

KINETIC METHOD BY USING CALORIMETRY TO MECHANISM OF EPOXY-AMINE CURE REACTION

Part VIII. A comparative study of some epoxy-amine reactions

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Four epoxy-amine reactions differing a number of the functional groups are compared. It has been shown that the main features of kinetics are similar for a whole family of model reactions. In series of epoxy-amine reactions analyzed, the reaction between resorcinol diglycidyl ether and *m*-phenylenediamine is one where increasing the viscosity of the reaction mixture leads to its vitrification during the reaction. This reaction proceeds very rapid compared with the model reactions. We demonstrate that application of kinetic techniques to analytical problems is facilitated by an understanding of the reaction mechanism involved. We report that thermokinetic method can be used for finding the activation energy in similar epoxy-amine systems through the use of times to point of the maximum in the experimental curve of the heat release rate vs. time. Our results indicate that independent of the initial reagent ratio, the conversion at the peak rate in the total curve the heat release ranges from 47 to 49%.

Keywords: aniline, DSC, epoxy-amine, kinetic calorimetry, *m*-phenylenediamine, phenyl glycidyl ether, resorcinol diglycidyl ether, solventless systems

Introduction

There are numerous publications where the calorimeters are used as analytical instruments [1, 2]. Thermokinetic experiment provides the data necessary to analyze important problems on the reaction mechanism that can not be approached easily in any other way. By the example of a series of reactions of amines with epoxides we have shown that the calorimetry is really powerful analytical tool for the determination of a reaction mechanism [3–6]. By studying the thermokinetics of such reactions we can obtain quite specific information about their kinetics.

The reactions between epoxides and amines are of considerable interest not only from the point of view their commercial importance, but also from the point of view a reaction mechanism in the solventless systems. By a solvent-free reaction is meant any system in which neat reagents react together in the absence of a solvent. Here the reactions actually take place in the molten phase even in these samples that outwardly appear to be solid [7].

It is noteworthy that the solventless reaction also accelerates the reaction rate dramatically even in viscous medium. For example, many of the reaction have been reported to occur more rapidly under solventless conditions than in solution [8, 9]. It is well known, using solventless reaction conditions, leads to an im-

provement in extent of conversion and shortened reaction times as well as a lower temperature than the solution reaction.

Consideration of the nature of epoxy-amine reactions led us to the finding that the beauty of epoxied curing systems analyzed previously is that they are not a solid-state reaction at all, but rather occurs in a liquid melt of the two reagents. Under vitrification epoxy-amine reaction must proceed also in the molten phase under conditions prevailing in melts. In systems of the latter type the rate enhancements can be achieved only by bringing functional groups together in viscous medium.

Using heat of the reaction as a measure of the extent of conversion, a series of epoxy-amine reaction mixtures within of which only a number of the functional groups varied was carried out [3–6]. We have shown the strict correlation existing between thermokinetics and reaction mechanisms. At that the problems inherent in this technique were discussed in detail. One very important problem is finding kinetic model for these reactions [10].

The results were somewhat surprising in that the proposed kinetic model fit the data about equally well to the measured the rate of the heat release as a function of time in the case of epoxy-amine reaction mixtures, which differ in the number of functional groups. The rate equations were tested to see how

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well they reproduced experimental results for a number of epoxy-amine reactions as a function of time and temperature under solventless conditions.

These studies have revealed that the kinetics of above epoxy-amine reactions, whether they are glass-forming or model reactions is found to be fundamentally the same. A feature distinguishes the reaction of epoxids with amines in neat (without solvent) systems from those of the same mixtures in solvents, this is the ready occurrence of structure forming processes whereas it is totally absent in dilute solutions.

From the point of view of kinetics as well, these reactions are of considerable interest. We observed rate law led us to suggest an occurrence of stable intermediates within which the reaction has been proposed to take place. According to this mechanism, the rate of the reaction as a whole is controlled by these intermediates. The experimental results indicate that two mechanisms are involved in the formation of the reaction product namely, the direct reaction (uncatalyzed pathway) and over persistent intermediate formation (catalyzed pathway).

In uncatalyzed pathway, the rate of reaction W is proportional to the product of the concentration of epoxy- ($[E]$) and NH- ($[A]$) groups

$$W = k[E][A] \quad (1)$$

The concentrations of epoxide and amine are denoted as $[E]$ and $[A]$ respectively.

As such, the uncatalyzed pathway involves bimolecular reaction epoxy-group with NH-group when portions of the reagent species may come sufficiently close for direct reaction to occur.

The catalyzed reaction has been proposed to take place involving intermediates formed by the reagent molecules [3–6]. The ability of the catalyst to hold reactants in a manner that organizes the complex for high reactivity and the subsequent release of products, provide a way for the chemical transformation by optimally locating functional groups. The use of the complexes as molecular- reaction vessels provides a basis for the kinetic treatment in the case of catalyzed reaction in all of four epoxy-amine reactions. This basic idea is expressed in equation:

$$W = k[\text{complex}][\text{cat}] \quad (2)$$

The role of catalyst in a reaction is to favour the movement of the electrons involved in the formation of a new C–N single bond and proton transference from the incoming amine nucleophile to the forming OH group. Equal reactivity of primary and second amines seems to point to processes in which the nucleophilicity of the nitrogen atom is nearly constant.

As mentioned above the mechanism of the catalyzed reaction is best accounted for on the basis of the

formation of the intermediates between the reagents. Their formation can be expressed as



The complex AE evolves to the final product P through a process, in which it is considered that the product is acting as a catalyst:



As is well known, the kinetic curves obtained by the experiment are a sigmoid function of time. This behaviour is reputed as evidence of autocatalysis. In outward appearance, these findings, indeed, point to catalysis by the molecules which are formed in the course of the reaction. Therefore product concentration is included in the rate Eq. (5):

$$\frac{dC_{x2}}{dt} = k_{ef2}(C_0 - C_p)C_p \quad (5)$$

where k_{ef2} – the rate constant of the catalytic reaction, C_0 is the initial concentration of the complex formed by the reagents; C_p is the concentration of the OH-functional groups, which are formed in the course of the reaction.

The validity of kinetic model (2) was tested by analyzing the effects of NH-/epoxy-groups ratio and temperature used on the reaction rate heat release. A comparison of observed and calculated reaction rate heat release of various reaction mixtures have been demonstrated in [3–5]. It turns out that all these reactions show similar kinetic behavior. Good agreement for every run lends support to the proposed kinetic model.

The present paper develops this idea further. We report here a comparative study of four epoxy-amine reactions. The set of epoxy-amine reactions chosen for our study is: resorcinol diglycidyl ether – aniline, resorcinol diglycidyl ether – *m*-phenylenediamine, phenyl glycidyl ether - aniline, phenyl glycidyl ether - *m*-phenylenediamine. They can be treated as reaction systems differing a number of the functional groups NH- and epoxy- in the molecules of amine and epoxied, respectively. These reactions were chosen primarily in order to be able to make such a comparison and thereby evaluate the advantages and disadvantages of the kinetic model. For this purpose, these reactions provide an excellent basis for the comparison of experimental data.

Experimental

Differential scanning calorimeter DSC-111 ('Setaram', France) was used to obtain the extent of reaction during the isothermal reactions of epoxy-amine systems. A mixture of epoxide and amine

(ca. 0.25g) of known composition was sealed in aluminium pans and subjected to isothermal reaction at different reagent ratios.

When the reactions were run to completion, the samples were annealed and a dynamical run was conducted at heating rate of 5°C per minute.

Results and discussion

Table 1 represents the structure formulas of all compounds of our concern. Reaction between resorcinol diglycidyl ether – *m*-phenylenediamine amine- and epoxy- functional groups produces oligomeric species. The latter react further to produce higher molecular weight polymers that eventually form a three dimensional infinite network which spans the dimensions of the reaction vessel. This reaction proceeds in highly viscous glassforming melt which stiffens to yield a glass solid where increasing the viscosity of the reaction mixture leads to its vitrification during the reaction. The most interesting property of resorcinol diglycidyl ether – *m*-phenylenediamine mixture is its vitrification. In series of epoxy-amine reactions analyzed the reaction between resorcinol diglycidyl ether and *m*-phenylenediamine is one where increasing the viscosity of the reaction mixture leads to its vitrification during the reaction.

It turned out that the effect of vitrification can be reliably established during kinetic experiment by isothermal calorimetry [3] since the onset of vitrification is reflected in the isothermal curves as a sharp decrease in the heat release rate.

To gain further understanding of cure reactions, we have studied the kinetics of linear polycondensation between resorcinol diglycidyl ether and aniline [5]. When this reaction proceeds in the stoichiometric mixture at 70°C, the reaction mixture becomes progressively viscous as product forms. However, the reaction does not by itself lead to vitrification. The product molecules represent the molten

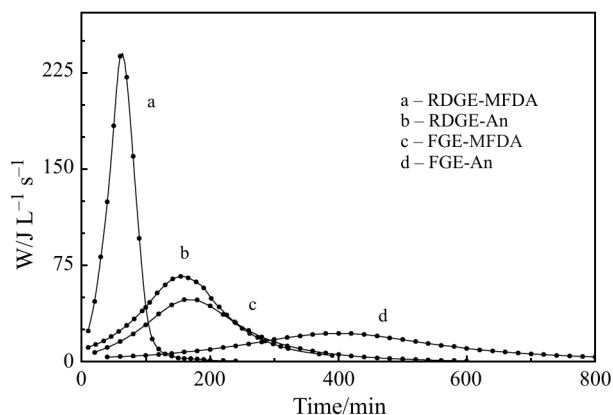


Fig. 1 Isothermal curves of heat release rate at 70°C

polymer. On cooling to room temperature this melt rapidly solidified yielding a glass solid. T_g of the neat polymer lies in the region 60–80°C.

Since the mechanism in above cases was found to be the same further attention has been given to a comparison of the thermokinetic parameters. In order to construct a probable reaction mechanism of epoxy- ring opening by amine, model experiments were performed with reagents bearing a different number of functional groups

Figure 1 shows a series of the kinetic measurements carried out with stoichiometric mixtures. Reactions were followed by calorimetry using the Mangelsdorf treatment of rate heat release - time data [3–6]. The reaction temperature was 70°C. It is notable that, the reaction rate between resorcinol diglycidyl ether and *m*-phenylenediamine is the most fast, while the reaction of phenyl glycidyl ether with aniline is slower than when aniline reacts with resorcinol diglycidyl ether. The increasing of the viscosity can be expected to have a marked effect on the reaction rate. In going from a reaction involving vitrification to model systems, the effect observed is in the opposite direction. The most reaction rate is observed in the reaction involving vitrification as compared to the model reactions (Fig. 1).

Table 1 Epoxy-amine systems differing a number of the functional groups. Their abbreviations, structure units and molar heats in uncatalyzed and catalyzed reactions. (← – NH-group, ⇐ – epoxy-group)

Reagents	Products	State at reaction temperature	$Q_{mol1}/$ kJ mol ⁻¹	$Q_{mol2}/$ kJ mol ⁻¹
Phenyl glycidyl ether – Aniline	$\leftarrow \leftrightarrow \rightarrow$	Viscous liquid	204	86
Resorcinol diglycidyl ether – Aniline	$\leftarrow \leftrightarrow \rightarrow \leftarrow \leftrightarrow \rightarrow \leftarrow \leftrightarrow \rightarrow$	Viscous liquid	200	88
Phenyl glycidyl ether – <i>m</i> -phenylenediamine	$\leftarrow \leftrightarrow \rightarrow$ $\leftarrow \leftrightarrow \rightarrow$	Glassy material	194	82
Resorcinol diglycidyl ether – <i>m</i> -phenylenediamine	$\leftarrow \leftrightarrow \rightarrow \leftarrow \leftrightarrow \rightarrow \leftarrow \leftrightarrow \rightarrow$ $\leftarrow \leftrightarrow \rightarrow \leftarrow \leftrightarrow \rightarrow \leftarrow \leftrightarrow \rightarrow$ $\leftarrow \leftrightarrow \rightarrow \leftarrow \leftrightarrow \rightarrow \leftarrow \leftrightarrow \rightarrow$	Crystalline solid	251	90

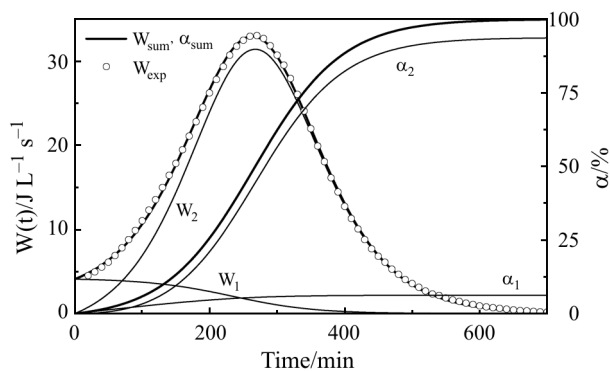


Fig. 2 Decomposing the total curve the heat release rate (W) vs. time into two-component parts. The magnitude of uncatalyzed α_1 and catalyzed α_2 reactions into the total curve conversion vs. time α_{sum} for the system of phenyl glycidyl ether – aniline at 70°C, epoxy- to NH-group ratio: 1.9

Figure 2 shows decomposing the total curve the heat release rate vs. time into two component parts, uncatalyzed W_1 and catalyzed W_2 reactions. In Fig. 2, there is also presented typical curve conversion vs. time. Decomposing the total curve conversion vs time into two component parts, one describing the uncatalyzed reaction and the other describing the catalyzed reaction demonstrates the magnitude of each type of reactions. In order to decompose the total kinetic curves conversion vs. time into the components we used the mass balance expressed in moles of the functional groups:

$$C_{t1} + C_{t2} = C_t \quad (6)$$

where C_{t1} and C_{t2} are the number of reagent moles reacted in each pathway. C_t is the total moles reacted to time t . C_{t1} , C_{t2} and C_t has the units the molar concentrations. Then it follows that degree of conversion at any time during reaction can be expressed as a sum of conversions of two pathways: the one conversion α_1 refers to uncatalyzed pathway and the other α_2 denotes the conversion in catalyzed pathway. Thus the total degree of conversion α at time t is expressed as the sum of two terms:

$$\alpha = \alpha_1 + \alpha_2 \quad (7)$$

α_1 and α_2 depend on the exothermic heat at time t during isothermal scan Q_t through the relation: $\alpha_1 = c_{01}Q_{t1}/Q_{\text{mol1}}$ and $\alpha_2 = c_{02}Q_{t2}/Q_{\text{mol2}}$ with the understanding that

$$Q_{t1} + Q_{t2} = Q_t \quad (8)$$

where Q_{t1} and Q_{t2} , are the heats evolved at time t and Q_{mol2} , Q_{mol1} are molar heats of epoxy ring opening for catalyzed and uncatalyzed pathways respectively. Q_t is the total heat evolved at time t . c_{01} and c_{02} are initial concentrations of the reagent in uncatalyzed and catalyzed reactions respectively. These data show that the

part of the uncatalyzed reaction is sufficiently small compared with the catalyzed reaction around 50% conversion in total curve. At that in all cases, catalyzed reaction is much faster than uncatalyzed pathway [3–5].

The molar heat Q_{mol2} for catalyzed reaction in the system of resorcinol diglycidyl ether- *m*-phenylenediamine is similar to those found for the model reactions, aniline with phenyl glycidyl ether and with resorcinol diglycidyl ether respectively. Here, molar heat of epoxy ring opening for uncatalyzed reaction, Q_{mol1} more than twice as much as Q_{mol2} (Table 1).

Another common feature of above systems is structure forming that can occur without a change in the underlying mechanism of epoxy ring opening. Following the reactions by calorimetry, we observed that near at the later stages of the reaction between aniline and phenyl glycidyl ether, there was an increase in the rate of heat evolution, which we associated with hydrogen-bonded aggregation of OH-containing molecules with other OH-containing molecules in the final product. The probability of this interaction is concentration dependent; it is not significant at sufficiently low concentration of aminoalcohol. As the concentration is increased, the isolated molecules of aminoalcohol in system are depleted in favor of aggregates. Thus, the products when present in high proportions at the later stages of the reaction might also influence the thermokinetics. The molar heat of this process was evaluated from the thermokinetic curves. The similar behavior was observed in the case of the reaction between aniline and resorcinol diglycidyl ether as well as in the reaction of phenyl glycidyl ether with *m*-phenylenediamine [5, 6]. In epoxy-amine reactions, the fact of the spontaneous association of the molecules of aminoalcohol into stable aggregates joined by hydrogen bonds has been pointed out by Harrod who investigated a series of model compounds and polymers in the 3- μ region of the infrared. He has demonstrated that all bulk materials show intense, broad peak around 3400 cm^{-1} , typical of hydrogen-bonded OH-groups [11].

Since the first points of the thermokinetic curve is subject to some error, the values of Q_{mol1} (molar heat in the uncatalyzed reaction) are not to be taken too seriously, but serve to emphasize the fact that the heat effect in uncatalyzed reaction is more than those in catalyzed pathway.

The kinetics found for the reaction of phenyl glycidyl ether with *m*-phenylenediamine is the same as those of the above epoxy-amine reactions [6]. However, contrary to them, the given reaction yields a crystalline solid during the reaction. The process of crystallization is seen in the thermokinetic curves. In this case, the time course of the reaction must be rep-

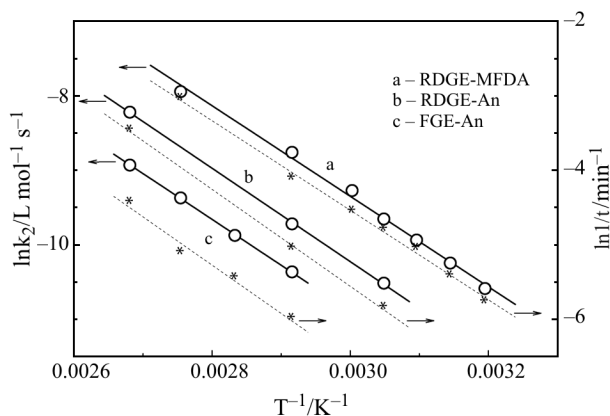


Fig. 3 Arrhenius plots for rate constants k_{ef2} (O). Symbol of * represents dependence of $\ln(1/t_{W=Wmax})$ on $1/T$

resented by a sum of three exothermic terms, the third of which is the initial stage of crystallization.

In model reactions, thermokinetic data show that the isothermic kinetic curve comprises of exotherms of three processes. However, in the reaction involving vitrification the third process is endothermic one. It is well seen in the curves of the heat rate release as a sharp decrease in the rate of heat evolution due to the endothermic process [3].

Figure 3 shows a plot of $\ln(k_2)$ vs. $1/T$ for three reactions. The calculated activation energies for the catalyzed reaction in the reacting systems of resorcinol diglycidyl ether and *m*-phenylenediamine, resorcinol diglycidyl ether and aniline and phenyl glycidyl ether with aniline were found to be 51, 52 and 51 kJ mol⁻¹ respectively. It is easy to observe from Fig. 2 that the values of activation energy are in good agreement for the three reactions.

An independent confirmation on the interpretation given to thermokinetic data can be obtained from the point of the maximal rate in the experimental curves of the heat release rate vs. time. It is clear from the Fig. 3 that the point of the maximum in the experimental curve of the heat release rate is in close agreement with the point of maximum in the curve of the catalyzed reaction. This feature allows direct comparison of the results obtained in above mentioned reactions through the time taken to reach the point of the maximum in the experimental curve of the heat release rate.

According to Eq. (5) the extent of conversion at which the catalysed reaction rate reaches the maximum value ($\alpha_{max} = C_x^{peak}/C_0$) is found by setting the first derivative of Eq.(5) to zero.

Thus, from Eq. (5) the following approximate expression is obtained:

$$\frac{dC_x}{dt} = [k(C_0 - C_x) - kC_x] = 0 \quad (9)$$

A solution of Eq. (9) for C_x gives $C_x^{peak} = 0.5 C_0$ or $\alpha_{max} = 50\%$.

From Eq. (9) it is clearly seen that α_{max} is independent of the initial reagent ratio. In other words, for a given kinetic model, the extent of conversion at the peak of the reaction isotherm in catalyzed reaction is a constant and equals 50%.

Under the conditions where catalyzed reaction plays the dominant role, the maximum in the experimental curve of the heat release rate is in close with the point of maximum in the curve of the catalyzed reaction, Fig. 1. In this case, the time required to reach the peak rate in the total curve the heat release rate, $t_{W=Wmax}$ in Fig. 2 would have the same Arrhenius plots as the reaction rate constant in catalyzed reaction.

It can be shown that

$$\ln(1/t_{W=Wmax}) = \ln(A/B) - E/RT \quad (10)$$

where $B = \ln(1/\alpha_{W=Wmax} - 1) / c_0$; $\alpha_{W=Wmax}$ is the extent of conversion at which the reaction rate reaches the maximum value; A is pre-exponential factor determined by the Arrhenius law:

$$k_{ef2} = A \exp(-E/RT) \quad (11)$$

In saying this we assume that the conversion at the peak rate in the total curve the heat release $\alpha_{W=Wmax}$ coincides closely with extent of conversion at which the catalysed reaction rate reaches the maximum value. Indeed, the experimental data demonstrates that independent of the initial reagent ratio, the conversion at the peak rate in the total curve the heat release ranges from 47 to 49%.

The catalysed reaction is given by the Eq. (5), its integrating gives:

$$k_{ef2} t c_0 = -\ln(1/\alpha - 1) + \ln(1/\alpha_0 - 1) \quad (12)$$

where α_0 is the extent of conversion at $t=0$. From the Eq. (12), neglecting the value of α_0 which is negligible compared to α , one obtains

$$k_{ef2} = -\ln(1/\alpha - 1) / c_0 t \quad (13)$$

The extent of conversion at the peak rate is independent of the reaction temperature; then term in braces is constant, and equals B , say. By taking logarithm of (13), we obtain

$$\ln k_{ef2} = -\ln B - \ln t_{W=Wmax} \quad (14)$$

If we linearize Arrhenius Eq. (11) by taking logarithm, combination with Eq. (14) gives

$$-\ln t_{W=Wmax} = \ln A - E/RT - \ln B \quad (15)$$

As a result, we obtain

$$\ln(1/t_{W=Wmax}) = \ln(A/B) - E/RT \quad (16)$$

The utility of Arrhenius plots (16) is illustrated in Fig. 2. Arrhenius plots show approximately parallel

straight lines; ordinates are logarithm of reciprocal time at the peak rate, the abscissas are reciprocal temperature. This approach can be used as an analytical tool to identify the reaction mechanism involving a prereaction stable complex formed by the reagent molecules. As a means of determining activation energies, this method of the Arrhenius plots (16), Fig. 2, is useful in confirming the absence of another processes during epoxide ring opening by amine.

A feature common to these reactions is also that under conditions of excess amine, the reaction rate increases with increasing amine concentration. This experimental finding further substantiates the molecular mechanism provided by the kinetic model for the reaction of epoxy-ring opening by amine. In Fig. 4, the rate constants of the catalytic activity of excess amine for two reactions are shown as linear function of the excess of amine ($C_a - C_E$). This trend of plots can be interpreted as indicating that, when the excess of amine becomes the solvent, high amine concentrations exerts a large catalytic effect. The slope of the lines is slightly different, as shown in Fig. 4. Thus the rate constants k_{ef2} tend to

$$k_{ef2} = k_{amine} (C_{A_0} - C_{E_0}) + k_{ef2(A=E)} \quad (17)$$

where $k_{ef2(A=E)}$ is the intercept and k_{amine} is the slope. $k_{ef2(A=E)}$ is the apparent rate constant of the stoichiometric composition; $(C_{A_0} - C_{E_0})$ is excess of amine over epoxide, mol/l. The term $k_{amine} (C_{A_0} - C_{E_0})$ can only play a role when the reaction proceeds under conditions of excess amine.

A linear plot of k_{ef2} , at 70°C vs. $(C_A - C_E)$ values, Fig. 4, for reactions of phenyl glycidyl ether with aniline and resorcinol diglycidyl ether with aniline yields k_{amine} values. Figure 4 demonstrates that k_{amine} values are very similar for both reactions whereas these reactions differ by $k_{ef2(A=E)}$ values. It is interesting that for the reaction phenyl glycidyl ether- *m*-phenylenediamine, k_{amine} value is more as compared with the reactions with aniline (Fig. 4).

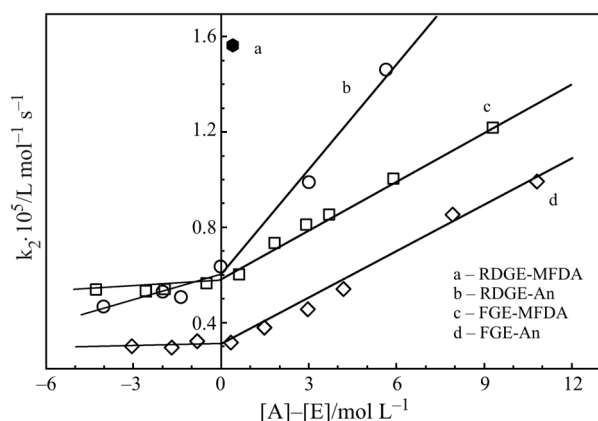


Fig. 4 Dependence an effective rate constant k_{ef2} on the amine excess, 70°C

The data on resorcinol diglycidyl ether – aniline and phenyl glycidyl ether – aniline tend to be more accurate because this reaction could be followed for a long time, as compared to the reaction of resorcinol diglycidyl ether with *m*-phenylenediamine which was half over in about ten minutes. The fact the reaction resorcinol diglycidyl ether – *m*-phenylenediamine proceeds very rapidly under conditions of excess amine made it practically impossible to get thermokinetic parameters at 70°C and this system has not been considered in Fig. 4 where this system is represented by the rate constant only for stoichiometric mixture.

An important point that should be noted is the existence of the structural changes which accompany the solventless reaction of epoxy ring opening. One cannot draw conclusion about kinetics and the mechanism of the reaction between amine and epoxide by the constructing kinetic models which consider only the simple picture of the interaction between the functional groups of the reagents. However, the activation energy can be evaluated from the time to reach the maximal reaction rate in the curve of experimental curve of the heat release rate vs. time.

In addition to these experimental results, the present report leads to a series of intriguing questions whose resolution may improve our understanding of the epoxy-amine reactant medium. One of them concerns the most reaction rate observed in the reaction involving vitrification compared with the model reactions. It is interesting the origin of the difference between the molar heat reactions in uncatalyzed and catalyzed pathways. Also intriguing are k_{amine} values that are observed under conditions of excess amine in catalyzed pathway. The nature of the epoxy-amine melts is itself worthy of further investigations.

Conclusions

Much of interest in chemical kinetics comes from the study of related reactions forming a series. The compounds included in this study are among the ones differing only a number of the functional groups. All these reactions show similar kinetic behavior. In these series of epoxy-amine reactions analyzed the reaction between resorcinol diglycidyl ether and *m*-phenylenediamine is one where increasing the viscosity of the reaction mixture leads to its vitrification during the reaction. This reaction proceeds very rapid compared with the model reactions. The latter is of particular interest as the demonstration that glass-forming reaction mixture is completely independent of increased viscosity.

The method for valuation of Arrhenius parameters and constant rate for catalyzed reaction is re-

ported which involves finding the time taken to reach the point of the maximum in the experimental curve of the heat release rate vs. time. This idea arose from the observation that the point of the maximum in the experimental curve of the heat release rate is in close proximity to the point of maximum in the curve of the catalyzed reaction which corresponds to 50% conversion. This is a very important feature as it allows direct comparison of the results obtained by isothermal calorimetry and might be useful as a practice of the study of the similar reactions by calorimetry.

The data that we present here demonstrate that thermokinetic method can be used for a rapid determination of the activation energy in similar epoxy-amine systems by measuring times to point of the maximum in the experimental curve of the heat release rate vs. time.

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Received: June 20, 2005

Accepted: April 28, 2006

DOI: 10.1007/s10973-005-7144-3