[21,22], and the second one takes place only at high temperatures and degrees of cure[7,23–25]. In our study, low degrees and temperatures of cure and very highly pure products with no external catalysts were used.

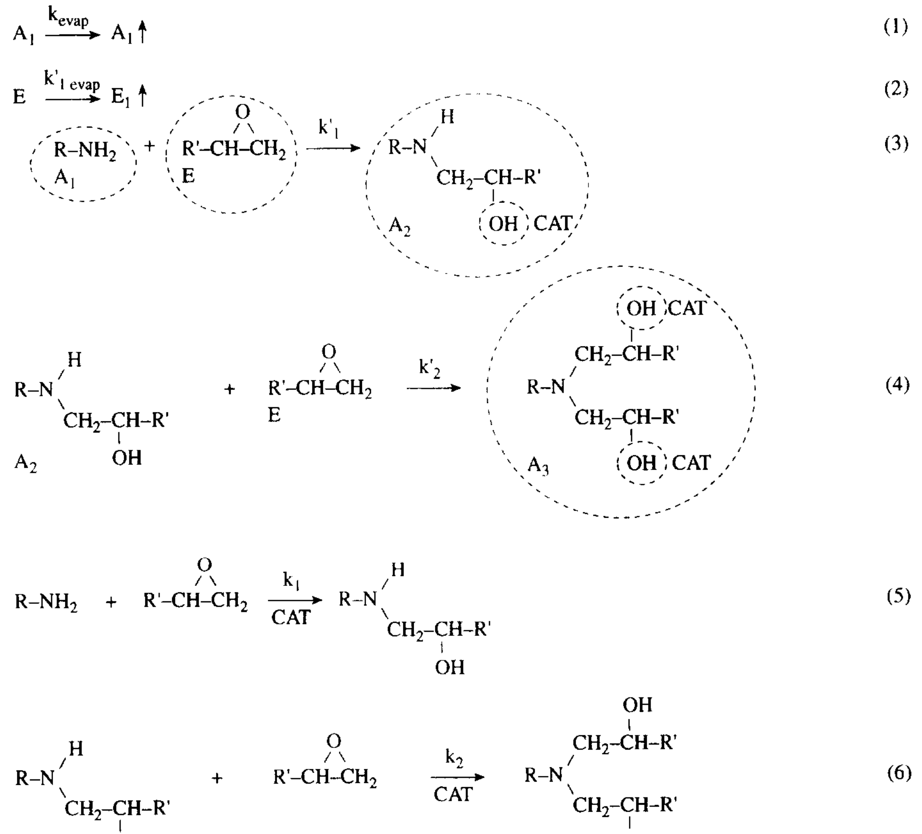
We would also like to point out that Rozenberg[13] finds a third overall order for the non-catalysed path (second order in amine). We also developed a mechanism considering this possibility, but we did not find any good theoretical or experimental agreement. From our point of view it is difficult to justify a catalytic effect of A_1 (in the whole course of the reaction) as the concentration of primary amine $[A_1]$ decreases much faster than the epoxy group (see *Figures 3* and *4*).

Rate equations

According to the kinetics scheme, equations (1)–(6), the following rate equations are obtained:

$$-\frac{\mathrm{d}[A_1]}{\mathrm{d}t} = k_{\mathrm{evap}}[A_1] + k_1'[A_1][E] + k_1[A_1][E][CAT] \quad (7)$$

$$-\frac{\mathrm{d}[E]}{\mathrm{d}t} = k_{\mathrm{evap}}'[E] + k_1'[A][E] + k_2'[A_2][E] + k_1[A_1][E][CAT] + k_2[A_2][E][CAT] \quad (8)$$



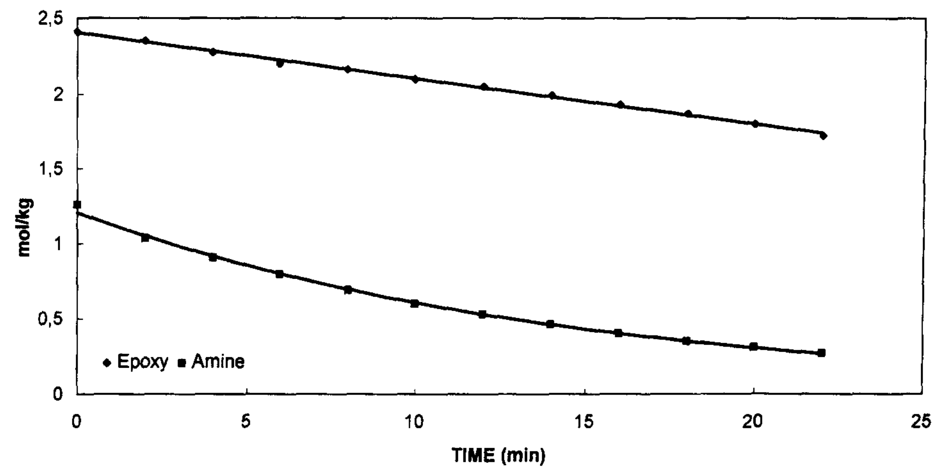


Figure 3 Variation of concentration against time at 50°C

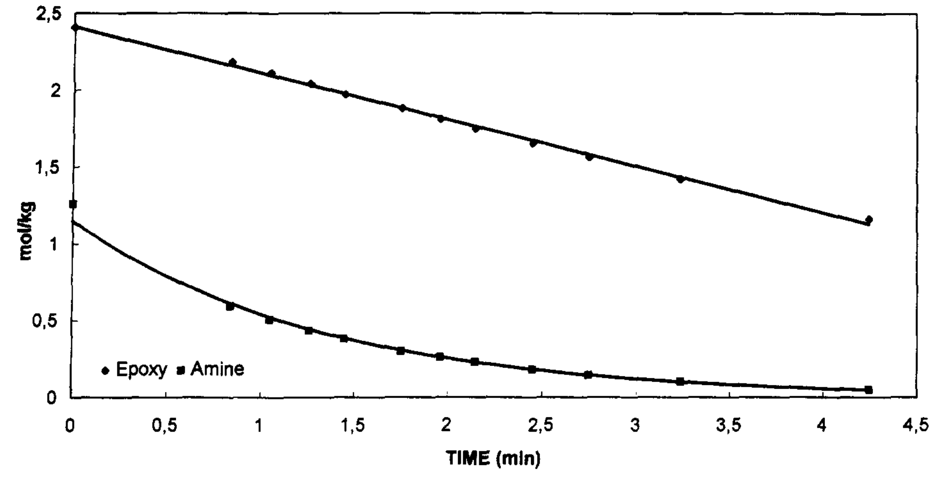


Figure 4 Variation of concentration against time at 90°C

$$\begin{aligned}\frac{d[\mathrm{CAT}]}{dt} = {} & k_1'[\mathrm{A}_1][\mathrm{E}] + k_1[\mathrm{A}_1][\mathrm{E}][\mathrm{CAT}] - k_2'[\mathrm{A}_2][\mathrm{E}] \\ & - k_2[\mathrm{A}_2][\mathrm{E}][\mathrm{CAT}] + 2k_2'[\mathrm{A}_2][\mathrm{E}] \\ & + 2k_2[\mathrm{A}_2][\mathrm{E}][\mathrm{CAT}]\end{aligned} \qquad (9)$$

and, from equations (8) and (9):

$$-\frac{d\mathrm{E}}{dt} = k'_{\mathrm{evap}}[\mathrm{E}] + \frac{d[\mathrm{CAT}]}{dt} \qquad (10)$$

Mass balances

Considering equations (1)–(6), the following mass balances can be established:

$$[\mathrm{A}_1]_0 = [\mathrm{A}_1]_{\mathrm{evap}} + [\mathrm{A}_1] + [\mathrm{A}_2] + [\mathrm{A}_3] \qquad (11)$$

$$[\mathrm{E}]_0 = [\mathrm{E}]_{\mathrm{evap}} + [\mathrm{E}] + [\mathrm{A}_2] + 2[\mathrm{A}_3] \qquad (12)$$

$$[\mathrm{CAT}] = [\mathrm{A}_2] + 2[\mathrm{A}_3] = [\mathrm{E}_0] - [\mathrm{E}] - [\mathrm{E}]_{\mathrm{evap}} \qquad (13)$$

where $[\mathrm{A}_1]_0$ is the initial concentration of primary amine, $[\mathrm{A}_1]_{\mathrm{evap}}$ the concentration of evaporated amine, $[\mathrm{A}_2]$ concentration of secondary amine, $[\mathrm{A}_3]$ concentration of tertiary amine, $[\mathrm{E}_0]$ initial concentration of epoxy, $[\mathrm{E}]_{\mathrm{evap}}$ concentration of evaporated epoxy and [CAT] concentration of catalyst.

Model development and rate equations

From equation (7), and defining the extension of reaction, α,

$$\alpha = \frac{[\mathrm{E}_0] - [\mathrm{E}]}{[\mathrm{E}_0]}$$

as

$$\begin{aligned}-\frac{d[\mathrm{A}_1]}{dt} = {} & [\mathrm{A}_1](k_{\mathrm{evap}} + k_1'([\mathrm{E}_0] - [E_0]\alpha) \\ & + k_1(([\mathrm{E}_0] - [\mathrm{E}_0]\alpha)(\alpha[\mathrm{E}_0] - [\mathrm{E}]_{\mathrm{evap}}))\end{aligned}$$

which leads to

$$\begin{aligned}-\frac{d\mathrm{A}_1/dt}{[\mathrm{A}_1]} - k_{\mathrm{evap}} = {} & K_1'(1-\alpha) + K_1(1-\alpha) \\ & \times \left(\alpha - \frac{[\mathrm{E}]_{\mathrm{evap}}}{[\mathrm{E}_0]}\right)\end{aligned} \qquad (14)$$

or

$$\frac{-\dfrac{\mathrm{d}[\mathrm{A}_1]/\mathrm{d}t}{[\mathrm{A}_1]} - k_{\mathrm{evap}}}{(1-\alpha)} = K_1' + K_1\left(\alpha - \frac{[\mathrm{E}]_{\mathrm{evap}}}{[\mathrm{E}_0]}\right) \qquad (15)$$

where $K_1' = k_1'[\mathrm{E}_0]$ and $K_1 = k_1[\mathrm{E}_0]^2$

From equation (8), and taking into account the mass balance equations (11)–(13),

$$\begin{aligned}\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (1-\alpha)[k_{\mathrm{evap}}' &+ k_1'[\mathrm{A}_1] + k_2'([\mathrm{E}]_{\mathrm{evap}} - [\mathrm{E}_0]\alpha \\ &+ 2([\mathrm{A}_1]_0 - [\mathrm{A}_1] - [\mathrm{A}_1]_{\mathrm{evap}})) \\ &+ k_1[\mathrm{A}_1]([\mathrm{E}_0]\alpha - [\mathrm{E}]_{\mathrm{evap}}) + k_2([\mathrm{E}]_{\mathrm{evap}} \\ &- [\mathrm{E}_0]\alpha + 2([\mathrm{A}_1]_0 - [\mathrm{A}_1] \\ &- [\mathrm{A}]_{\mathrm{evap}}))([\mathrm{E}_0]\alpha - [\mathrm{E}]_{\mathrm{evap}})]\end{aligned} \qquad (16)$$

If we assume that the ratios k_2/k_1 and k_2'/k_1' are independent of the path (catalytic, non-catalytic) the next equation is derived:

$$\begin{aligned}\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (1-\alpha)[k_{\mathrm{evap}}' &+ K_1'\lambda + K_1'R(B - 2\lambda - 2\phi_{\mathrm{A}} + \phi_{\mathrm{E}} \\ &- \alpha) + K_1\lambda(\alpha - \phi_{\mathrm{E}}) + K_1R(B - 2\lambda - 2\phi_{\mathrm{A}} + \phi_{\mathrm{E}} \\ &- \alpha)(\alpha - \phi_{\mathrm{E}})]\end{aligned} \qquad (17)$$

where $K_1' = k_1'[\mathrm{E}_0]$, $K_1 = k_1[\mathrm{E}_0]^2$, $\phi_{\mathrm{E}} = [\mathrm{E}]_{\mathrm{evap}}/[\mathrm{E}_0]$, $\phi_{\mathrm{A}} = [\mathrm{A}]_{\mathrm{evap}}/[\mathrm{E}_0]$, $\lambda = [\mathrm{A}_1]/[\mathrm{E}_0]$, $B = 2[\mathrm{A}_1]_0/[\mathrm{E}_0]$ and $R = k_2/k_1 = k_2'/k_1'$.

It is noteworthy that, according to the mechanism, R is constant with the conversion. Equation (17) describes the evolution of the reaction for a general mechanism, and it can be simplified under different considerations:

(1) If no evaporation takes place, $\phi_{\mathrm{E}} = 0$, $\phi_{\mathrm{A}} = 0$, $k_{\mathrm{evap}}' = 0$; then

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (\lambda + R(B - 2\lambda - \alpha))(1-\alpha)(K_1' + K_1\alpha) \qquad (18)$$

(2) Also, if the resin and the amine are in stoichiometric relation, $B = 2[\mathrm{A}_1]_0/[\mathrm{E}_0] = 1$.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (\lambda + R(1 - 2\lambda - \alpha))(1-\alpha)(K_1' + K_1\alpha) \qquad (19)$$

As stated, R represents the ratio of rate constants for hydrogens in primary and secondary amine groups, and its ideal value is frequently a matter of much controversy. For some authors[1,7,26,27] this value is unity and for others[8,19,20,28–31] 1/2. Both may be correct, but they have to agree with the kinetic and mass considerations *for each proposed kinetic model*. If in equation (19) we put $R = 1/2$, then

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (1/2K_1' + 1/2K_1\alpha)(1-\alpha)^2 \qquad (20)$$

Equation (20) is the very well known expression derived from the Horie model. This and other expressions which are 'generalizations' of such an equation, $\mathrm{d}\alpha/\mathrm{d}t = (K_1' + K_1\alpha^m)(1-\alpha)^n$, where m and n are adjustable parameters, have been extensively applied by many investigators[1–4,9,18–20,28,32–34]. Three important remarks must be made concerning this equation.

(1) The rate constants of our model equation (19) are double those defined in the Horie model, $\mathrm{d}\alpha/\mathrm{d}t = (K_1' + K_1\alpha)(1-\alpha)^2$, but the elemental constants have the same meaning; $K_1' = 1/2k_1'[\mathrm{E}_0]\ c_0, c_0$ being the initial concentration of OH groups, and $K_1 = 1/2k_1[\mathrm{E}_0]^2$.

(2) According to our definition the ideal value of R is 1/2. $R > 1/2$ implies that either the hydrogen of the substituted amine (A_2) is more reactive than that of the nonsubstituted one (A_1) or the proposed kinetic model is inadequate. $R < 1/2$ implies that the reactivity of the secondary hydrogen (A_2) is less than that of the primary one.

(3) To eliminate λ in equation (19), necessarily $R = 1/2$. The Horie equation can *only* be applied in such an ideal case. It is noteworthy that the necessary substitutions to obtain this equation come from the *mass balances*.

Rate constants

The rate constants were obtained through equation (15) by plotting the first term of this equation against $(\alpha - ([\mathrm{E}]_{\mathrm{evap}}/[\mathrm{E}_0]))$; K_1' and K_1 are calculated from the intercept and the slope. For this purpose we need to determine k_{evap} and $[\mathrm{E}]_{\mathrm{evap}}$. While $[\mathrm{E}]_{\mathrm{evap}}$ is easily obtained from thermogravimetric analysis (t.g.), k_{evap} can be more difficult to evaluate because evaporation and reaction are parallel events. For this reason we carried out t.g. experiments not only for the reactive mixture, but also for a mixture of the amine and a high boiling point plasticizer (dioctyl-phthalate) with the same amine concentration. As the dioctyl-phthalate is not necessarily an inert medium and could react with such a strong amine, another, 'non-saponifiable' plasticizer was tested. This was di-(phenoxy-ethyl)-formal (Desavin from Bayer AG), and we did not observe any noticeable difference. As the volatility of the amine could be influenced by the different hydrogen bonding between the ester and the real reacting medium, we carried out several preliminary 'blank' tests using different products, concentrations and thermal conditions. Of course we found variations, but at the beginning of the reaction (we only need to know when the epoxy–amine reaction starts in order to evaluate k_{evap}, in fact the values are obtained from the epoxy–amine t.g. data) we found reproducible results using the aforementioned plasticizer. *Figure 5* shows the difference between the two systems at one temperature (80°C). From a series of experiments carried out with different blanks made with the resin alone and with resin/plasticizer in several proportions, we were able to establish, for the thermal range used in this study, that only the evaporation of the amine is important. The epoxy evaporation, $[\mathrm{E}]_{\mathrm{evap}}$, is quite negligible.

From equation (1) $-\mathrm{dA}_1/\mathrm{d}t = k_{\mathrm{evap}}[\mathrm{A}_1]$, which in integrated form leads to

$$\ln\left(\frac{[\mathrm{A}_1]_0}{[\mathrm{A}_1]_0 - x}\right) = k_{\mathrm{evap}}t \qquad (21)$$

where x is the concentration (mol kg^{-1}) of the evaporated amine. *Figure 6* shows plots of $\ln([\mathrm{A}_1]_0/[\mathrm{A}_1]_0 - x)$ against time. Deviations from linearity are related to the beginning of the reaction. According to this, only a few points (depending on the temperature) can be taken to obtain k_{evap}. In order to minimize the errors, we have obtained values of k_{evap} from the tangents of the curves at the origin. *Table 1* shows the values of k_{evap} at the four test temperatures. With respect to the evaluation of k_{evap}, it is very important to point out that all values obtained

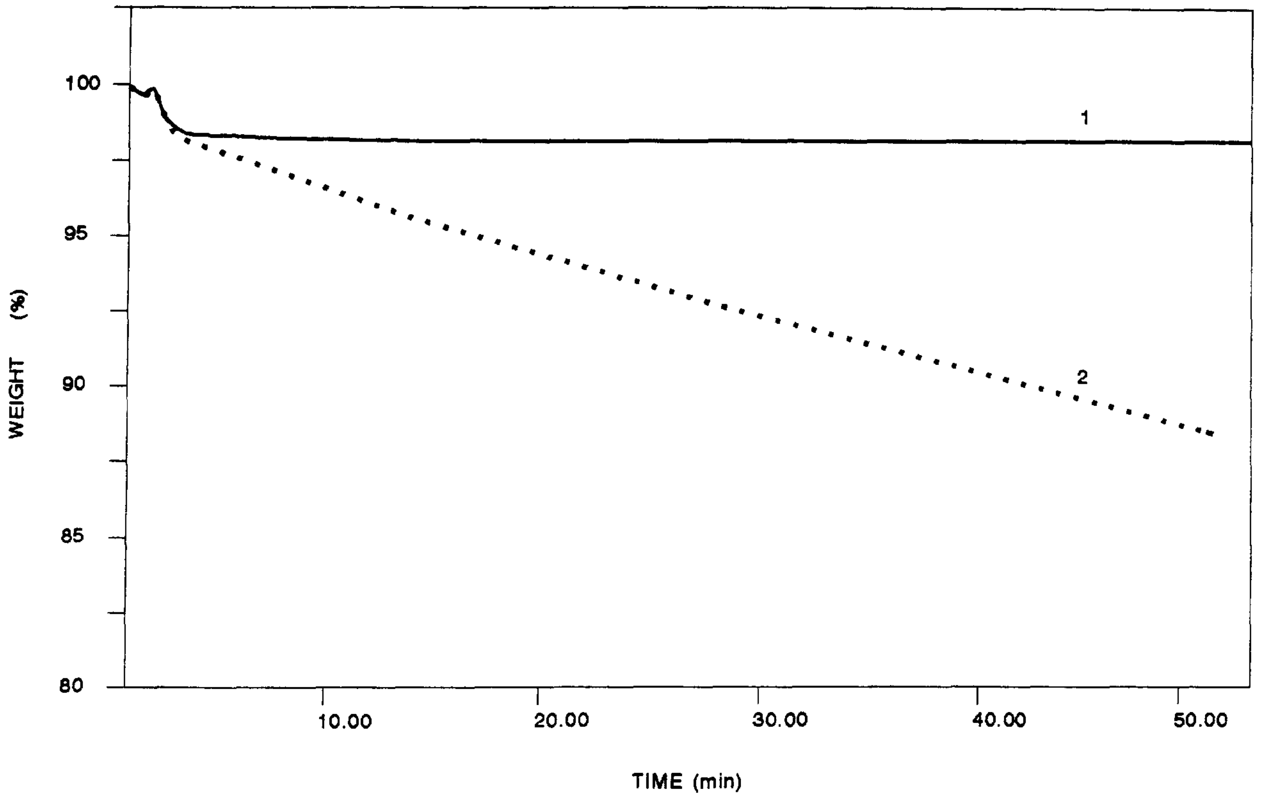


Figure 5 T.g. isothermal curves: 1, epoxy/amine; 2, dioctyl-phthalate/amine at 80°C

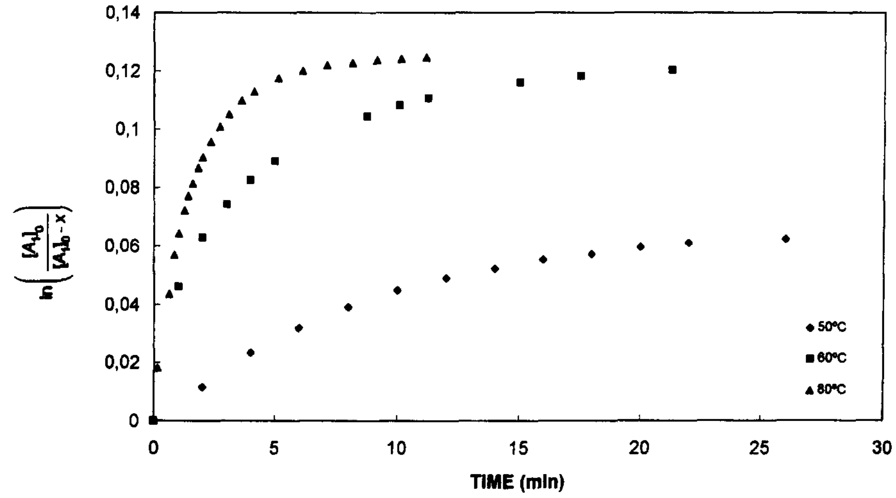


Figure 6 Plots for evaluation of k_{evap} at 50, 60 and 80°C

Table 1 Kinetic parameters

	T (°C)					
	50	60	80	90	E_a (kJ mol^{-1})[a]	A[b]
k_{evap} (s^{-1})	8.20×10^{-5}	1.63×10^{-4}	9.40×10^{-4}	1.15×10^{-3}	68.5	1.1×10^{7}
K_1 (s^{-1})	2.30×10^{-3}	3.70×10^{-3}	1.25×10^{-2}	1.90×10^{-2}	52.8	8.3×10^{5}
K_1' (s^{-1})	4.20×10^{-4}	1.30×10^{-3}	3.80×10^{-3}	6.00×10^{-3}	62.3	6.7×10^{6}
R	0.43	0.41	0.37	0.36		
k_1 (kg^2 mol^{-2} s^{-1})	3.90×10^{-4}	6.26×10^{-4}	2.11×10^{-3}	3.21×10^{-3}	52.8	1.4×10^{5}
k_1' (kg (mol s)$^{-1}$)	1.73×10^{-4}	5.35×10^{-4}	1.56×10^{-3}	2.47×10^{-3}	62.3	2.7×10^{6}
k_2 (kg^2 mol^{-2} s^{-1})	1.68×10^{-4}	2.57×10^{-4}	7.81×10^{-4}	1.15×10^{-3}	48.1	1.1×10^{4}
k_2' (kg (mol s)$^{-1}$)	7.44×10^{-5}	2.19×10^{-4}	5.77×10^{-4}	8.90×10^{-4}	57.8	2.2×10^{5}

[a] E_a = activation energy
[b] A = pre-exponential factor

have to refer to the experimental conditions. Among them we consider external pressure (in our case atmospheric pressure, which was practically constant during all experiments $\simeq 1020 \pm 15$ mbar), surface area of the unit (we used circular pans, diameter = 5 mm), and thickness of the layer (approximately 60 μm).

Figure 7 shows a plot of equation (15) for the four temperatures studied. Considering $[\mathrm{E}]_{\mathrm{evap}} = 0$ for the reason mentioned above, from the linearity of the plot it can be deduced that equation (15) is well fulfilled.

From the general rate equation (17), and considering that $k'_{\mathrm{evap}} = 0$, $\phi_{\mathrm{E}} = 0$ and that for stoichiometric conditions $B = 1$,

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (\lambda + R(1 - 2\lambda - 2\phi_{\mathrm{A}} - \alpha))(1 - \alpha)(K'_1 + K_1\alpha) \tag{22}$$

This equation allows us to calculate R after integration, introducing the values of K_1 and K'_1. In *Table 1* the values of K_1, K'_1 and R for the four experimental temperatures are given after fitting equation (22) to the experimental points; we can also see the values of the four elemental rate constants determined from R, K_1, K'_1, the activation energies and the pre-exponential factors.

We must emphasize the excellent chemical–physical sense of the values obtained. The activation energies of the catalytic mechanism are lower than those of the noncatalytic. The values of the activation energies for the formation of tertiary amines are lower than those for the secondary amines, probably due to the stabilization of the activated complex through the OH group. The pre-exponential factors are lower too, which is quite consistent with the collisional efficiencies against active sites, taking into account the great size of the secondary amines in relation to the primary amines.

The values of R agree and disagree with values given by different authors (in this respect it is worth observing that R varies by more than one for different epoxy–aromatic amine systems, collected by Mijovic *et al.*[35]). However, with respect to aliphatic polyamines, it is usually accepted that R is close to 1/2[11,20,29]; substitution effects are more significant in the aromatic amines, the cycloaliphatic polyamines probably being an intermediate case, but the dependence of R on the temperature is not considered in such references.

It can be seen in *Table 1* that R decreases when the temperature increases and the value obtained $< 1/2$; its tendency with temperature (negative substitution effect) again agrees with the findings of some authors[36–39] but disagrees with others[40–42]. The value of R may be directly related to the network morphology. If $R = 1/2$ a randomly crosslinked network would be expected. If $R \ll 1/2$ a predominance of linear chains should be expected; if $R < 1/2$, a random distribution of linear and crosslinked chains is the most probable path. These facts are, experimentally, well known by applicators and formulators of epoxy resins. They normally start the cure at a lower temperature than the final cure temperature. The temperature is then increased through a previously established cure ramp, depending on the particular epoxy system. The aim of such a thermal ramp is to achieve the optimum mechanical and chemical properties. On the basis of our model, where $R = 1/2$ represents the ideal case, it is difficult to justify values of $R > 1/2$, at least from a purely morphological point of view.

The values given in *Table 1* for the rate constants indicate a relative rate of only about 2 or less for catalysed compared to non-catalysed processes. For most systems encountered in the literature, the catalysed process is commonly around 30–50 times faster than the non-catalysed[1,13], but these authors used aromatic amines while we used a much more reactive amine.

The value of the ratio of rate constants is directly related to the reactivity of the system. The difference between the activation energy of the non-catalysed and the catalysed path obtained for our system is lower than for aromatic amine systems. The activation energy for the catalysed path is similar for all epoxy–amine systems; it is the non-catalysed path which strongly depends on each particular amine.

Reaction rates

Figure 8 compares the experimental d.s.c. results with the theoretical ones obtained from equation (22) up to ~ 50% conversion. The agreement, at least from our point of view, is highly satisfactory. Conversions above 50% are not included in the aim of this work.

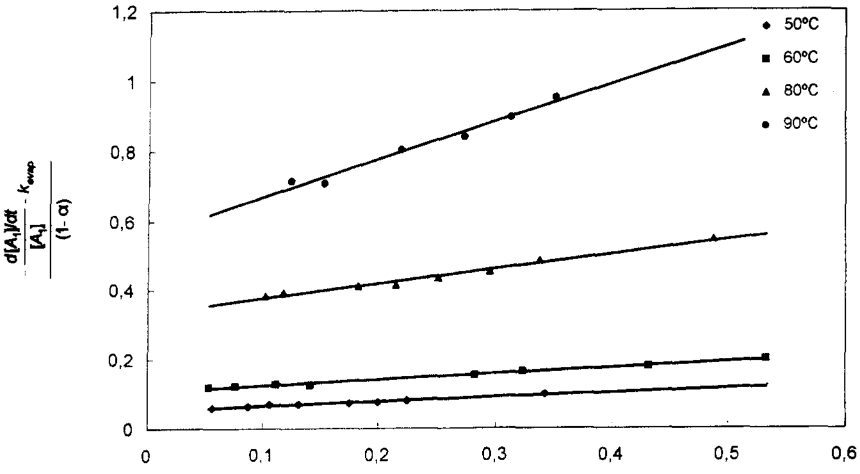


Figure 7 Evaluation of the rate constants by equation (15), at 50, 60, 80 and 90°C

Equation (22) would be expected to operate between two extremes. For $\lambda \rightarrow [A_1]_0/[E_0]$, which corresponds to the beginning of the reaction, and for the other extreme, where $\lambda \rightarrow 0$, practically the end of the chemically controlled process, this equation can also be expressed by the sum of two terms in the following way:

$$\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dt}\right)_1 + \left(\frac{d\alpha}{dt}\right)_2$$

$$\left(\frac{d\alpha}{dt}\right)_1 = \lambda(1-\alpha)(K_1' + K_1\alpha)$$

$$\left(\frac{d\alpha}{dt}\right)_2 = R(1-2\lambda-2\phi_A-\alpha)(1-\alpha)(K_1'+K_1\alpha) \tag{23}$$

then

$$\frac{(d\alpha/dt)_1}{(d\alpha/dt)_2} = \frac{\lambda}{R(1-2\lambda-2\phi_A-\alpha)} \tag{24}$$

A plot of the right-hand side of equation (24) against α can be seen in *Figure 9*. It is noteworthy that when $t \rightarrow 0$, $\alpha \rightarrow 0$, $\lambda \rightarrow 1/2$, $\phi_A \rightarrow 0 \Rightarrow (d\alpha/dt)_1/(d\alpha/dt)_2 \rightarrow \infty$. On the other hand, when $\lambda \rightarrow 0 \Rightarrow$ equation (24) $\rightarrow 0$.

If we further assume in equation (23) that $\lambda = 0$, then

$$\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dt}\right)_2 = R(1-2\phi_A-\alpha)(1-\alpha)(K_1'+K_1\alpha) \tag{25}$$

For $R = 1/2$ and $\phi_A = 0$ this equation is converted again into the Horie equation. However, for $R \neq 1/2$, apart from the considerations previously stated, great mistakes can be made in the evaluation of rate constants by application of this equation. In fact, one can see that in this case one evaluates the products K_1R and $K_1'R$. R does not necessarily take the same values for all epoxy–amine systems and, according to our results, is temperature dependent.

Figure 9 allows us to estimate [OH] when the mechanism changes. For $\alpha = 0.2$ both mechanisms take the same value. As $\alpha = [E_0] - [E]/[E]_0$, from the mass balances $[CAT] = [OH] = [E_0] - [E] = 0.486\,mol\,kg^{-1}$ ($[E]_{evap} = 0$). This interesting, quantitative finding does not agree with the Shechter[21] and Smith[43] postulates. These authors respectively consider that this reaction goes through either a termolecular concerted mechanism or a rate-controlling step which involves only two-body collisions. They also assume that

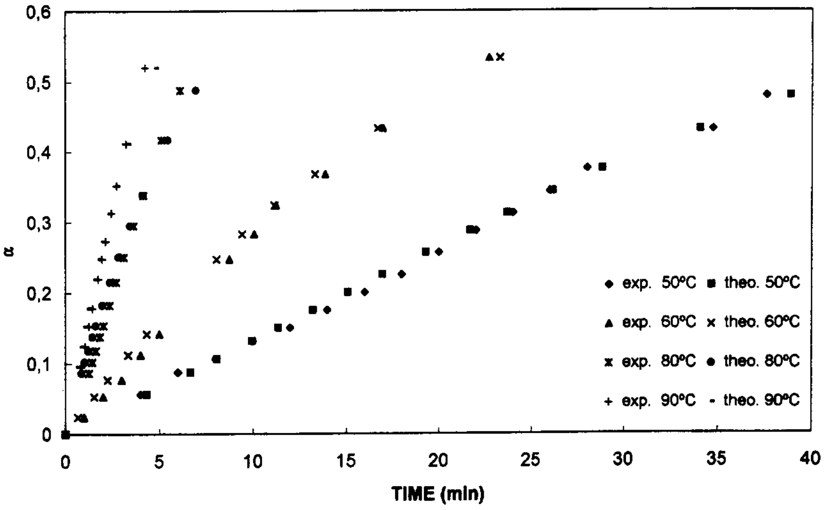


Figure 8 Comparison between theoretical and experimental results (conversion/time) at 50, 60, 80 and 90°C

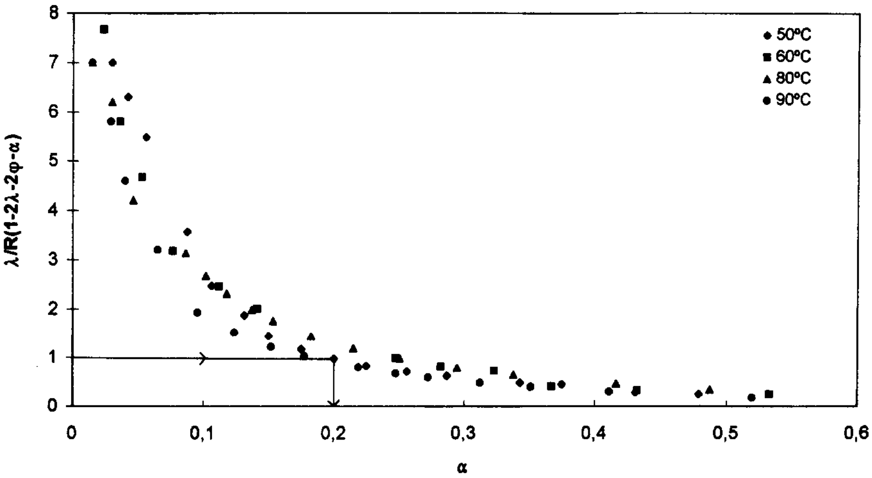


Figure 9 Variation of the ratio of reaction rates (noncatalytic/catalytic) against conversion at 50, 60, 80 and 90°C

the presence of initial impurities (water, glycols, alcohols or in general –H donors) markedly accelerates the course of the epoxy–amine reaction, such impurity being the third molecule involved in the termolecular mechanism. From our experimental results, and assuming that we have no contaminants at all in our highly purified products, we can say that the epoxy–amine reaction starts with an order two (initiation) and becomes order three (propagation) when [OH] is close to 20% [E_0].

It is worthwhile to point out the significance of the evaporation of the amine on the rate of reaction during the course of the reaction. For $\alpha_{50} = 0.48$, $\lambda_{50} \simeq 0.04$, $2\phi_{50} \simeq 0.06$; for $\alpha_{60} = 0.53$, $\lambda_{60} \simeq 0.03$, $2\phi_{60} \simeq 0.12$; for $\alpha_{80} = 0.49$, $\lambda_{80} \simeq 0.04$, $2\phi_{80} \simeq 0.13$ and for $\alpha_{90} = 0.52$, $\lambda_{90} \simeq 0.04$, $2\phi_{90} \simeq 0.13$. The evaporation term, $2\phi_A$, is not at all negligible when the reaction reaches conversion values above 20% and is obviously temperature dependent. Evaporation decreases the rate of reaction up to 25–30% of the α value.

CONCLUSIONS

We have carried out a study of the kinetics of cure for an epoxy–amine system. From the equations derived from our theoretical model the ratio of elementary rate constants (R), as well as the rate constants themselves, are obtained directly. The effects on rate of reaction of the evaporation of monomers are shown; evaporation becomes very important when the reaction reaches values of conversions above 20–25%.

We want to point out that it was not our aim to obtain a superposition of theoretical and experimental curves. One could do that with a multiparameter equation, e.g. a phenomenological equation, in which the parameters have not necessarily any physical meaning at all. Our main idea was to obtain the best parameters according to the established mechanism and to observe whether this mechanism is able to explain the main features of the experimental data obtained.

Our results also show that the Horie model is an excellent and suitable one for specific cases, but it cannot be used indiscriminately because the parameters obtained may not have a physical meaning.

To end, and considering the more than one hundred g.c.–m.s. experiments carried out in this study, we can say that such a technique is excellent for quantification of amines in epoxy–amine mixtures.

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