

Kinetic Effects on the Impurities in Epoxy-Resin/*m*-Xylylenediamine Reaction

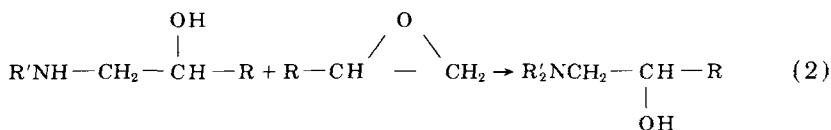
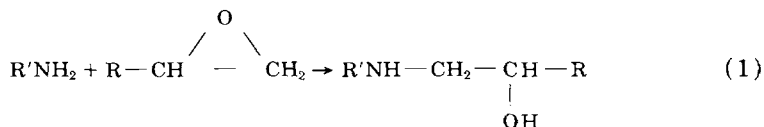
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Synopsis

Different isolated or competitive mechanisms have been experimentally observed in order to predict the kinetics of an epoxy-amine reaction in terms of various mathematical models based on different possibilities of reaction. Impurities such as water, glycols, and in general all donors of active hydrogen even at low concentrations significantly change the course of the reaction. We therefore decided to study the curing reaction of the epoxy resin, first as a commercial product and later purified, with *m*-xylylenediamine of known purity. The extent of cure has been followed and determined by differential scanning calorimetry (DSC) and infrared spectroscopy (FT-IR). Purity, epoxy content and OH content were measured by liquid chromatography HPLC and wet analysis.

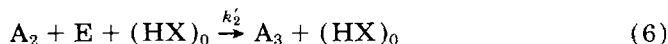
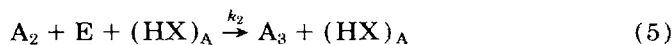
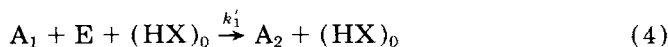
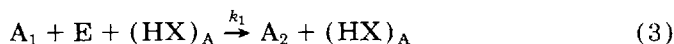
INTRODUCTION

Shechter et al.¹ studied the different mechanisms of epoxy-amine reactions, and observed that they follow two steps:



They found that the hydroxyl groups generated during the reaction, and or the presence of initial impurities, such as water, glycols, solvents, etc., markedly accelerate the course of the epoxy-amine reaction.

Owing to this, and faced with the possibility that the catalytic effect could originate either from impurities or from the OH groups generated in the course of the reaction, many investigators²⁻⁷ have studied the following mechanisms,



where $(\text{HX})_A$ and $(\text{HX})_0$ represent the hydroxyl groups and the initial impurities, respectively. A_1 , A_2 , and A_3 , primary, secondary and tertiary amines, and E epoxy.

From these equations, admitting that any autocatalytic [eqs. (3) and (5)] or externally catalyzed mechanism, n -order path, [eqs. (4) and (6)] could be produced, and assuming equal reactivity for all the hydrogen amines (Horie et al.⁴), the following expression in terms of basic concentrations⁸ can be derived:

$$\frac{d\alpha}{dt} = (K'_1 + K_1\alpha)(1 - \alpha)(B - \alpha) \quad (7)$$

where $K_1 = \frac{1}{2}k_1e_0^2$ and $K'_1 = \frac{1}{2}k'_1e_0c_0$ (e_0 and c_0 are initial concentrations of epoxy and $(\text{HX})_0$, respectively), B the epoxy-amine molar relation, and when the resin and amine are in stoichiometric relations

$$\frac{d\alpha}{dt} = (K'_1 + K_1\alpha)(1 - \alpha)^2 \quad (8)$$

or, in general,

$$\frac{d\alpha}{dt} = (K'_1 + K_1\alpha^m)(1 - \alpha)^n \quad (9)$$

The reduced reaction rate α^0 is defined as

$$\alpha^0 = \frac{d\alpha/dt}{(1 - \alpha)^n} = K'_1 + K_1\alpha^m \quad (10)$$

EXPERIMENTAL

Materials. The resin used was diglycidyl ether or bisphenol A (Epikote 828 from S. P. E. Shell) and *m*-xylylenediamine, MXDA, (Aldrich Chemical Co., 99% pure) as curing agent.

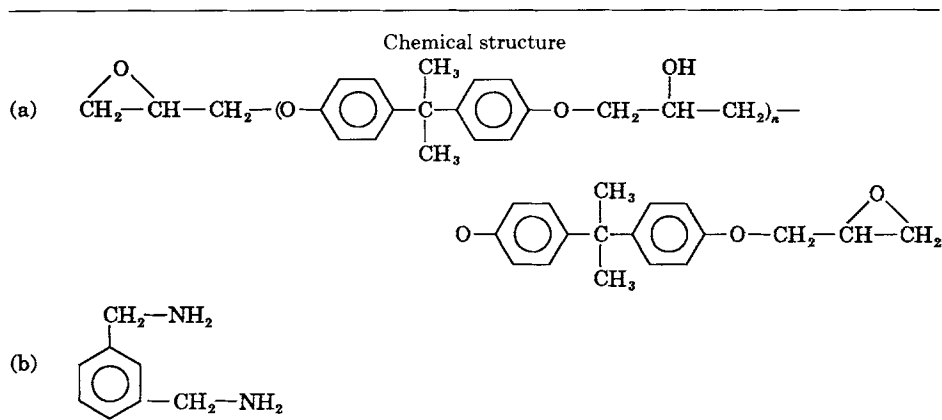
The first series of experiments was done using resin as supplied. In a second series the resin was purified by distillation *in vacuo* (180°C and 1 mm Hg) and further crystallizations in methanol.

From HPLC analysis data, the fall of the OH content can be attributed both to the loss of different substituted glycols and also to the practically total disappearance of all fractions different from $n = 0$. The final product can almost be considered as the pure diglycidyl ether of bisphenol A, DGEBA (Table I).

The MXDA was used as supplied, and its purity checked to be 99.2%, by calorimetric measurements (van 't Hoff isobar method⁹) and wet analysis.¹⁰

Techniques. Differential scanning calorimetry (DSC) and infrared spectroscopy FT-IR were used. A DSC-7 Series Delta Perkin-Elmer equipped with a 3700 data computer and TAC 7/3 controller with both dynamic and isothermal software was used. The DSC was calibrated in the range of selected temperatures

TABLE I



	Data of resins	
	Epikote 828 commercial	Epikote 828 purified
Wet analysis		
Epoxide eq g resin/g eq epoxy	180	171
OH content eq OH/100 g resin	0.06	0.008
hydrolyzable chlorine ppm	631	Negligible
HPLC analysis		
α -Glycol (mmol/kg)	60	8-10
Sap. chlorine (mmol/kg)	8	Negligible
% fractions $n = 0$	94	99.9
% fractions $n = 1$	5.7	0.1
% fractions $n = 2$	0.3	—

^a Idealized chemical structure of an epoxy resin, epichlorhydrin, and diphenylolpropane (bisphenol A).

^b *m*-xylylenediamine (MXDA).

using high purity elements. The performance was as described in the DSC procedure manual. The system was continually under nitrogen and the baseline was adjusted daily. Also following the manual instructions, the DSC holder was frequently cleaned. The weight of samples taken varied between 12 and 18 mg.

The spectrophotometer was a FT-IR Md 1720/ \times Perkin-Elmer equipped with software installed in the electronic module, permitting the necessary calculations previously marked. Dry nitrogen was used in every run, thus minimizing the background/baseline problems inherent to this type of equipment. The signal/noise relation, was in the range 1500/1-2500/1. In order to prevent the high reactivity to humidity and the tendency to form carbonates of the MXDA, both the weighing and mixing took place in a nitrogen atmosphere with a silica gel as desiccant.

DSC and FTIR Measurements. The best weight ratios for $B = 1$ were determined by dynamic runs ($10^\circ\text{C}/\text{min}$) to obtain the highest value of the heat of reaction and the maximum value of the glass transition temperature. These were 100 parts of resin/18 parts of MXDA for the commercial resin and 100/19.5 in the case of the purified resin agreeing with the results obtained through wet analysis data.¹¹ Both the resins and the amine were kept at 10°C before mixing to avoid premature reactivity during the mixing process.

Isothermal runs were carried out in the most appropriate temperature range of the dynamic curve (50 – 110°C), and performed as follows: For each test the samples contained in a closed aluminum pan were placed in the DSC at 30°C for 1 min, and programmed to increase temperature at $150^\circ\text{C}/\text{min}$ by the DSC computer. A second "blank" run was carried out to minimize transient interference in the first seconds of the isothermal reaction and later deducted from the first run through the computer. The samples from the calorimeter (after isothermal runs) were used to get the residual heat and T_g by DSC ($10^\circ\text{C}/\text{min}$). The extent of cure was obtained by FT-IR, measuring at each temperature, the relative absorbance of the epoxy band (916 cm^{-1}) against a reference band (1610 cm^{-1}).¹²

RESULTS AND DISCUSSION

Results. Maximum values of the reaction enthalpies, from -30 to 220°C , were -516 J/g (22.29 kcal/eq) for the commercial resin and -555 J/g (22.78 kcal/eq) for the purified one. These results are similar to those found by other authors.^{3,4,7} Figures 1(a) and 1(b) show the agreement between both methods, DSC and FT-IR. The differences observed may be attributed to the limitations of the isothermal calorimetric method in which the stabilization and heating times cannot be measured by DSC.

To check the validity of the kinetic model in eq. (10) plots of the reduced rate α^0 versus the extent of cure, α , are necessary. According to this model the dependence of α^0 on α must be linear. Different tests with different values of n and m in eq. (10) were tried. It was found that the best straight line corresponds to values of $n = 1.5$ and $m = 1$ (correlation better than 0.995).

Figures 2(a) and 2(b) show the validity of the model used, at the three different temperatures chosen, 50 , 80 , and 110°C . Deviation from linearity marked by a sharp decrease of the reduced rate (corresponding to 60–80% conversion) can be related to the post-gelification reaction, viscosity of the medium and to some extent to effective molecular collisions being controlled by diffusion.^{3,4,6,7} Plots of the reduced rate versus conversion were used to calculate K'_1 and K_1 from the intercept and the slope of the linear part of the curve.

The activation energies corresponding to the commercial and to the purified resin are obtained from the Arrhenius plots in Figures 3(a) and 3(b). (Correlation values were in the range 0.991–0.993.)

Plots of the reaction rate versus time for experimental (taken as $d\alpha/dt = (dH/dt)/\Delta H_f^{13}$) and theoretical values, at the three chosen temperatures, are shown in Figures 4(a), 4(b), 5(a), 5(b), 6(a), and 6(b). As can be observed a good correlation is found.

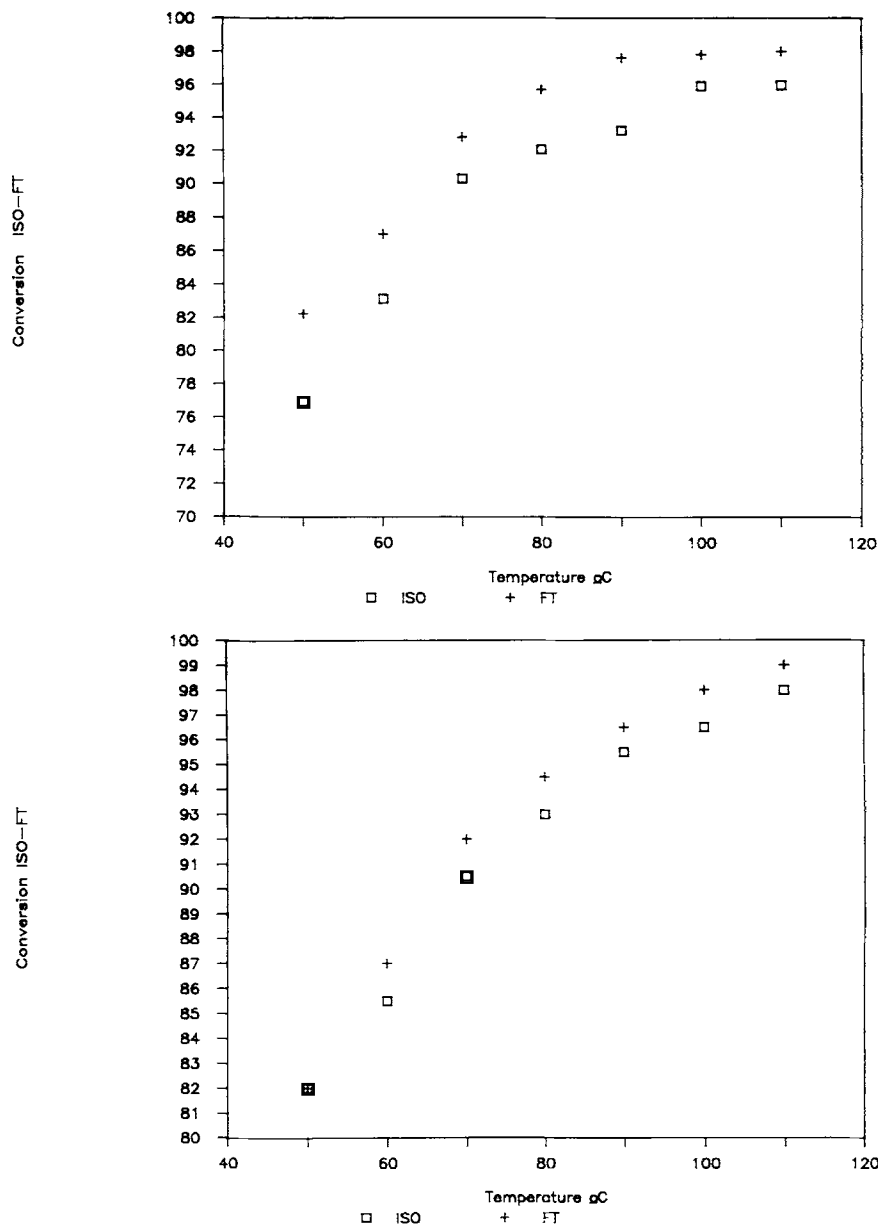


Fig. 1. Isothermal/FT-IR conversion against temperature: (A) commercial resin; (B) purified resin.

Discussion. Table II shows the differences existing both in kinetic and thermodynamic parameters between the commercial and the purified resin. From eq. (9), if c_0 tends to zero, K'_1 tends to zero corresponding to an autocatalytic reaction. Conversely, if $K'_1 \gg K_1\alpha$, the reaction would correspond to a typical n -order mechanism.

Figure 7 shows a linear behavior of K_1/K'_1 versus temperature for the purified resin, which suggests an autocatalytic mechanism. Also from the HPLC data

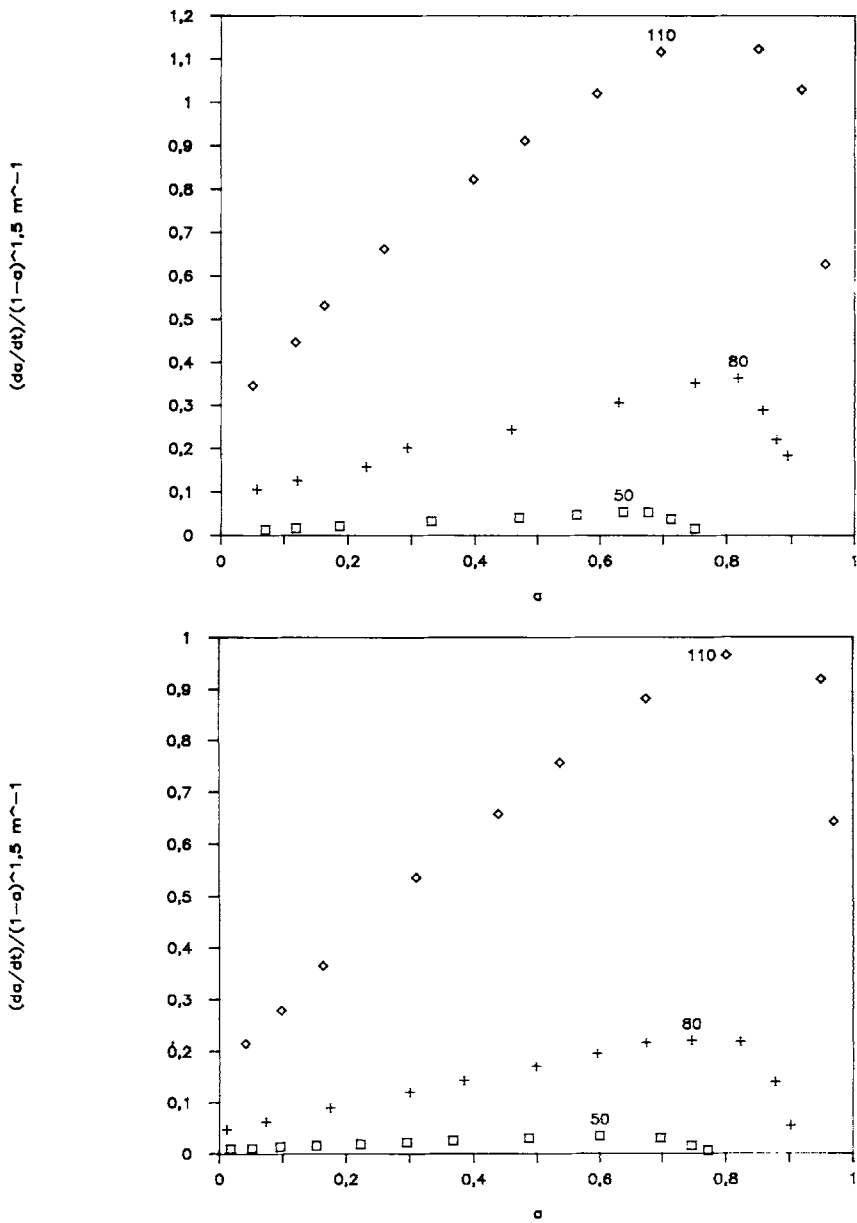


Fig. 2. Variation of reduced rate α^0 with the extent of cure at different temperatures ($^{\circ}\text{C}$): (A) commercial resin; (B) purified resin.

we observe that c_0 is close to zero (10 mmol/kg as α -glycol), which indicates, in agreement with the previous paragraph, an autocatalytic reaction. For the commercial resin, K_1/K'_1 varies nonlinearly with temperature which can be interpreted as a superposition of the two mechanisms in favor of the n -order one when the temperature increases.

The activation energies show general agreement but some difference in E'_{a1} with other investigators. Referring to the purified resin, we found values

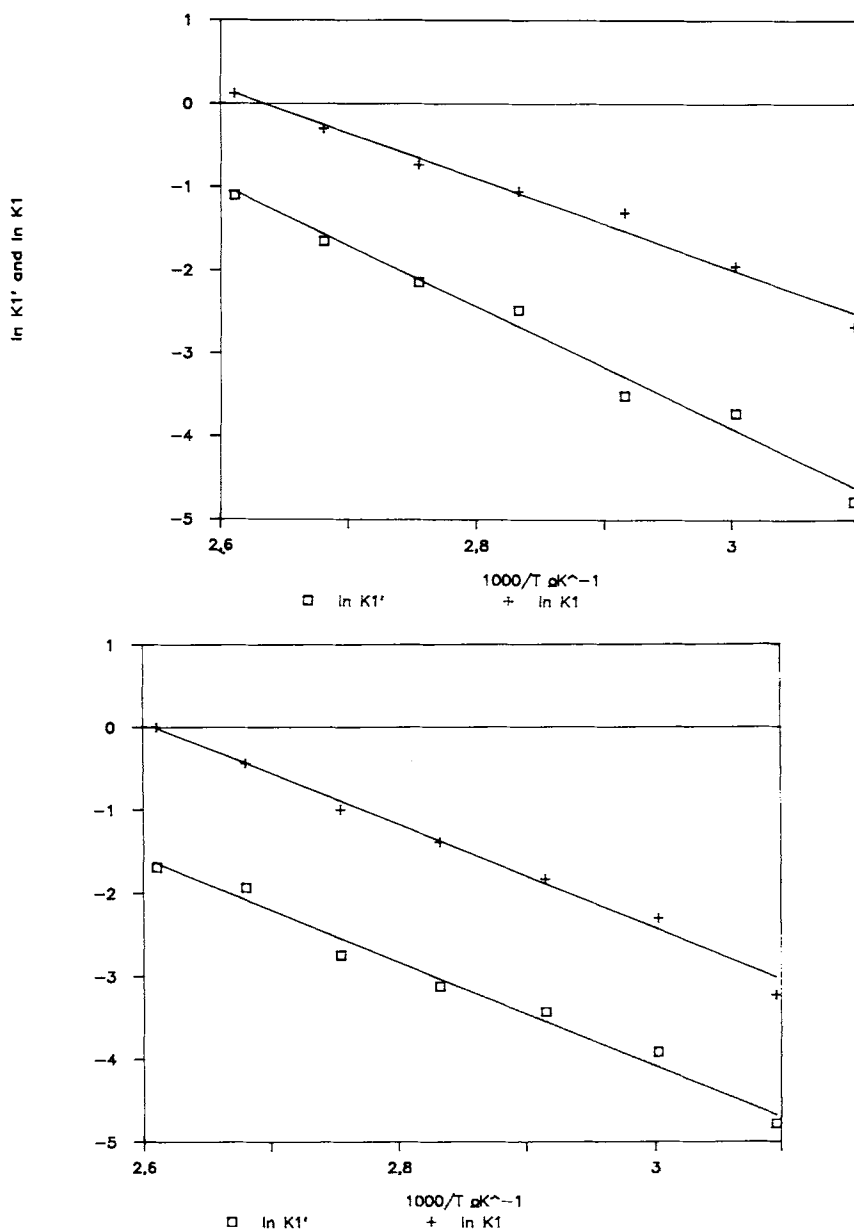


Fig. 3. Arrhenius plot: (A) commercial resin; (B) purified resin.

of the activation energies for the autocatalytic mechanism E_{a1} of 12.35 kcal/mol and E'_{a1} of 12.40 for n -order path. Horie et al.⁴ find E_{a1} of 13.9 kcal/mol using the model reaction phenyl glycidyl ether and butylamine. They also find a value of E_{a1} 12.9 kcal/mol for the epoxy resin-hexamethylenediamine reaction in fairly good agreement with our own result. Even though they have not reported E'_{a1} , they themselves suggest that there may be little difference between activation energies of the four rate constants.

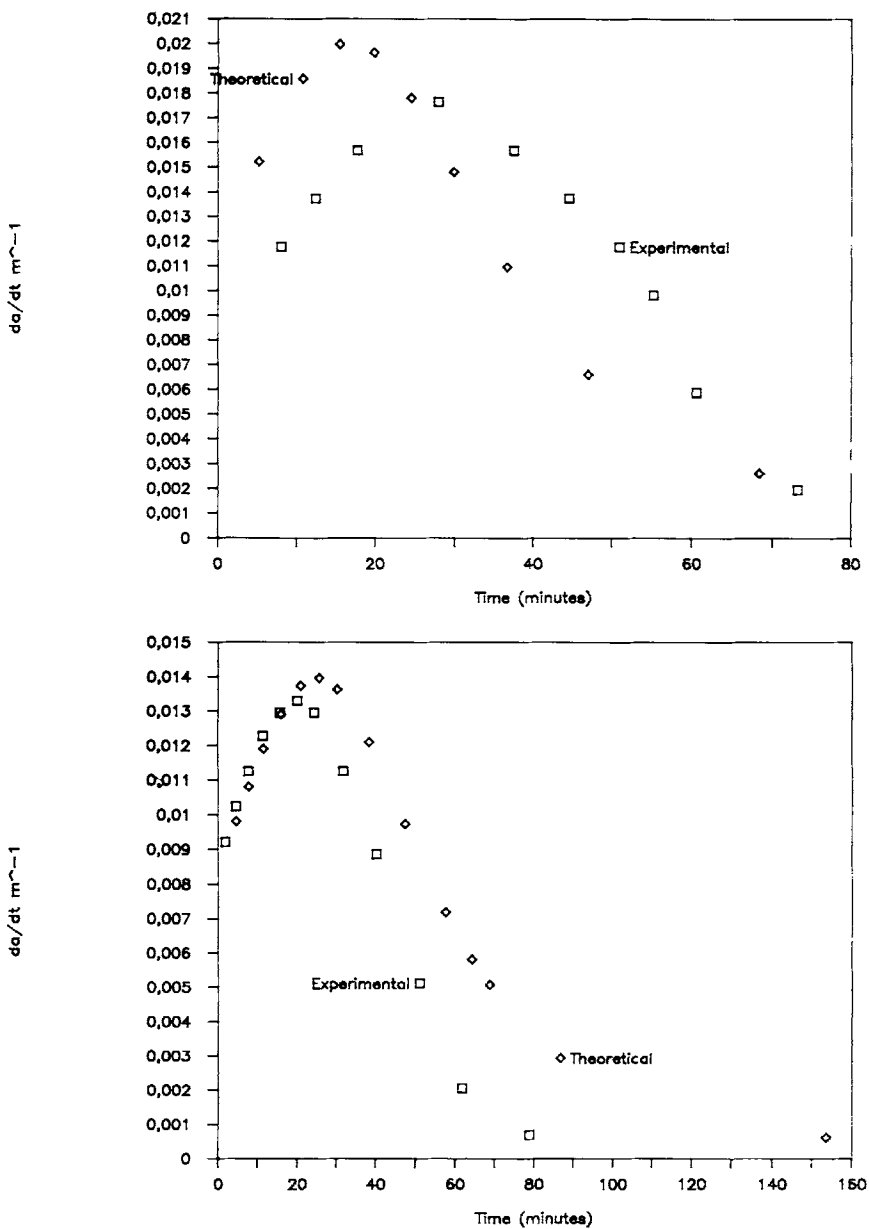


Fig. 4. Rate of reaction against time at 50°C : (A) commercial resin; (B) purified resin.

With respect to the commercial resin, E_{a1} (10.80 kcal/mol) corresponding to the autocatalytic path is generally in good agreement with other published data^{3,6,7}; however, E'_{a1} (14.60 kcal/mol) is lower than that found by them (19–25 kcal/mol). We note that our value is in good agreement with the results for the purified resin. The differences in purity and fractions $n \neq 0$ are not enough to justify a 5 kcal/mol or more difference, so that this could be accounted for by structural considerations. The molecular distances between active sites

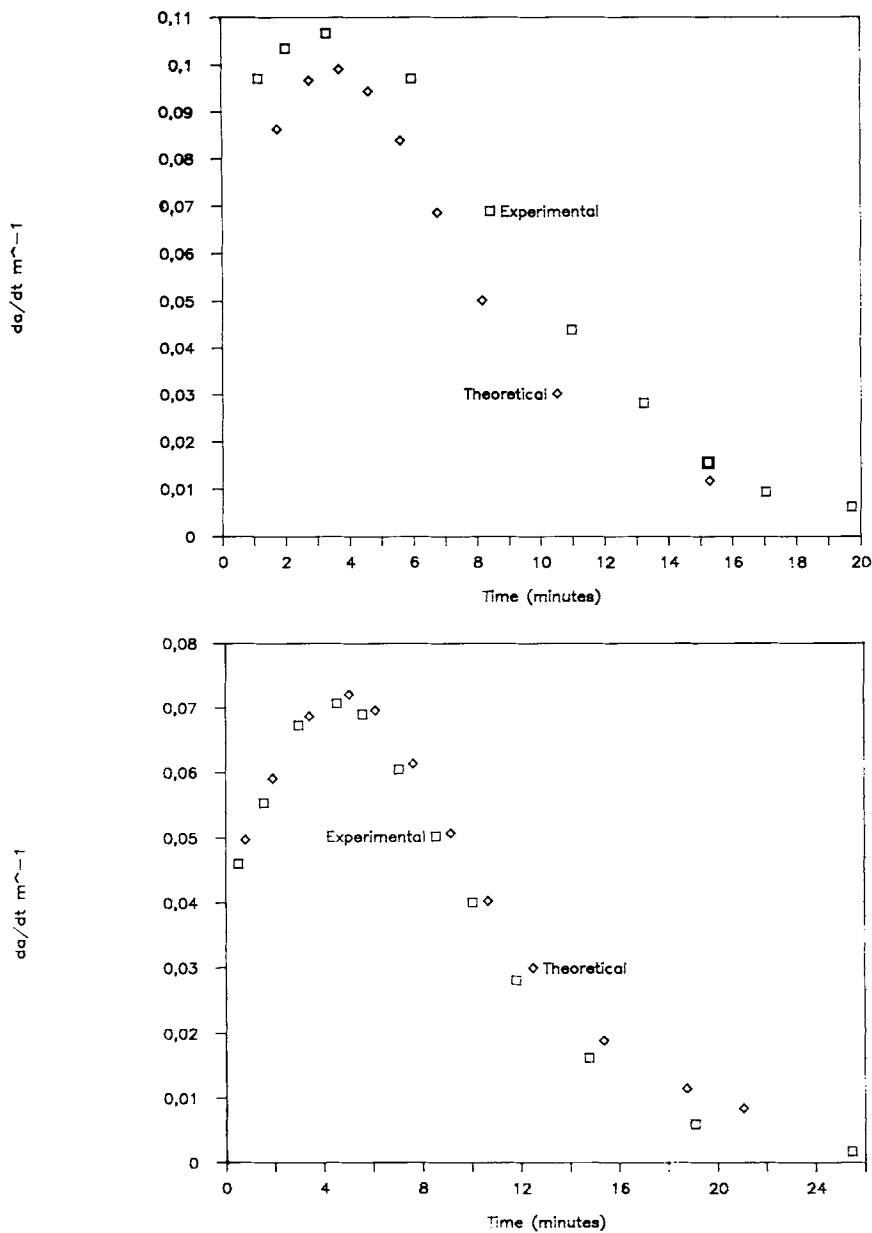


Fig. 5. Rate of reaction against time at 80°C : (A) commercial resin; (B) purified resin.

on epoxy and the amine compared are; ethylenediamine $<$ *m*-phenylenediamine $<$ *m*-xylylenediamine which are in inverse order to E'_{a1} (24.5,⁷ 19.4,³ and 14.6). The greater flexibility of *m*-xylylenediamine is reflected in Figure 2, where the critical conversion for the infinite network is over 0.58.¹⁴ This case could be similar to that found by Horie et al.,⁴ who observed different critical conversions related to the flexibility of the epoxy-amine chains.

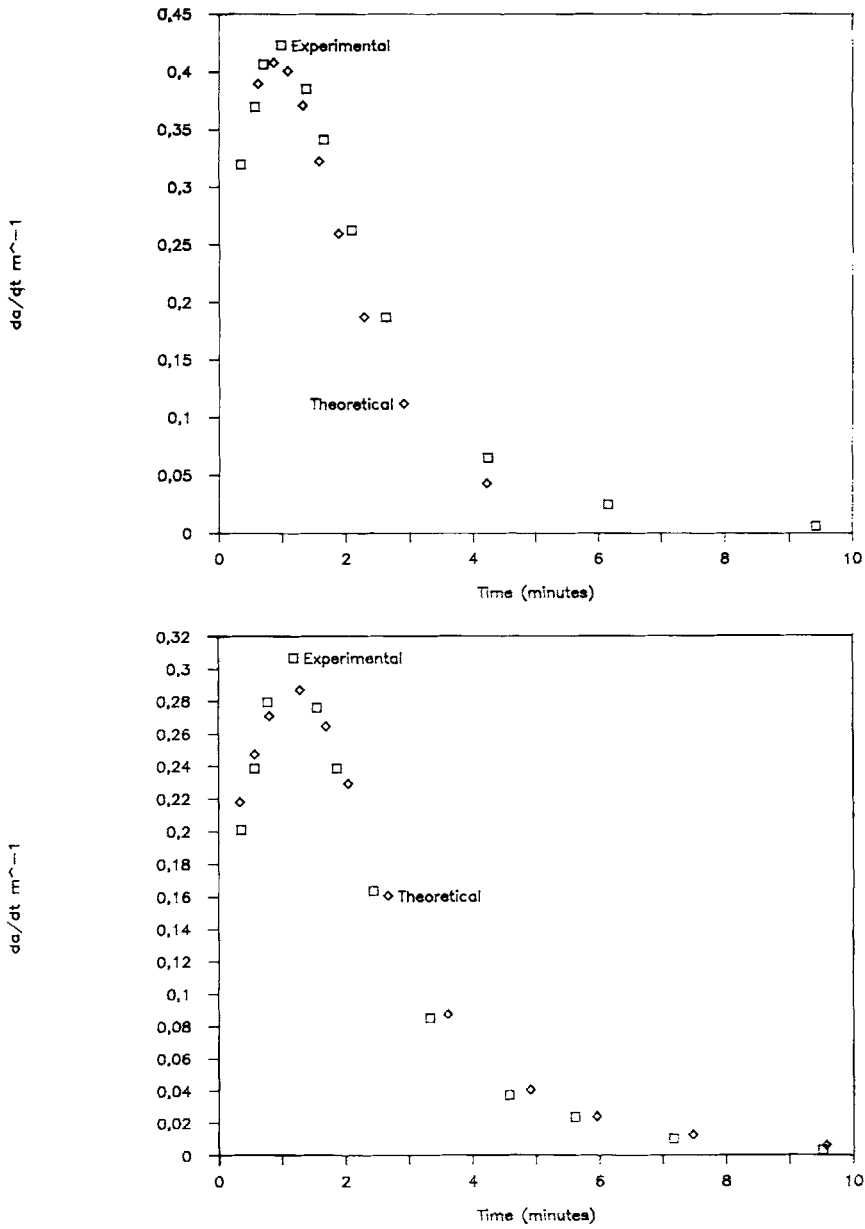


Fig. 6. Rate of reaction against time at 110°C : (A) commercial resin; (B) purified resin.

Table II shows values $n = 1.5$ and $m = 1$ for the reactions studied. Smith,² Sourour and Kamal,³ and Horie et al.,⁴ using techniques and models similar to ours, find an n -order to 2 and an overall order of 3.

According to Smith,² who reports that the epoxy-amine reaction can be considered as a termolecular mechanism, the order of reaction can vary under certain conditions. For example in a third-order reaction if K'_1 were large compared with K_1 the reaction would tend to pseudo-second-order. This is not so

TABLE II
 Thermodynamic and Kinetic Parameters

	Commercial resin	Purified resin
ΔH_T (J/g)	516	555
α_{\max} exptl ^a	0.26	0.29
α_{\max} theoret ^b	0.22 ^c	0.28 ^d
$T_{g\infty}$ (°C)	109	114
K_1 (min ⁻¹)	$1.68 \cdot 10^6 \cdot e^{-10.80/RT}$	$1.16 \cdot 10^7 \cdot e^{-12.35/RT}$
K_1' (min ⁻¹)	$7.17 \cdot 10^7 \cdot e^{-14.60/RT}$	$2.38 \cdot 10^6 \cdot e^{-12.40/RT}$
$(d\alpha/dt)_{\max}$ theoret (110°C) (min ⁻¹)	0.40	0.30
$(d\alpha/dt)_{\max}$ exptl (110°C) (min ⁻¹)	0.43	0.31
Time to reach $(d\alpha/dt)_{\max}$ theoret (min)	0.86	1.29
Time to reach $(d\alpha/dt)_{\max}$ exptl (min)	0.98	1.19
<i>n</i> order	1.5	1.5
Overall order	2.5	2.5

^a $\alpha_{\max} = \Delta H$ at the peak where the rate is maximum/ ΔH_T .

^b From the eq. (9), for $n = 1.5$ and $m = 1$, $(d^2\alpha/dt^2) = 0$.

^c 0.22 (at 110°C, varies with temperature).

^d 0.28 (constant with temperature).

in our case. However, we have observed that the *n*-order of 2 can also manifest itself, but the correlation obtained by us (for $n = 2$ and $m = 1$) was less than 0.97 while we found values between 0.995 and 0.999 for $n = 1.5$ and $m = 1$. Of course, in the latter case this reaction seems more probable.

Stoichiometric defaults could justify these differences, but lack of evidence of this type of anomalism obliges us not to pass judgement in this sense. The

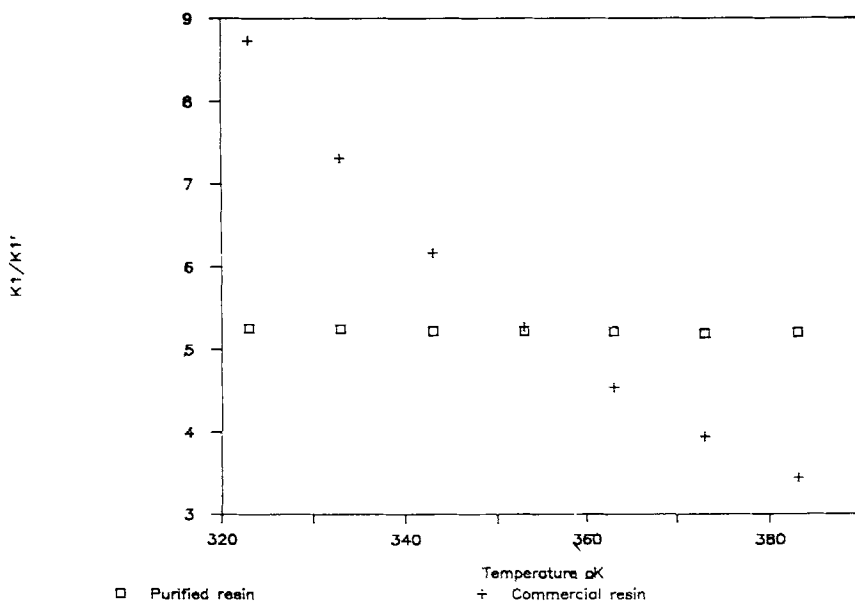


Fig. 7. Variation of the ratios of the rate constants against temperature (K).

order of reaction does not vary between the two resins. The differences in the range of impurities found are not significant enough to change the order of reaction.

There exists one other fact not yet reflected. The rate of reaction for the commercial resin at 50°C shows some differences between the theoretical model and the experimental values. This could be justified in terms of impurities different to those of the glycols.¹⁵ The presence of hydrolyzable chlorine (Table I) can inhibit the reaction's catalysis. At high temperatures this phenomenon is clear but almost vanishes under the thermal effect when the reaction tends to *n*-order.

This fact is well known in the electrical and electronic industries where the use of resins with low hydrolyzable chlorine is recommended.

CONCLUSION

The results obtained by us for the two reactions studied show that:

- The kinetic model used reflects good experimental-theoretical agreements in the whole range of the temperatures observed.
- Due to the fact that in this reaction the reduced rate for an infinite network is over 0.58, a good correlation between conversion-time and high conversion values can be found.
- The curing is practically autocatalytic and independent of the temperature when the products are highly pure. The epoxy resin used as the commercial product follows two mechanisms; at low temperatures the autocatalytic one and the *n*-order path at high temperatures.
- The values of the activation energies for the autocatalytic path are close to 11–13 kcal/mol.
- The energy of activation for an *n*-order mechanism can vary for different diamines.
- The rate of reaction for the commercial resin is faster than the purified one. The effect of the hydrogen donors such as α -glycols is in fact significant.
- The reaction is typically termolecular; however, an overall order less than 3 can be found. Within the limits of the impurities found by us there was no effect on the order of reaction.

However, it is clear that our results are based on the hypothesis of equal reactivity of all the amine hydrogens. To check this assumption, and according to Duffy et al.,¹⁶ we carried out experiments at different heating rates and different epoxy-amine ratios. The existence of only one exothermic peak shows the validity of the model used by us.

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