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Method for determination of the ratio of rate constants, secondary to primary amine, in epoxy–amine systems

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In epoxy–amine kinetic studies, the determination of the ratio of rate constants (*R*) for hydrogens on primary and secondary amine groups is very important; in fact *R* is related to the network morphology. In this paper we show that *R* can be directly calculated from the ratio of the concentrations of primary to secondary amine at $(d[A_2]/dt)_{max}$, $d[A_2]/dt$ being the reaction rate for the formation of the secondary amine. Experimental measurements were carried out in the near infrared. © 1997 Elsevier Science Ltd.

(Keywords: reactivity ratio; infrared spectroscopy; substitution effect)

Introduction

In epoxy–amine kinetic studies, a critical parameter is the ratio of the rate constants (*R*) for the hydrogens on primary and secondary amine groups.

However, one can find such oscillations for the *R* values that it often becomes highly difficult to choose any for a given epoxy system. For instance, Rozemberg[1] observed that some values of *R* obtained by different authors vary by more than one unit. For aliphatic amines cured with a diglycidyl ether of bisphenol-A (DGEBA) it is usually accepted that *R* is close to 1/2 (stated by some authors as the ideal value)[2-4], but for aromatic and cycloaliphatic polyamines the situation is not so clear. For instance, Dusek[5] established a practically nil substitution effect for two typical aromatic diamines (4,4′-diaminodiphenylmethane and 4,4′-diaminodiphenylsulfone) in contradiction with other authors[6,7]. With reference to cycloaliphatic diamines there is less information[8,9]. For *R* determination, two types of experimental methods are normally used: critical molar ratio[4,10] based on gel considerations and the comparison between theoretical and experimental curves[9,11,12]. The aim of this work is to determine *R* through a simple and reliable method based on infrared (i.r.) measurements. In our method, *R* is directly evaluated from an equation with only one unknown. In consequence, it is not an adjustable parameter obtained from a general rate equation where *R* is fitted to experimental points. This method can seriously affect the true *R* value as all types of theoretical and experimental errors can be considered as a part of *R*. The effect of the temperature on *R*, which was practically not considered until a few years ago[11], is also included.

Experimental

The epoxy resin chosen was a purified DGEBA (molecular weight 348 g mol^{-1}) and three amines as curing agents: a pure aliphatic diamine, ethylenediamine (EDA), an aliphatic diamine with aromatic substituent, *meta*-xylene diamine (*m*-XDA) and a very common cycloaliphatic diamine, isophorone diamine (IPD), which were all purchased from Aldrich.

Stoichiometric amounts of epoxy resin and amines were used. The resin was previously melted and both weighting and mixing took place in a N_2 atmosphere.

Fourier transform i.r. spectroscopy was performed using a Perkin-Elmer Spectrum 2000, equipped with a Dynascam Interferometer cooled i.r. source, KBr beam splitter and DTGS detector. All spectra were collected in the near-i.r. (7000–4000 cm^{-1}) at 8 cm^{-1} resolution with a scanning rate of 4 cm s^{-1} and 20 scans per slice. For thermal control, a temperature controller was used (Specac 20140) equipped with a circular cell with NaCl windows and a Teflon spacer (pathlength 1 mm). To optimize the thermal equilibrium an external thermostatic bath was used, pumping water (flow rate 500 ml min^{-1} at 10°C) through the cell. The reactive mixture was injected with a syringe when the controller showed the programmed temperature. A silicone grease moulding release (previously tested to know the possible interferences with the quantifiable bands) was used to prevent the adhesion resin/windows.

The spectra were recorded using software for kinetic determinations (Perkin-Elmer) programmed at different previously established times. The epoxy systems were all tested at different temperatures.

Results and discussion

The mechanism of the curing of the epoxy–amine reaction has been studied by several investigators[3,13-16] and can follow two different but simultaneous paths, uncatalysed and catalysed (and/or autocatalysed). We also showed[17] that when no evaporation of the starting

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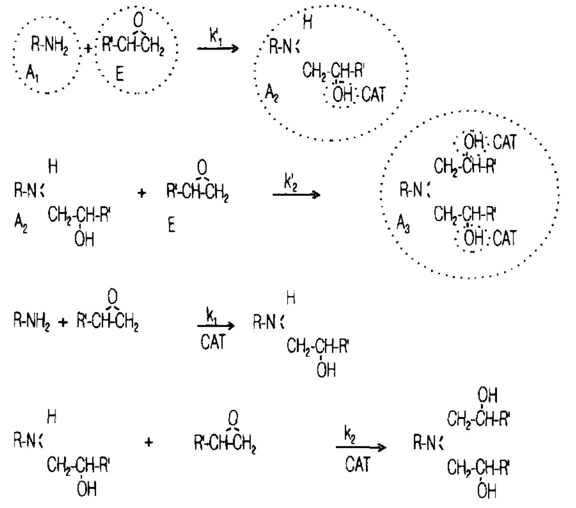
monomers (epoxy and/or amine) occurs, the kinetic scheme can be expressed by the following equations:



(1)

(2)

(3)

(4)

Evaluation of the ratio of rate constants. Considering equations (1) and (4) the rate of the reaction for the formation of secondary amine is:

$$\frac{d[A_2]}{dt} = k_1'[A_1][E] - k_2'[A_2][E] + k_1[A_1][E][CAT] - k_2[A_2][E][CAT] \tag{5}$$

If we assume that the ratios of rate constants k_2'/k_1' and k_2/k_1 are independent of the path[17], the non-catalytic reactions represented by equations (1) and (2) and the catalytic one by equations (3) and (4), then $k_2/k_1 = k_2'/k_1' = R$. Equation (5) becomes

$$\frac{d[A_2]}{dt} = k_1'[A_1] - k_1'R[A_2] + k_1[A_1][CAT] - k_1R[A_2][CAT]$$

Under the condition of maximum

$$\left(\frac{d[A_2]}{dt}\right)_{max} = 0$$

then

$$R = \frac{[A_1](k_1' + k_1[CAT])}{[A_2](k_1' + k_1[CAT])} \Rightarrow R = \frac{[A_1]}{[A_2]} \tag{6}$$

$[A_1]$ being directly evaluated from the experiments and $[A_2]$ from the mass balances:

$$[A_1]_0 = [A_1] + [A_2] + [A_3] \tag{7}$$

$$[E]_0 = [E] + [A_2] + 2[A_3] \tag{8}$$

$$[CAT] = [CAT]_0 + [A_2] + 2[A_3] = [CAT]_0 + [E_0] - [E] \tag{9}$$

where $[A_1]_0$ and $[E]_0$ are the initial concentrations of amine and epoxy; $[A_1]$, $[A_2]$, $[A_3]$, $[E]$, $[CAT]$ and $[CAT]_0$ the concentrations of primary, secondary and tertiary amines, epoxy and catalyst (OH^- groups generated during the course of reaction) and catalyst initially present (OH^- groups from impurities or OH^- donors added to the system).

By combining equations (7) and (8):

$$[A_2] = [E_0] * (\beta * B - \alpha) \tag{10}$$

and also $[A_3]$ can be obtained:

$$[A_3] = [E_0] * (\alpha - \beta * B/2) \tag{11}$$

where

$$\alpha = \frac{[E_0] - [E]}{[E_0]}, \quad \beta = \frac{[A_1]_0 - [A_1]}{[A_1]_0}, \quad B = \frac{2[A_1]_0}{[E_0]}$$

($B = 1$ for the stoichiometric mixtures used in our case).

Measurements. The assignments of bands of primary amines and the epoxy group in the near-i.r. have been well documented by several authors[18-24]. Different concentrations of epoxy and amines were used to investigate the dependence of absorbance/concentration. The linear plots obtained show that Beer's law is obeyed in this region (primary amine at 4937 cm^{-1} and the epoxy group at 4530 cm^{-1}).

The quantification of epoxy and amine was carried out by considering the ratio of absorbances at different times

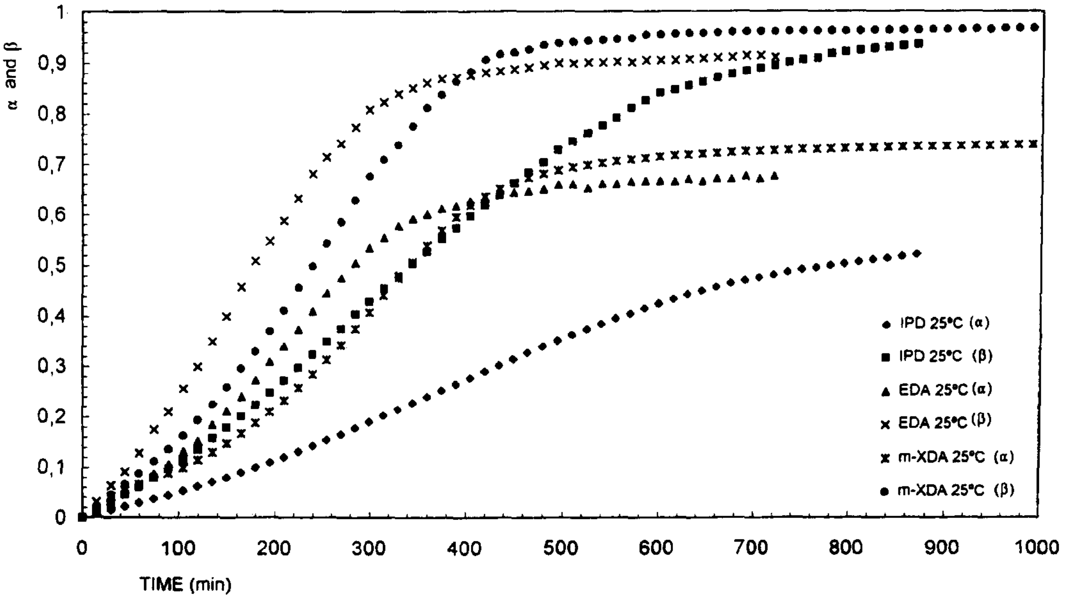


Figure 1 Extension of reaction for epoxy (α) and primary amine (β) for the three epoxy–amine systems studied at 25°C

with respect to the absorbance at $t = 0$. A fixed path-length (1 mm), but no reference band, was used for all experiments.

Analysis of results. *Figure 1* shows the experimental results obtained plotting epoxy and amine conversions (α, β) against time of reaction at 25°C in the three systems studied. As expected, in considering equations (1) and (2) and equations (3) and (4), the consumption of primary amine is faster than that of the epoxy group. According to these equations a relationship between α and β can be established:

$$\frac{\mathrm{dE}}{\mathrm{dA}_1} = 1 + R\frac{[\mathrm{A}_2]}{[\mathrm{A}_1]}$$

as $\alpha = (\mathrm{E}_0 - \mathrm{E})/\mathrm{E}_0$ and $\beta = (\mathrm{A}_{10} - \mathrm{A}_1)/\mathrm{A}_{10}$, then

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\beta} = \frac{[\mathrm{A}_1]_0}{[\mathrm{E}_0]} * \left(1 + \frac{[\mathrm{A}_2]}{[\mathrm{A}_1]}R\right) \tag{12}$$

As a consequence and for stoichiometric mixtures, if $R \rightarrow 0$ $(k_2 \rightarrow 0$ or $k_1 \gg k_2) \Rightarrow \alpha = 1/2\beta$. This case only occurs (from the beginning to the end of the reaction) if there is no formation of tertiary amines. On the other hand, at the beginning of the reaction $[\mathrm{A}_2] = 0 \Rightarrow \alpha = 1/2\beta$; α/β changes as the reaction continues in the same direction as the factor $([\mathrm{A}_2]/[\mathrm{A}_1])^*R$. For instance, if $([\mathrm{A}_2]/[\mathrm{A}_1])^*R \rightarrow 1 \Rightarrow \mathrm{d}\alpha/\mathrm{d}\beta \rightarrow 1$.

Figure 2 (epoxy/*m*-XDA at 80°C) shows the variations of concentration of $[\mathrm{A}_1]$, $[\mathrm{A}_2]$ and $[\mathrm{A}_3]$; R is directly obtained under the condition $(\mathrm{d}[\mathrm{A}_2]/\mathrm{d}t)_{\max}$ according to equation (6) (see marks on figure). The same procedure was applied for other temperatures and systems (*Table 1*) where the effect of a very well known diluent, benzyl alcohol (Merck), 12.8% on DGEBA/*m*-XDA, on R is also included.

It is worthwhile to point out that, from our point of view, the method proposed for R determination is reliable and is not necessarily under the influence of a different hypothesis for the epoxy–amine mechanisms. For instance, if we assume a pure non-catalysed path, equations (1) and (2), or a pure catalysed path, equations (3) and (4), the result is the same as if we suppose a simultaneous catalysed/non-catalysed mechanism: $[\mathrm{A}_1]/[\mathrm{A}_2] = k_2'/k_1'$ from equations (1) and (2) and $[\mathrm{A}_1]/[\mathrm{A}_2] = k_2/k_1$ from equations (3) and (4). Other possibilities for the reaction, such as catalysis by primary amine, were also considered, with the same results.

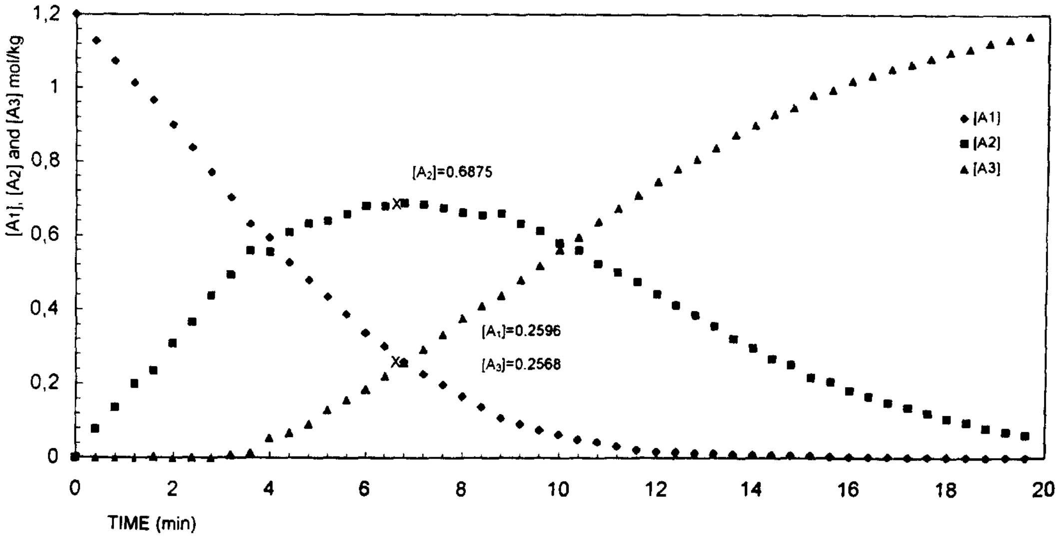


Figure 2 Variation of the concentrations of primary $[\mathrm{A}_1]$, secondary $[\mathrm{A}_2]$ and tertiary $[\mathrm{A}_3]$ amines as a function of reaction time. Epoxy/*m*-XDA at 80°C

Table 1 Results obtained for R, α and β at $(\mathrm{d}[\mathrm{A}_2]/\mathrm{d}t)_{\max}$

	m-XDA			IPD			EDA			Benzyl alcohol/*m*-XDA		
Temperature (°C)	R	α	β	R	α	β	R	α	β	R	α	β
15	–	–	–	–	–	–	–	–	–	0.40	0.49	0.77
25	0.42	0.50	0.77	0.166	0.45	0.92	0.42	0.50	0.77	0.47	0.47	0.76
40	0.40	0.49	0.77	–	–	–	0.39	0.50	0.78	0.41	0.49	0.77
50	0.39	0.50	0.78	0.131	0.46	0.89	–	–	–	0.40	0.49	0.77
60	0.38	0.50	0.78	–	–	–	0.39	0.50	0.78	0.39	0.49	0.78
70	0.38	0.50	0.78	–	–	–	0.38	0.51	0.79	0.38	0.49	0.78
80	0.38	0.50	0.78	0.099	0.45	0.92	0.38	0.50	0.78	–	–	–
90	–	–	–	0.089	0.48	0.92	–	–	–	–	–	–
100	–	–	–	0.077	0.49	0.93	–	–	–	–	–	–
110	–	–	–	0.075	0.46	0.93	–	–	–	–	–	–

Conclusions

We have proposed a method for the determination of the ratio of rate constants (R) for secondary amine/primary amine. This method, based on near-i.r. measurements, allows the calculation of R by the simple evaluation of $[A_1]$ and $[A_2]$. Also, the results show that:

- the established method is highly reproducible (the values given are the average of three determinations with variations of less than 5%) and not necessarily under the influence of different hypothesis of mechanisms;
- R is directly obtained without any theoretical assumption on its possible value;
- if we assume that in the aliphatic diamines the substitution effect is not markedly important, the values of R for epoxy/EDA should be 1/2. In no case does R take such an ideal value. It is interesting to point out the influence of benzyl alcohol on R at 25°C;
- R decreases with the temperature, but it becomes constant. There is probably a maximum at a given temperature for each system (see the benzyl alcohol case);
- the extension values of epoxy and amine (α, β), at $(d[A_2]/dt)_{max}$, are practically constant and independent of the temperature for each system;
- any general kinetic model should consider the possibility that $R \neq 1/2$.

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