Thermokinetics of the reaction of phenyl glycidyl ether with aniline

R. M. Vinnik,[a] E. A. Miroshnichenko,[a] and V. A. Roznyatovsky[b]★

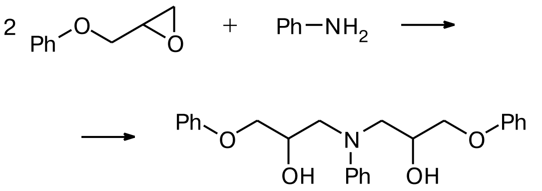
[a]N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 119991 Moscow, Russian Federation.
Fax: +7 (095) 137 8318
[b]Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119992 Moscow, Russian Federation.
E-mail: vit.rozn@chem.msu.ru

The thermokinetic curves in the reaction of phenyl glycidyl ether with aniline were calculated for various compositions of the reaction mixture and temperatures. In addition to the main exothermic effect related to the epoxide ring opening, another exothermic effect of unknown nature was observed. The kinetic data obtained are explained in terms of structural changes caused by the self-aggregation of the reaction product molecules. The "kinetic investigation" approach provides a quantitative analysis of calorimetric data.

Key words: "kinetic investigation" approach, thermokinetics, phenyl glycidyl ether, thermochemistry, epoxy compounds, self-aggregation.

Epoxide—amine systems are the subject of many thorough studies, although the kinetics of many reactions in these systems had not been extensively studied. In particular, this is true for the reaction of phenyl glycidyl ether with aniline (Scheme 1).

Scheme 1



This reaction has a high exothermic effect and, hence, it can conveniently be studied using the thermokinetic method.[1] However, the association of the reaction product molecules and the formation of a new phase result in the situation when the kinetic equation that takes into account only the mechanism of reactant consumption fails to describe the rate of heat evolution (W) as a function of time observed in experiments.

The purpose of this work is to analyze thermochemical data for the reaction of phenyl glycidyl ether with aniline by scanning calorimetry.

Experimental

Phenyl glycidyl ether (E) and aniline (A) (both purchased from Merck) were purified by vacuum distillation under argon. A mixture of reactants of a known composition was prepared at ~20 °C. A weighed sample of the mixture (0.25 g) was placed in a standard aluminum cell, and the cell was sealed and placed in an DSK-III differential scanning calorimeter (Setaram, France). Kinetic measurements were carried out in the isothermal regime. The reaction product was studied in the dynamic regime, and the measurements were carried out after the samples were stored for a long time at ~20 °C. The heating rate with the temperature scan was 5 °C min^{-1}. The conversion at each time moment was calculated from the ratio Q_t/Q_{mol}, where Q_t is the quantity of heat released at a given moment, and Q_{mol} is the molar heat of the reaction referred, in all cases, to 1 mole of functional groups of a deficient reactant.

Results and Discussion

The typical curve of the rate of heat evolution (W_{exp}) obtained by the kinetic experiment in the isothermic regime is presented in Fig. 1. Some results obtained by scanning the samples in the dynamic regime are presented in Fig. 2. The thermograms contain the characteristic endotherm, whose size depends on the ratio of reactants in the reaction mixture (see Fig. 2). This peak cannot be registered upon the repeated scan. An additional heat release is observed during the kinetic experiment in the thermograms of the reacting mixtures that contain the endotherm.

The thermokinetics of the reaction considered can be presented by Scheme 2, which shows that the chemical reaction proceeds *via* two routes: noncatalytic and autocatalytic (their parameters, *viz.*, rate constants (k) and heats of reactions (Q), are marked by indices 1 and 2,

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 371—375, February, 2005.

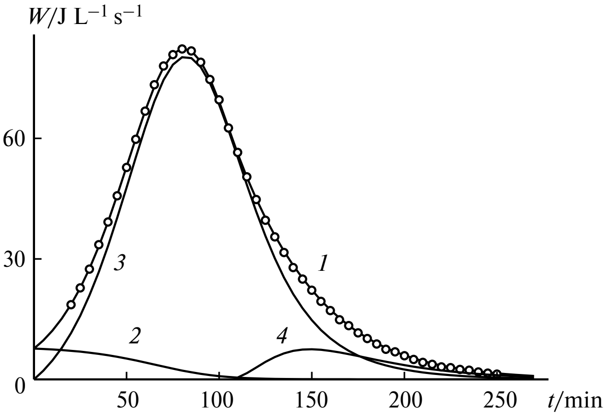


Fig. 1. Experimental (W_{exp}) (*1*, points) and calculated (W_{calc}) (*1*, line) curves of the heat release rate deconvoluted into components W_1 (*2*), W_2 (*3*), and W_3 (*4*).

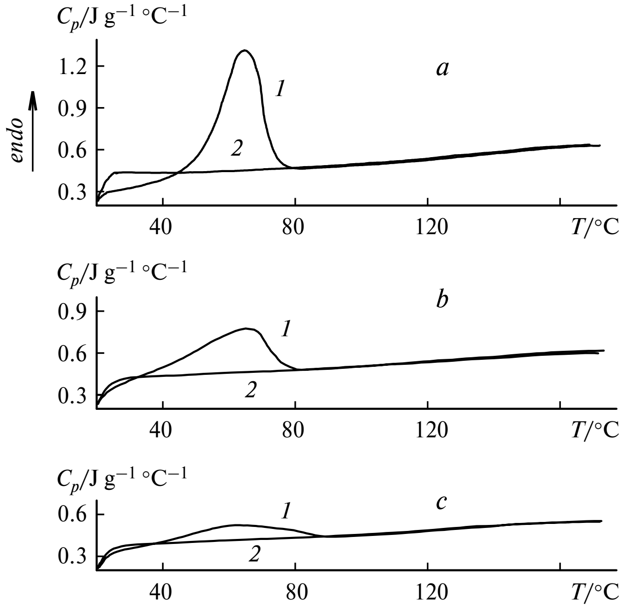
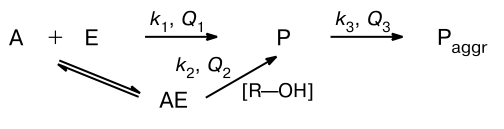


Fig. 2. Temperature plots of the heat capacity (C_p) in the reacted mixture with the ether to aniline ratios: 1.06 (*a*), 0.7 (*b*), and 0.47 (*c*); *1*, first scan and *2*, second scan (reaction temperature 100 °C).

respectively). According to the autocatalytic route, the OH groups that formed catalyze the epoxide ring opening. Index 3 designates an additional heat release process, which can be explained by the formation of aggregated molecules of the reaction product (P_{aggr}).

Scheme 2



A is aniline, E is phenyl glycidyl ether,
AE is reaction complex,
P is reaction product

Scheme 2 is described by the kinetic equation

$$W = Q_{mol,1}k_{app,1}[E][A] + Q_{mol,2}k_{app,2}[AE][P - P_{inact}] + \\ + Q_{mol,3}k_{app,3}[(P - P_{sat}) - P_{inact}][P - P_{sat}], \qquad (1)$$

$P_{inact} = 0$ for $P < P_{sat}$,

where $k_{app,1}$ and $Q_{mol,1}$ are the apparent rate constant and molar heat of the noncatalytic reaction; $k_{app,2}$ and $Q_{mol,2}$ are the apparent rate constant and molar heat of the autocatalytic reaction. An additional heat release ($Q_{mol,3}$) was observed during the kinetic experiment for all reacted mixtures that show the endotherms (see Fig. 2). To take into account the contribution of the additional heat effect to the exothermic behavior of the reaction, we assumed that the interaction process involves the period of nucleation and development of crystallization nuclei, and precipitation occurs at a temperature lower than the reaction temperature. Then in Eq. (1) P_{inact} is the concentration of the catalytically active OH groups leaving the reaction volume during saturation, and P_{sat} is the saturated concentration of the crystallization nuclei.

The expression for the autocatalytic reaction was obtained under the assumption that the reactants are involved in the equilibrium formation of a 1 : 1 AE complex, which is autocatalytically transformed into the reaction product P with the apparent rate constant $k_{app,2}$. This assumption is based on the kinetic data for the epoxide—amine system with different functionalities of the reacting molecules. For example, we have previously shown[2] that the kinetics of the reaction of diamine with monofunctional epoxide is based on the autocatalytic reaction of a complex formed by the reactants. The kinetics of the epoxide ring opening remains unchanged when monofunctional epoxide is replaced by its bifunctional analog.[3]

In addition to the noncatalytic and autocatalytic reactions, another process contributes to the overall exothermic effect. We interpret this process as the formation of intermolecular associates by the product molecules followed by the loss of catalytic activity due to association.

The formation of crystallization nuclei from the reaction product molecules can result in the loss of catalytic activity. Based on the spectral study of the reaction of aniline with phenyl glycidyl ether, we assumed that complexes with a hydrogen bond between the OH groups are formed at high conversions.[4] Since these are the OH groups that are active in the autocatalytic reaction, the association of the reaction product molecules can result in the catalytic activity loss. Therefore, the first two terms of Eq. (1), which describe the consumption of the reactants, can be supplemented by another term that takes into account structural changes in the reaction mixture introduced by the molecules formed in the reaction.

Table 1. Thermokinetic data for the reaction of aniline (A) with phenyl glycidyl ether (E) at 70 and 100 °C

70 °C					100 °C				
[A]/[E]	$Q_{mol,1}$	$Q_{mol,2}$	$Q_{mol,3}$	C_{sat} (%)	[A]/[E]	$Q_{mol,1}$	$Q_{mol,2}$	$Q_{mol,3}$	C_{sat} (%)
	kJ mol^{-1}					kJ mol^{-1}			
0.52	335.6	89.86	14.72	73.2	0.48	29.9	72.5	15.5	63.1
0.72	169.6	92.95	26.75	69.0	0.70	262.0	87.1	45.7	60.6
0.86	152.8	84.57	46.47	63.5	0.90	98.0	91.1	52.1	67.9
1.06	204.3	85.83	38.10	69.8	1.06	68.7	78.2	25.8	73.7
1.28	204.3	97.97	26.13	74.2	2.20	201.0	98.4	0	100
1.54	377.2	99.23	25.96	76.3	3.06	213.0	106.0	0	100
1.90	201.3	107.20	0	100	4.08	201.0	87.7	0	100
3.10	522.5	86.08	0	100					
4.50	258.7	93.78	0	100					

The P_{inact} concentration in Eq. (1) is related to the number of functional groups of the product molecules leaving the reaction sphere. In this case, P_{sat} is the concentration of catalytically active species. Once the value of P_{sat} is reached an additional heat release commences accompanied by the establishment of a saturated concentration of the OH groups in the reaction medium; $Q_{mol,3}$ is the molar heat of this process; and $k_{app,3}$ is the apparent rate constant of the decrease in the catalytic active species in the reaction volume.

The kinetic curve of the heat release calculated by Eq. (1) and the results of deconvolution of the total rate of heat release to components W_1, W_2, and W_3 are presented in Fig. 1. Indices 1, 2, and 3 designate the rates of the noncatalytic and autocatalytic reactions and the self-aggregation of the reaction product molecules, respectively. The deviation of the calculated kinetic curve from the experimental one was estimated by the *R* factor.[5] In all experiments, the *R* factor did not exceed 1.5%. The heats $Q_{mol,1}$, $Q_{mol,2}$, and $Q_{mol,3}$ for the considered processes are presented in Table 1.

The initial points in the thermokinetic curve were obtained by extrapolation, which especially affects the $Q_{mol,1}$ values. The rate of the noncatalytic reaction W_1 achieves remarkable values within the first 75 min. The $k_{app,1}$ and $k_{app,2}$ values calculated by Eq. (1) satisfactorily fit the Arrhenius equation with an almost equal slope (Fig. 3). The apparent activation energy (E_a) values are equal to 50.6 and 51.2 kJ mol^{-1}, respectively. These data agree with the experimentally found E_a values. For the autocatalytic reaction between bifunctional amine and epoxide, E_a is 51 kJ mol^{-1}, whereas that for the noncatalytic reaction is 52 kJ mol^{-1}.[6] The Arrhenius plot for the noncatalytic reaction has a higher pre-exponential factor than that for the autocatalytic reaction.

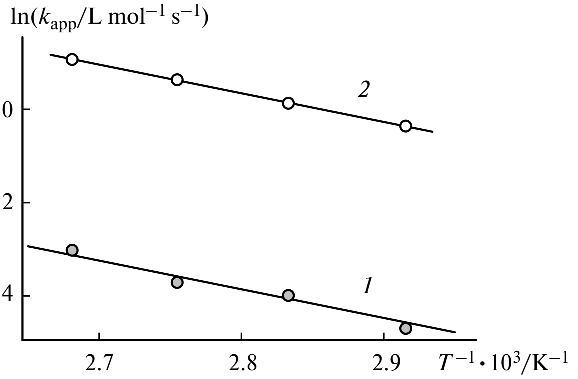


Fig. 3. Arrhenius dependences of $k_{app,1}$ (*1*) and $k_{app,2}$ (*2*).

The processes with the heat release rates W_1, W_2, and W_3 differ by the molar heats Q_{mol}. Due to this, they were separated quantitatively. As can be seen from the obtained data, the consumption of the reactants in the reaction (see Scheme 1) proceeds mainly *via* the autocatalytic route (see Table 1).

The reaction rate always increases with an increase in the amount of aniline in the mixtures with an excess of the latter, while the mixtures with excess epoxide react more slowly than the stoichiometric mixtures[2–7] (see Table 1). The increase in the conversion rate of the mixture containing excess aniline can be explained by the catalytic activity of its excessive amount. This conclusion is confirmed by the data presented in Fig. 4, indicating that the $k_{app,2}$ values are virtually constant in the region where the reactant ratios change from excess epoxide to the stoichiometric composition. On further increase in the aniline content in the reaction mixture a linear dependence of $k_{app,2}$ on the excessive (compared to the stoichiometric composition) concentration of the NH groups is observed

$$k_{app,2} = k_A(C_{A_0} - C_{E_0}) + k_{app,2}{}^{A=E}, \qquad (2)$$

where the product $k_A(C_{A_0} - C_{E_0})$ is related to the catalytic activity of excess aniline, $k_{app,2}{}^{A=E}$ is the apparent reaction rate constant at the stoichiometric composition of

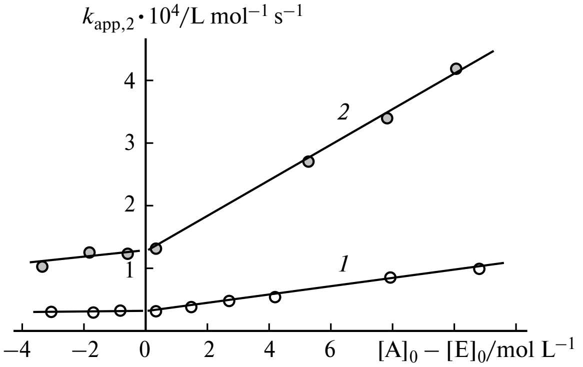


Fig. 4. Dependences of $k_{app,2}$ on excess aniline at 70 (*1*) and 100 °C (*2*) ($[A]_0$ and $[E]_0$ are the concentrations of aniline and phenyl glycidyl ether in the initial mixture, respectively).

the reactants, and $C_{A_0} - C_{E_0}$ is excess aniline with respect to phenyl glycidyl ether in the starting mixture.

In the region of an excessive concentration of the epoxide groups, a constant $k_{app,2}$ value is inherent in these systems. The catalytic activity observed for excess amine is a characteristic feature of the reactions in epoxide—amine systems and additionally confirms our hypothesis on the pre-associative mechanism of the autocatalytic reaction.[3]

The process, whose heat release rate is designed through W_3 (see Fig. 1), manifests itself during the reaction as an additional heat release. This process begins when the concentration of the OH groups in the reaction medium reaches saturation. The kinetically determined conversions above which the additional heat release appears (C_{sat}) are presented in Table 1. It follows from these data that C_{sat} is independent of the experimental conditions and corresponds to conversions of ~70%.

As can be seen from the data in Fig. 2, the thermograms with the endotherms are similar to the melting thermograms. However, judging from the position of these peaks observed within 45—80 °C with a minimum about 70 °C, we can conclude that no crystallization should occur when the reaction is carried out at temperatures above 80 °C. The kinetic data obtained at 70 and 100 °C are similar, implying that crystallization could occur only during cooling of the samples, while their heating during temperature scanning induces precipitate melting.

Evidently, the intermolecular interaction of the product molecules results in their self-aggregation followed by crystallization. The latter occurs at temperatures lower that the temperature of a kinetic experiment. Since the crystallization occurs only in overcooled or oversaturated solutions (melts), molecular clusters are predominantly formed at low overcooling or oversaturation.[8]

Thus, we explain the additional heat release found using the "kinetic investigation" approach by the self-aggregation of the product molecules preceding crystallization. This section of the kinetic curve corresponds to the induction period of nucleation and nuclei development. Analogous two-step precipitation processes preceded by the formation of a metastable amorphous phase have been described.[9,10]

We have previously[2] mentioned a tendency to the structural organization of the molecules produced in the reaction of phenyl glycidyl ether with *m*-phenylenediamine. Unlike the system with aniline analyzed in the present work, crystallization was observed at the end of the kinetic experiment. After the reaction completion, the kinetic curve of heat release was characterized by a new exotherm and the reacted samples contained a crystalline precipitate.

The kinetic model proposed for the description of the epoxide ring opening by the amino group in the aniline—phenyl glycidyl ether system reflects structural changes in the reaction medium in addition to the mechanism of reactant consumption. The exothermic effect observed during the reaction is composed of the effects of three processes, two of which are chemical reactions, and the third process is an induction period of crystallization nucleation in the reaction of aniline with phenyl glycidyl ether. The heat release kinetics of this process calculated by Eq. 1 as the phase separation process is shown in Fig. 1 (curve *4*).

Thus, using the "kinetic investigation" approach we found that the aniline—phenyl glycidyl ether reaction system is a typical example of the structure directing medium in which the main reaction occurs between reactants bound in a stable complex and stable molecular aggregates are the reaction product.

It has been known long ago that the behavior of the system can kinetically be studied at the supramolecular level. Such examples were described for hydrophobic interactions.[11,12] However, the appearance of similar structural aggregates during the reaction in nonaqueous media is not usually considered, because the self-organization of particles is most often ascribed to hydrophobic interactions. The spontaneous aggregation of hexanoic acid in acetonitrile indicates that a similar mechanism is significant for organic media as well.[13] Evidently, these are the solvophobic interactions that contribute mainly to the stability of molecular aggregates in the reaction of phenyl glycidyl ether with aniline.

Thus, using the reaction of phenyl glycidyl ether with aniline, we showed that the thermokinetic study of the process makes it possible to construct the kinetic model of the reaction involving the kinetic description of both the epoxide ring opening and supramolecular organization of the reaction product molecules.

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Received July 18, 2003;
in revised form July 12, 2004