

KINETIC METHOD BY USING CALORIMETRY TO MECHANISM OF EPOXY-AMINE CURE REACTION Part VI. Phenyl glycidyl ether–aniline

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Abstract

The thermokinetic behavior of the reaction between phenyl glycidyl ether and aniline closely resembles the analogous diepoxy diamine cure reaction in that the reactants are assembled before bond-breaking step occurs, and does not proceed through free reacting groups. The mechanism of the reaction between phenyl glycidyl ether and aniline in solventless system involves in addition to mechanism of the epoxy ring opening, structure changes accompanied by phase separation related to the self-aggregation.

In an attempt to obtain further information about the reaction mechanism, the DSC heating runs of the reacted samples have been examined. These results suggest that the observed endothermic peaks are associated with additional ordering. The latter takes place only at lower temperature than reaction temperature.

Since the rate constant k_2 values for autocatalysed reaction follow of Arrhenius behavior, it is possible to calculate the activation energy, which is $E=51$ kJ mol⁻¹. Analysis of the kinetic experiments demonstrates that the heat of reaction that are detected in kinetic measurements provide correct information about the mechanism of the process.

Keywords: aniline, DSC, epoxy-amine, phenyl glycidyl ether, reaction kinetics in solventless systems, thermokinetics

Introduction

The old increase of interest in mechanism of epoxy-amine reactions is partly the result of calorimetric method that is readily available. The relevance of calorimetry to physical organic chemistry has been emphasized by Arnett [1]. Previously, we have shown that the kinetic method for determining kinetic parameters by calorimetry should be of considerable generality and for favorable cases can permit research of the kinetic of the reaction where the other methods would be very difficult to employ [2–4].

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In preceding work [5] calorimetry has been successfully applied to study a simple molecular epoxy-amine reaction such as phenyl glycidyl ether–aniline. Our aim was to construct a kinetic model which reproduces the most important features of this solventless system.

The reaction kinetics of a simple molecular epoxy-amine reaction was found to be analogous to kinetic behavior of the curing reaction. A characteristic property of epoxy-amine reaction is a preassociation mechanism in which the reactants are assembled before bond-breaking step occurs, and does not proceed through free reacting groups. A similar mechanism holds both in epoxy-amine curing reaction [2–4] and in a simple molecular epoxy-amine system in solventless systems [5].

Calorimetric study on reaction kinetics of phenyl glycidyl ether–aniline system revealed the existence another exothermic process apart from exothermic effect of the reaction of the epoxy ring opening [5]. The most probable explanation may be found in that this exothermic process reflects the self-association tendency in the behaviour of the reaction product. The product molecules containing OH-group (Fig. 1) have a potential for spontaneous association through hydrogen bonding [6]. There is evidence for the formation of new hydrogen-bonded complexes between OH-groups [7]. The authors suggest that these complexes are related to the increase in viscosity of the reactive mixture in the later stages of the reaction.

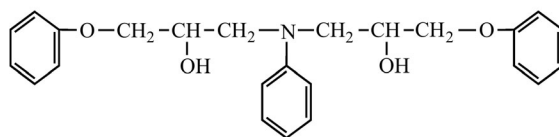


Fig. 1 Structure formula of the product of the reaction between phenyl glycidyl ether and aniline

These data let us consider such typical behaviour of aggregation as molecular organisation of the reaction product. It seems therefore important to gain insight into the physicochemical character of molecular organisation of the reaction product.

We could not anticipate that our kinetic analysis of the reaction would provide direct evidence of the nature of the patterns of molecular aggregation that exist in reaction medium. What we did hope for, however, is that we would be able to explore the extend to which our analysis appear to confirm or refute ideas as we had formulated from previous study [5].

According to kinetics of the reaction [5] we attribute the increase in the viscosity during the course of the reaction to the assumption that the product molecules undergo a structural transition leading to the production of large aggregates in the reaction medium. These molecules assemblies are constructed through non-covalent bonding interactions, presumably, hydrogen bonding. Since solvation of the molecules of the product is not favourable resulting in their self-aggregation, these aggregates can be referring to irreversible aggregates [8]. Irreversible aggregates are formed when spontaneous separation becomes energetically unfavourable. For example, in the case of acid-base interaction, owing to hydrophobic interaction butyric acid in water prefer self-aggregation to interaction with pyridine [9]. Evidently, in our case, these aggre-

gates are stabilized by hydrogen-bond interaction which results in appearance of the locally ordered phases. The latter imply that further reaction proceeds in saturated medium with respect to the molecules of the product and must occur with phase segregation process. Therefore in [5], kinetic data have been analyzed through the application of saturation model. The possibility of determining by kinetic method whether a compound is aggregated can be traced back to the works reported in 1970s [10, 11], where it was noticed extensive aggregation without detectable turbidity.

A possible involvement of such aggregates in reaction in nonaqueous media has generally been ignored, because 'stacking' is commonly attributed to 'hydrophobic' interactions unique to an aqueous environment, and is not thought of as being important in organic media. This is illustrated by the example of self-aggregation of hexanoic acid in acetonitrile [9].

Thus, the magnitude of three effects, i.e. an exothermic effect for epoxide ring opening in uncatalysed reaction, an exothermic effect for epoxide ring opening in autocatalysed reaction and an additional exothermic process should be reflected in thermochemistry of the reaction under consideration.

In spite of the large amount of significant work that has been published on the epoxy-amine reactions, there are many fundamental questions that remained unanswered, especially in thermokinetics. A very important point which has not been noted concerns the occurrence molecular organization organisation of the reaction product. At the present stage of research the mechanism of product structuring is mostly unknown.

The kinetics and mechanism of the reaction of phenyl glycidyl ether-aniline has been the object of several studies [12, 13]. However the results have been indefinite. The object of this work is to extend our knowledge of the thermokinetics of the reaction of epoxide ring opening by amine in the case of the reaction of phenyl glycidyl ether-aniline system. Whereas in the previous paper we have restricted ourselves to cases with different reagent ratios but the same temperature of the reaction, here we will particularly focus on the thermokinetic curve obtained at various reaction temperatures.

Experimental

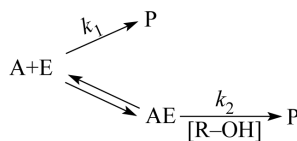
A mixture of epoxide and aniline with the same reagent ratio was subjected to isothermal reaction at four temperatures within the range 70–100°C. Thermokinetic curves were obtained employing stoichiometric quantities of aniline.

Sample preparation and the details of the kinetic measurements were carried out as described previously [5]. The treatment of experimental kinetic curves was conducted by 'kinetic investigation' approach to reaction mechanism. A detail discussion of this approach is described in a series of the works [2–4].

After the studies of isothermal kinetics the samples were stored under room temperature at least some months before any DSC analysis. DSC heating runs of the reacted samples were conducted at heating rate of 5°C per min.

Results and discussion

The results obtained previously [5] are consistent with the following mechanism, where the epoxide, amine and reaction product molecules are designated as E, A and P, respectively.



Scheme 1

In the path corresponding to k_1 the reaction product P is formed by uncatalyzed reaction. The amount of product formed via uncatalysed pathway is small but the occurrence of this reaction cannot be ignored. The ‘uncatalyzed’ reaction evolving heat at a rate W_1 , plays an important part in early stage of the process [5]. The reaction pathway k_2 is regarded as an autocatalytic reaction in which catalytic effect is ascribed to the complex formation AE between the reagents E (epoxy) and A (aniline), owing to the formation of hydrogen bonds between the hydrogen atoms of NH_2 -group of aniline and the oxygen atoms of epoxy-group.

In autocatalytic pathway there is equilibrium between intermediate AE and reactants [2]. From Scheme 1 the heat release rate can be formulated as in Eq. (1).

$$W = Q_{\text{mol}1} k_{\text{ef}1} [E][A] + Q_{\text{mol}2} k_{\text{ef}2} [AE][P - P_{\text{inactive}}] + Q_{\text{mol}3} k_{\text{ef}3} [(P - P^{\text{sat}}) - P_{\text{inactive}}] \quad (1)$$

where the reagent concentrations are represented in terms of the concentration of functional groups. $Q_{\text{mol}2}$ is the molar heat of the epoxy ring opening for autocatalyzed reaction; $Q_{\text{mol}1}$ and $Q_{\text{mol}2}$ are the molar heat of the epoxy ring opening for uncatalyzed reaction and autocatalyzed reactions respectively; $k_{\text{ef}1}$ is a rate constant for uncatalyzed reaction; $k_{\text{ef}2}$ is (observed) effective rate constant for the reaction catalyzed by OH groups formed in the reaction.

The heat release rate of the reaction phenyl glycidyl ether with aniline have been shown previously to follow the rate law of Eq. (1), in which the reaction of epoxy ring opening is given by the first two terms, one is uncatalyzed and the other, the main, is autocatalyzed. To complete the kinetic description we have to add a term ascribed to phase separation. In the present case, phase separation is related to the loss of catalytic activity by the molecules of the reaction product by reason of aggregation.

The problem of aggregation can be considered as alternative process with respect to protein folding. As is well known, unfolded parts of the polypeptide chain are more susceptible than folded regions to attack by proteolytic enzymes [8]. These data indicate that conformational changes are responsible for the loss in activity by protein folding. Similar situation was demonstrated by the example of hydrolysis of ribonuclease polypeptide chain [14].

In Eq. (1), the concentration of OH groups denoted as P_{inactive} corresponds to the situation when the reaction mixture undergoes microphase separation. Then, P^{sat} is

the concentration of OH groups the reaction product corresponding to the onset of additional exothermic process. In other words, P^{sat} corresponds to the saturated concentration of hydroxyl groups. For this process, Q_{mol3} and k_{ef3} are the molar heat and a rate constant, respectively.

The data [2–5] show that the kinetic model represented by Scheme 1 is generally valid for epoxy-amine reaction including model reaction of phenyl glycidyl ether with aniline. The heat release rate of the reaction phenyl glycidyl ether with aniline have been shown previously to follow the rate law of Eq. (1), in which the reaction kinetics of epoxy ring opening is given by the first two terms, one is uncatalyzed and the other, the main, is autocatalyzed. The third term represents the expression giving the rate of escape of OH groups from the reaction medium. This process is observed after 70% of conversion.

Complete mathematical details of our models were presented earlier [1, 5] and thus, only a brief outline is given here. In our model we seek to connect the reaction kinetics with corresponding structural changes in the reaction medium. The latter term in Eq.(1) is assumed evaluate the contribution from these structural changes to the total reaction heat.

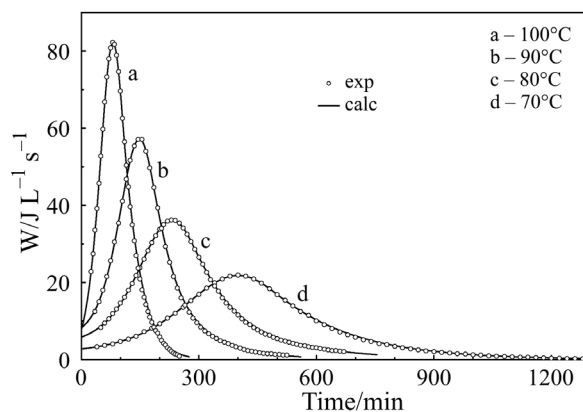


Fig. 2 Rate curves on the reaction time at various reaction temperatures

Figure 2 shows the experimental curves obtained for the reaction phenyl glycidyl ether–aniline at different temperatures. The symbols represent the experimental data and the lines show the calculated curves. The differences between observed and kinetic curves computed according to Eq. (1) are within 1.5%. This agreement between the experimental data and the theoretical Eq. (1) indicates that above kinetic model is valid.

The results of computer treatment of experimental kinetic curves obtained at different temperatures are summarized in Table 1. The latter lists the molar heats of the epoxy ring opening and the rate constants of the two pathways, uncatalysed and catalysed. The rate constant values for the uncatalysed reaction is not of high precision for the reason previously mentioned [4]. However, it is evident that the values of k_1 obtained from Eq. (1) are much less than the rate constants k_2 for catalysed reaction.

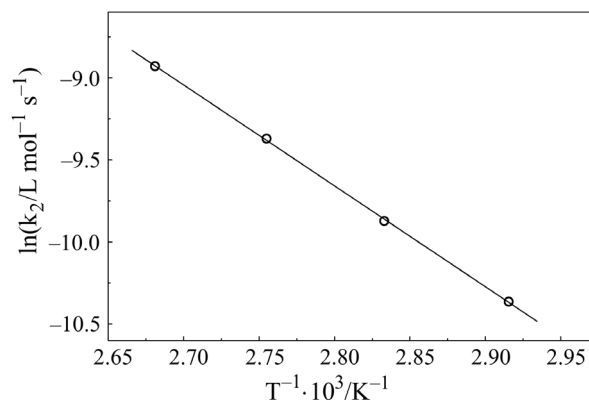


Fig. 3 Arrhenius plot of the reaction rate constants for the reaction phenyl glycidyl ether–aniline

In the temperature range of 70 to 100°C the Arrhenius plot gives straight line. The plot is shown in Fig. 3. The obtained Arrhenius activation energy is 51 kJ mol⁻¹. This value is close to the value 52 kJ mol⁻¹ obtained for the cure reaction between diepoxy and diamine [4].

Table 1 Summary of thermokinetic parameters for the reaction phenyl glycidyl ether–aniline at 70, 80, 90 and 100°C

Temperature/ C	70	80	90	100
$Q_{\text{mol1}}/\text{kJ mol}^{-1}$	204	210	223	68.7
$Q_{\text{mol2}}/\text{kJ mol}^{-1}$	85.5	86.8	84	78.2
$Q_{\text{mol3}}/\text{kJ mol}^{-1}$	38.1	53.4	45	25.8
$k_1 \cdot 10^7 / \text{l mol}^{-1} \text{s}^{-1}$	4.12	8.39	11.1	33.9
$k_2 \cdot 10^5 / \text{l mol}^{-1} \text{s}^{-1}$	3.16	5.16	8.51	13.3
$C^{\text{sat}}/\%$	69.8	68.6	69.5	73.7
$Q_{\text{sum}}/\text{kJ L}^{-1}$	577	606	509	475
$Q_2/\text{kJ L}^{-1}$	461	460	448	407
$Q_1/\%$	9.4	11	12	6.4
$Q_2/\%$	80.1	82.8	88	88.7
$Q_3/\%$	10.5	13.3	14	7.7

The value of α^{sat} is the degree of conversion when the increasing in the rate of evolving of the heat due to the onset of additional exothermic process is observed.

The onset of additional exothermic process α^{sat} corresponds to the ascertainment of the saturated concentration of OH groups in reaction medium. These kinetically determined values of α^{sat} which range from 68 to 74% are reported in Table 1. As can be seen these values did not show definite temperature dependence. We have also used Eq. (1) to estimate the magnitude of all three processes in the total re-

action heat. The values of the total reaction heat denoted as Q_{sum} are reported also in this Table 1.

As can be seen from Table 1, in percentage terms, the magnitude of the integral heats Q_1 , Q_2 and Q_3 to the total heat each little dependent on the reaction temperature. Results given in Table 1 show also that although the yield of the product in uncatalysed reaction do not exceed 12%, this reaction makes the major contribution on the total exothermic at the beginning of the reaction. However, the major portion of the total reaction heat is given by k_{ef2} route.

Some time after the completion of the kinetic experiments just described we were prompted to perform DSC heating runs. The DSC measurements revealed that on heating the samples endothermic peak was observed, which could be attributed to a melting transition.

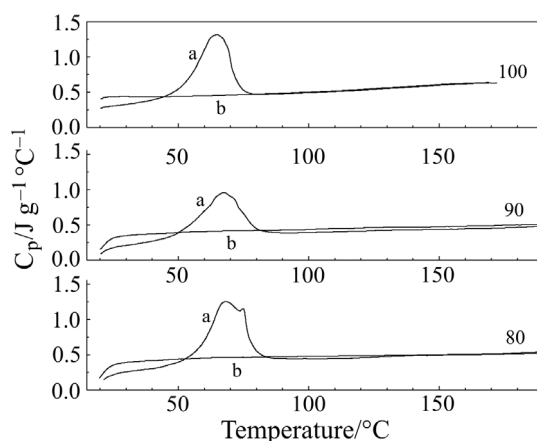


Fig. 4 The a – first and b – second DSC heating scan of the reacted samples

Figure 4 shows these DSC curves. An endothermic peak can be seen at approximately 70°C in the range between 45 and 80°C. As evident from Fig. 4, there are no endotherms occurring at temperature higher than 80°C. Therefore, one might think that crystallisation could not occur under reaction temperatures more than 80°C. These data imply that crystallisation might be initiated after the completion of the reaction when the samples were subjected to annealing.

From all these considerations, it is reasonable to assume that in the course of the reaction, molecules of product associate, and then these particles stick together in aggregates and precipitate from solution at lower temperature. We suppose that interaction between the aromatic rings also contributes to formation of these non-covalent supramolecular assemblies. In other words, the reaction involves, in addition to mechanism of the epoxy ring opening, ordered regions formation. However, a significant ordering (crystallisation) takes place only at lower temperature than reaction temperature when molecules take thermodynamically favorable conformation. Thus, the crystallisation would therefore represent merely by additional ordering of the aromatic rings, with their newly adopted conformation, into a lattice. Aggregation of the

molecules of the reaction product in the course of the reaction can be solely the precursor of their crystallisation.

According to this interpretation, endothermic peak in DSC heating scans may be explained by a two-step melting process for the reaction under consideration: in the first stage melting of the ordered structure present and in the second stage the microphase mixing of disordered molecules occurs.

This study may thus point out that thermokinetic investigation is very effective in the case of epoxy-amine reactions. Aforesaid thermokinetic model promise to be a useful starting point for understanding the structural changes in the reaction medium, where more traditional methods would be very difficult to employ.

Conclusions

Analysis of the kinetic data led to the conclusion that mechanism of the reaction between phenyl glycidyl ether and aniline in solventless system involves in addition to mechanism of the epoxy ring opening, structure changes accompanied by phase separation related to the self-aggregation.

Detailed analysis of thermokinetic curves was used to show that it is possible to obtain quantitative information from calorimetric investigation of the reaction in order to draw a kinetic picture of structural changes in the reaction of phenyl glycidyl ether–aniline.

It may be assumed that the observed change of the reaction mechanism in solventless system is not due to the increasing the viscosity of the system, but due to the association tendency in the behavior of the reaction product.

The results reported above show that the major route for product formation is by autocatalysed reaction. The amount of product formed via uncatalysed pathway is small. However the occurrence of this reaction cannot be ignored especially in early stage of the reaction.

It was found to be the onset additional exothermic process at conversions more than 70%. We believe that additional exothermic process observed in the course the reaction is closely related with the ordered regions formation. Since such structural organisation leads to the microphase separation, the discussion of the kinetics of the reaction at conversions more than 70% was focused on a microphase separation occurring in reaction medium. This type of the kinetic behaviour arises when aggregated species remain soluble during the progress of the aggregation process. At the same time crystallisation takes place only at lower temperature than reaction temperature. This situation presents an interesting problem for further study.

References

- 1 E. M. Arnett, *J. Chem. Therm.*, 31 (1999) 711.
- 2 R. M. Vinnik and V. A. Roznyatovsky, *J. Therm. Anal. Cal.*, 73 (2003) 807.
- 3 R. M. Vinnik and V. A. Roznyatovsky, *J. Therm. Anal. Cal.*, 73 (2003) 819.
- 4 R. M. Vinnik and V. A. Roznyatovsky, *J. Therm. Anal. Cal.*, 71 (2003) 531.

- 5 R. M. Vinnik and V. A. Roznyatovsky, *J. Therm. Anal. Cal.*, 74 (2003) 29.
- 6 M. C. Etter, *Acc. Chem. Res.*, 23 (1990) 120.
- 7 J. Mijović and S. Andjelić, *Macromolecules*, 28 (1995) 2787.
- 8 C. J. Roberts, *J. Phys. Chem., B* (2003) 1194.
- 9 S. Moshizuki, Y. Usui and A. Wakisaka, *J. Chem. Soc., Faraday Trans.*, 94 (1998) 547.
- 10 J. P. Guthrie, *Can. J. Chem.*, 51 (1973) 3494.
- 11 J. B. Jones and K. D. Gordon, *Biochemistry*, 12 (1973) 71.
- 12 V. P. Kuznetsova, PhD Thesis, Moscow 1976.
- 13 J. Mijović, A. Fishbain and J. Wijaya, *Macromolecules*, 25 (1992) 979.
- 14 J. A. Rupley and H. A. Scherrega, *Biochemistry*, 2 (1963) 421.