NEW ASPECTS OF THE NUCLEOPHILIC OPENING OF EPOXIDE RINGS

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Abstract—The mechanism of nucleophilic opening of epoxide rings has been investigated by studying the kinetics of (i) amine-epoxide reactions both in the absence and presence of hydroxyl-containing catalysts, (ii) reactions of commercial epoxydiane oligomers of different molecular weights with aromatic diamines (*m*-phenylene diamine), and (iii) reactions of epoxides with phenols in the absence and presence of alkali.

Despite the fact that the opening of α-epoxy rings under the action of nucleophilic agents has been reported in many papers, much effort is needed to make the picture of the mechanism complete. The well known works of Parker, Smith, Pritchard[1-3] and others, deal with kinetics, stereochemistry and products of the reaction of nucleophilic addition to epoxides. However, more detailed study of this reaction is necessary, including the effect of the nature of the nucleophile on reactivity, consideration of various complexes in the reaction mechanism, the presence of side-reactions, the rôle of secondary products, possible influence of the medium, etc. The study of these problems is important, in particular, for the understanding of the widely used curing of epoxy resins which gives three-dimensional polymers, and also the reaction of epoxy-resin formation from low molecular weight epoxides and phenols. In the present report I deal with the work in this field which has been done in the Inst. Chem. Phys. Acad. Sci. USSR in recent years.

The mechanism of amine-epoxide reactions has been studied with both monofunctional substances such as phenyl-glycidyl ether, aniline, *N*-ethylaniline, *N,N*-diethylaniline, aromatic diamines, secondary oxyamines etc. and commercial epoxydian oligomers of various molecular weights cured with *m*-phenylenediamine.

The following basic processes take place in amine-epoxide reactions

In reactions with aliphatic amines, a tertiary amine group is formed which is capable of catalyzing the polymerisation of the epoxy group, in the case of aromatic amines, such a reaction does not take place. But it is known that even tertiary aromatic amines undergo addition to the epoxide ring with the formation of quarternary ammonium bases that break down at a rate much greater than the rate of the addition reaction:

$$C_6H_5-N(CH_3)_2 + CH_2-CH-CH_3 \xrightarrow[\text{slow}]{\text{HOR}}$$

$$\longrightarrow [C_6H_5N^+(CH_3)_2CH_2-\underset{\underset{OH}{|}}{C}HCH_3]OR^-$$

$$\xrightarrow[\text{rapid}]{} PhN(CH_3)_2 + ROCH_2\underset{\underset{OH}{|}}{C}HCH_3$$

Quarternary bases breakdown easily through the well-known Hoffman reaction. Introduction of electron acceptor substituents into the nucleus of a tertiary aromatic amine does not eliminate its nucleophilic activity towards the epoxide ring. Anionic polymerization of epoxide rings is excluded since quarternary aromatic bases break down at a rate much greater than that of the addition reaction.

The precise molecular scheme of the reaction can be established only by use of highly sensitive methods. From thin-layer chromatography data we have shown that in the case of reaction of aniline with phenyl-glycidyl ether at

$$PhNH_2 + PhOCH_2CH-CH_2 \longrightarrow PhNH-CH_2-\underset{\underset{OH}{|}}{C}H-CH_2OPh$$

$$(PhNHR) + PhOCH_2CH-CH_2 \longrightarrow PhN \underset{CH_2-CH-CH_2OPh}{\overset{CH_2-\overset{\overset{OH}{|}}{C}H-CH_2OPh}{<}}$$

$$\underset{HO}{} \qquad (PhNR_2)$$

Scheme 1.

However, amine-epoxide reactions are not limited to the above addition scheme. Quite possible are reactions of epoxide isomerization in the presence of bases at elevated temperatures, for example:-

$$CH_2-CH-CH_2OR \xrightarrow{B^-} CH_2-CH-CHOR \longrightarrow$$
$$\underset{O^-}{|}$$
$$\underset{|}{} \qquad \underset{OH}{|}$$
$$CH-CH=CH_2OR \xrightarrow{BH} CH_2-CH=CH-OR$$

60–90°C, likewise in the reaction between an amine with an electron acceptor substituent (diaminodiphenylsulfone) and this ether at 110–160°C, the above by-processes are absent. Numerous selective high-sensitive qualitative chemical surface reactions verified this with the precision of 10^{-11} mol. Apart from this by various chemical and physical methods, products of the reaction have been isolated and identified as the products of normal addition of amine to epoxide, as follows from the Schemes (1, 2).

The reactions of aliphatic amines with epoxides are more intricate. For example, the heat of the reaction of hexamethylenediamine and butylamine with phenylglycidyl ether per mole of epoxy groups depends on the initial ratio of reagents. As the amine ratio is increased, the heat of reaction increases by more than 10%. Along with this, gel- and thin-layer-chromatography data show that deviation from stoichiometry leads to the appearance of by-products of the reaction.

It is well known that added small amounts of hydroxylic substances markedly increase the rate of amine-epoxide reactions due to significant activation of the carbon atom in the epoxide ring to nucleophilic attack by amine (Scheme 2):

$$PhNH_2$$

$$PhOCH_2CH\!-\!CH_2$$
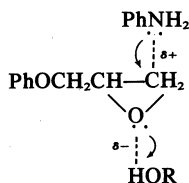
Scheme 2.

Usually the formation of such complexes is considered to be the cause of the acceleration of amine-epoxide reaction which is of markedly autocatalytic type due to the accumulation of hydroxyl groups in the course of the reaction (see Scheme 1). Besides, complexes of the type $\rangle N:\!\rightarrow HOR$ are sure to exist, and to lessen the reactivity of the amine.

We have made experiments in which previously isolated products of 1st and 2nd addition of phenylglycidyl ether to aniline were introduced into the system phenylglycidyl ether-aniline. In this case the induction period is absent and the rate reaches its maximum in the very beginning of the reaction (Fig. 1), demonstrating that the formation of hydroxyl-containing reaction products is the cause of autocatalysis. It is also confirmed by small change of the dielectric constant during the reaction (from 7.5 to 5.5).

Meanwhile the question of the possibility of this reaction being non-catalytic, i.e. amine directly interacting with epoxy group, was unanswered. Solution of this problem required special methods of purification of
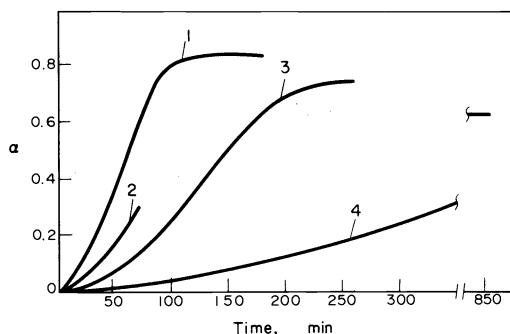
Fig. 1. Kinetic curves of precision purified phenylglycidyl ether and aniline at 90°C. $E_0 = 2.8$ mol/l; A_{10}, mol/l: 1—6.1; 2—4.4; 3—3.6; 4—2.1.

reagents and reaction vessels from traces of water and other hydroxyl containing foreign substances.

It turned out that even under these conditions when the reagents were pure up to 10^{-6} mol/l, phenylglycidyl ether reacts with aniline (Fig. 1), the rate of the process being proportional to the square of the aniline concentration (Fig. 2).[4] The presence of even small amounts of water diminishes the reaction order with respect to amine. Quadratic dependence of the reaction rate on amine concentration (A_1) means that the latter acts both as a proton donor forming an intermediate complex (A_1E) with the epoxide (E):

$$A_1^+ E \underset{\kappa_-}{\overset{\kappa_+}{\rightleftarrows}} (A_1 E).$$
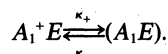
and as a nucleophilic agent

$$(A_1 E) + A_1 \overset{\kappa_1}{\longrightarrow} A_1 + A_2$$
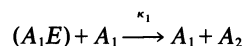
which results in the addition product formation A_2. It follows from the above scheme, that

$$\left(\frac{d\alpha}{dt}\right)_{t\to 0} = \kappa_1 \frac{\kappa_+ A_{10}^2}{\kappa_- + \kappa_1 A_{10}}$$

and when $\kappa_- \gg \kappa_1 A_{10}$ (A_1 is a very weak acid) $(d\alpha/dt) = \kappa_1 \kappa_p A_{10}^2$ where $\kappa_p = (\kappa_+/\kappa_-)$, which is in accordance with the experimentally found dependence of the reaction rate
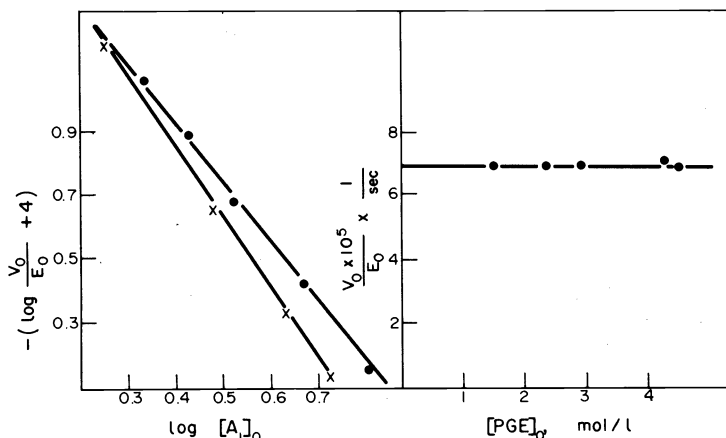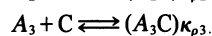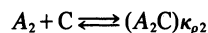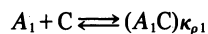

Fig. 2. Dependence of the initial reaction rate of phenylglycidyl ether and aniline at 90°C on reagents concentration: (a) $E_0 = 3.0$ mol/l; (b) $A_{10} = 4.4$ mol/l. 1—precision purified reagents; 2,3—in presence of hydroxyl substances.

on amine concentration. Decrease of the reaction order with respect to amine in the presence of hydroxyl-containing impurities, is due to the partly catalytic mechanism of the reaction, when the more acidic hydroxyl-containing substance plays the role of proton donor. When there are enough hydroxyls in the system the reaction order with respect to amine is unity. It should be noted that the usual methods of purification leave enough water in the reaction system, so that the reaction order with respect to aniline differs considerably from quadratic and is near unity.

Thus, the data obtained show that the amine-epoxide reaction can proceed in absence of any proton-donor substances, the amine being both a nucleophilic and a proton-donor reagent.

The second principal problem arising in the study of epoxide curing with amines is the peculiarities of the reaction at high conversions.[5] It is well known that the curing reaction often stops long before functional groups of one of the reagents are consumed, which fact was usually explained by diffusion hindrance in a hard polymer matrix. However, investigation of the kinetics of reaction of phenylglycidyl ether-aniline in o-

$$A_1 + C \rightleftharpoons (A_1C)\kappa_{p1}$$
$$A_2 + C \rightleftharpoons (A_2C)\kappa_{p2}$$
$$A_3 + C \rightleftharpoons (A_3C)\kappa_{p3}$$
$$E + C \rightleftharpoons (EC)\kappa_{p}$$
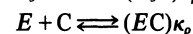
Scheme 3.

It should be emphasized that the retardation at high conversions would be observed only if the basicity of the forming secondary or tertiary amine groups or both of them is higher than the basicity of primary amine groups. Only in this case a progressive relative decrease of free hydroxyl groups would be observed, and as a consequence, a decrease of the rate of the process as a whole.

The consequence of the above propositions on the formation of complexes between amines and hydroxyl groups should be a considerable decrease of the viscosity of the reaction system at high conversion due to the formation of a network possessing labile hydrogen bonds in the knots, since the formation of tertiary amine groups leads to the appearance of tri-functional reagent in the system (one tertiary amine group and two hydroxyl groups).
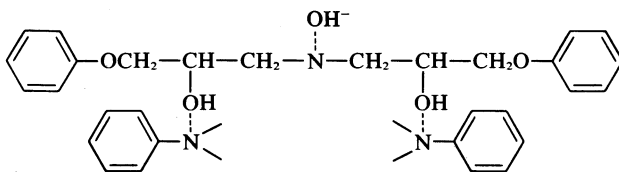
dichlorobenzene proved the same effect to exist in this system, i.e. considerable retardation of the reaction before the reagents are consumed (Fig. 3). This effect is observed when the reaction is conducted en bloc. It was natural to look for the cause of this phenomena not in the change of physical properties of the media and diffusion hindrance of the reaction but in some chemical processes that lead to the retardation of the reaction.

We assumed the observed retardation effect at high conversion to be caused by the formation from primary amines (A_1) of more basic secondary (A_2) and tertiary (A_3) amine groups and subsequent binding by them of hydroxyl groups (C) into nonreactive complexes (A_1C). Complex formation, on the one hand, decreases the concentration of reactive complex (EC) of epoxy group with hydroxyl group through the decrease of free hydroxyls and, on the other hand, decreases the free amine concentration, leading to a sharp retardation of the process (Scheme 3).
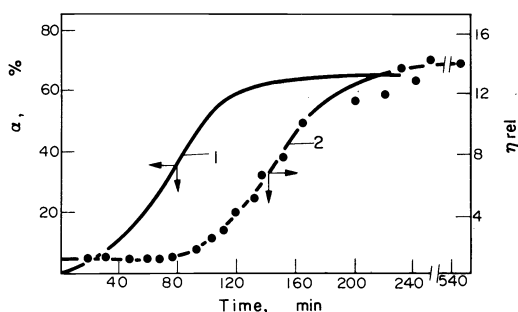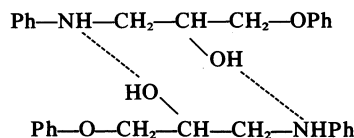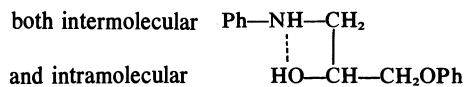
In accordance with these results are the data on the kinetics of the relative viscosity change in course of the reaction (Fig. 3). Special experiments have shown that the increase of the viscosity is connected with the formation of poly (phenyl-glycidyl ether) at high conversion, since phenylglycidyl ether is not polymerized by N,N-diethylaniline. As expected, the effect of the viscosity increase becomes greater as the ratio A_{10}/E_0 increases. Thus, when A_{10}/E_0 1,8; 1,0; 0.454, $\eta_{rel\infty} = 3.5$; 14; 32.5 respectively. As was expected, introduction of a stronger base into the system leads to a sharp viscosity decrease of the latter due to disintegration of polyfunctional complexes.

Increase of the reaction temperature decreases the fraction of amine that is associated with hydroxyl groups, and as a consequence, increases the conversion at which retardation of the process is observed. If the reaction is carried out in adiabatic regime, conversion of epoxy groups is 100%. In agreement with the expected behaviour is the dependence of conversion at which retardation takes place on the ratio of reagent concentration; "limiting" conversion increases with the ratio A_{10}/E_0 (Fig. 4).

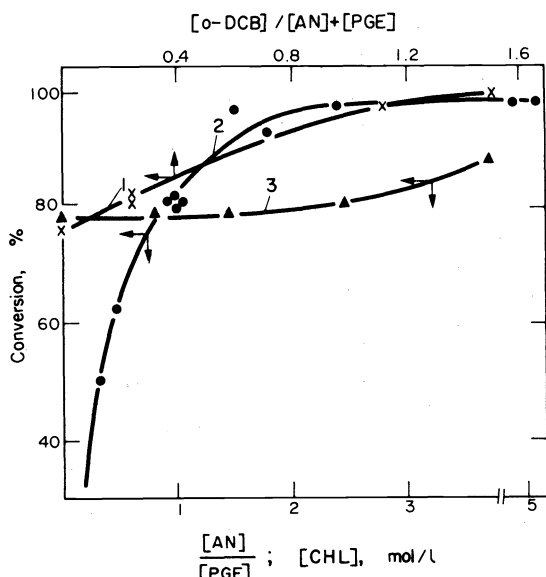Hydrogen bonds in amine-hydroxyl group complexes can be

both intermolecular   Ph—NH—CH₂

and intramolecular   HO—CH—CH₂OPh

Fig. 3. Kinetics of phenylglycidyl ether consumption (1) and relative viscosity change (2) for phenylglycidyl ether–aniline reaction at 90°C. $A_{10} = 4.4$ mol/l; $E_0 = 4.44$ mol/l.

Fig. 4. Dependence of "limiting" conversion of phenylglycidyl ether on dilution (1), ratio A_{10}/E_0 (2) and initial concentration of cyclohexanol (3).
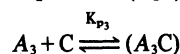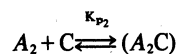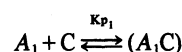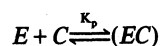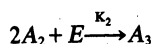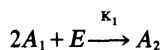
Dilution of the reaction system with o-dichlorobenzene while keeping reagents ratio constant, (Fig. 4) has shown that the conversion at which the rate decreases sharply, becomes greater as dilution increases. This result points to the major role of intramolecular association reactions and is in accordance with data on relative viscosity change kinetics.

To observe directly the process of complex formation by hydroxyl groups with each electron-donor component of the reaction system of epoxides and aromatic amines and to characterize these reactions quantitatively, thermodynamic parameters of complex formation reactions in model systems (cyclohexanol + phenylglycidyl ether + aniline) N-ethylaniline and N,N-diethyl aniline) have been obtained from calorimetry and i.r. spectrometry data.[6] Thermodynamic parameters of these reactions are presented in Table 1.

As data in Table 1 show, the obtained values of thermodynamic parameters are in accordance with the above conceptions on the cause of autoinhibition in amine-epoxide reactions.

Thus, reaction retardation in real processes of epoxide curing by amines can happen not only because of diffusion control of reaction but also chemical processes caused by complex formation reactions between more basic secondary and tertiary amine groups and hydroxyl groups.

From the obtained data the curing process of epoxides by amines can be presented as the following sequence of reactions[7,8]

$$2A_1 + E \xrightarrow{K_1} A_2$$

$$2A_2 + E \xrightarrow{K_2} A_3$$

$$E + C \underset{}{\overset{K_p}{\rightleftharpoons}} (EC)$$

$$A_1 + (EC) \underset{}{\overset{K_1'}{\rightleftharpoons}} (Az)$$

$$A_2 + (EC) \underset{}{\overset{K_2'}{\rightleftharpoons}} A_3$$

$$A_1 + C \underset{\phantom{K_{P_1}}}{\overset{K_{P_1}}{\rightleftharpoons}} (A_1C)$$

$$A_2 + C \underset{\phantom{K_{P_2}}}{\overset{K_{P_2}}{\rightleftharpoons}} (A_2C)$$

$$A_3 + C \underset{\phantom{K_{P_3}}}{\overset{K_{P_3}}{\rightleftharpoons}} (A_3C)$$

Scheme 4.

Thus, interaction of epoxides with aromatic amines is a rather complex reaction proceeding through both catalytic and non-catalytic processes and including quite seldom occuring phenomena—simultaneous processes of autocatalysis and auto-inhibition.

To characterize the above reactions quantitatively and to prove the scheme of reaction, the kinetics of phenylglycidyl ether reaction with aniline and N-ethylaniline has been studied both in presence and absence of cyclohexanol. But before we come to the obtained results, it is necessary to consider an important methodical question, since the conversion [$\alpha = (E_0 - E/E_0)$] is determined from calorimetry in a complex way, because the observed integral heat of reaction Q_1, in general, for the Scheme 4, should be non-linear with respect to conversion due to non-linearity of the second term in eqn (5) which includes the heat of complex-formation reactions.

$$Q_1 = Q\alpha + q(\alpha) \tag{5}$$

where Q is the heat of reaction of the epoxy group with the N-bond of amine (Q is assumed to be equal for primary and secondary amines, since the main contribu-
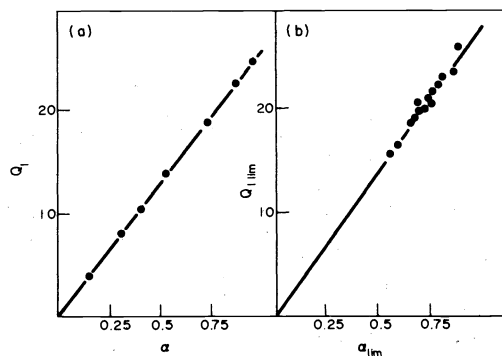

Fig. 5. Dependence of heat of reaction (Q_1) on conversion (α).

Table 1

	$-\Delta H$, kcal/mol	$-\Delta S$ cal/mol °K	K_{pi}^{97} l/mol (calor.)	K_{p1}^{97} l/mol (i.r.-spectr)
(A_1C)	4.5	16.0	0.45	0.5
(A_2C)	2.8	10.0	0.73	0.63
(A_3C)	0.9	2.0	0.55	0.28
(EC)	3.4	11.0	0.48	0.6

tion to Q is the heat of epoxide ring opening). But, luckily enough, the dependence of Q_1 on α, determined chemically or spectroscopically, turned out to be linear and originating at the beginning of coordinates (Fig. 5). The value of Q is equal to 26.3 kcal/mol. This result implies that $Q\alpha \gg q(\alpha)$.

From the analysis of Scheme 4, the following kinetic equations can be written that are useful for experimental verification and determination of kinetic and thermodynamic constants:

1.
$$V_{01} = \left(\frac{d\alpha}{dt}\right)_{t\to 0} = k_1 A_{10}^2, \quad C_0 = 0$$

2.
$$\frac{C_0}{V_{02} - V_{01}} = \frac{k_{p1}}{k_p \cdot k_1'} + \frac{1}{k_1' k_p A_{10}} + \frac{E_0}{k_1' A_{10}} C_0 \neq 0$$
$$A_{10} \gg C_0$$

3.
$$B \equiv \frac{\alpha_{\lim} E_0(1-\alpha_{\lim})k_p[k_1' A_{10} - (k_1' - k_2')\alpha_{\lim}E_0]}{V_{\lim}A_{10}}$$

$$-\frac{1+k_p E_0 + k_{p1}A_{10}}{A_{10}} = \frac{k_{p2} - k_{p1} - k_p}{A_{10}}\alpha_{\lim}E_0$$

Scheme 6.

Where V_{01} and V_{02} are the initial rates in absence and in presence of alcohol, respectively, $\alpha_{\lim}$-conversion, corresponding to reaction retardation, $V_{\lim}$-rate of reaction at conversion α_{up}. The rest notations are as in Scheme 4. Similar equations can be written for the reaction of phenylglycidyl other with N-ethylaniline.

Several examples of experimental verification of these equations are presented in Figs. 6–8. The determined values of kinetic and thermodynamic constants are presented in Tables 2 and 3.

The obtained values of rate and equilibrium constants adequately describe experimental kinetic curves. Thus, Fig. 9 presents the dependence of the rate of phenylglycidyl ether-aniline reaction on conversion, calculated from eqn (7):

Fig. 6. Dependence of reaction rate for phenylglycidyl ether–aniline in presence of cyclohexanol on concentration of reagents in terms of eqn (6.2).

Fig. 7. Dependence of "limiting" reaction rate for phenylglycidyl ether–aniline on phenylglycidyl ether concentration in terms of eqn (6.3).

reaction rate increases with increasing basicity of amine, which is clearly illustrated by the data of Dobaš and Eichler[9] (Fig. 10) on the reaction of n-tolyl glycidyl ether

$$\frac{d\alpha}{dt} = k_2\left[A_{20}\left(1-\frac{k_{p0}C_0}{1+k_{p2}A_{20}}\right)-\alpha E_0\right]^2(1-\alpha) + k_2' k_p\left[A_{20}\left(1-\frac{k_{p2}C_0}{k_{p2}A_{20}}\right)-\alpha E_0\right]$$

$$\times(1-\alpha)\frac{C_0 + \alpha E_0}{1+k_p E_0(1-\alpha)+k_{p2}\left[A_{20}\left(1-\frac{k_{p2}C_0}{k_{p2}A_{20}+1}\right)-\alpha E_0\right]+k_{p3}\alpha E_0} \tag{7}$$

derived from Scheme 4. Experimental results are denoted by dots.

Thus, quantitative investigations of model reactions of phenylglycidyl ether with primary and secondary aromatic amines prove the proposed mechanism of epoxide-aromatic amine reactions.

From this mechanism, proposing nucleophilic attack of the amine on a carbon atom of the epoxide ring, the
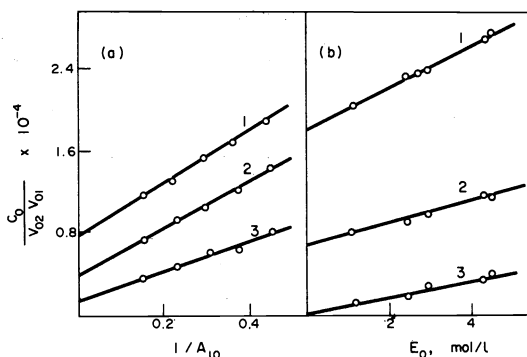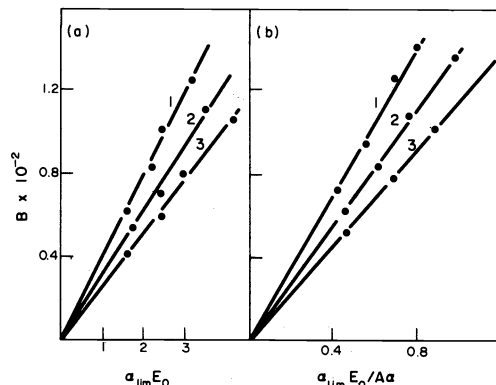
with substituted anilines. This reaction is adequately described by the Hammett equation (Fig. 11) with parameters ρ −1.32 and −1.27 for K_1' and K_2' respectively. Low values of ρ indicate the opening of the epoxide ring to be the stage limiting the reaction rate.

An important problem in primary amine-epoxide reactions is the relative reactivity of primary amine and secondary hydroxy-amine, the product of addition to the

Table 2. Kinetic and thermodynamic parameters of the phenylglycidyl ether-aniline reaction

90°C	k_0 1/mol sec	E, kcal/mol	$-\Delta H$, kcal/mol	$-\Delta S$, cal/mol °K
$k_1 (5+0.5) \times 10^{-6}$	19.5 ± 3	11 ± 0.5		
$k_1' (2.2+0.2) \times 10^{-4}$	7.3 ± 8	9.2 ± 0.4		
k_p 0.20 ± 0.02			2.3 ± 0.2	7.0 ± 1.0
k_{p1} 0.46 ± 0.04			3.5 ± 0.3	8.5 ± 1.5
k_{p2} 0.7 ± 0.05			2.2 ± 0.2	6.5 ± 1.0

Table 3. Kinetic and thermodynamic parameters for the phenylglycidyl ether–N-ethylaniline reaction[8]

90°C	k_0 1/mol sec	E, kcal/mol	$-\Delta H$, kcal/mol	$-\Delta S$ cal/mol °K
$k_2(3.2 \pm 0.3) \times 10^{-7}$	40 ± 5	13.5 ± 0.3		
$k_2'(5.5 \pm 0.6) \times 10^{-5}$	22 ± 3	9.8 ± 0.3		
$k_p 0.22 \pm 0.02$			2.5 ± 0.3	8.0 ± 1.0
$k_{p2} 0.75 \pm 0.06$			2.5 ± 0.2	10.0 ± 2.0
$k_{p3} 1.2 \pm 0.05$			1.1 ± 0.2	1.2 ± 0.2
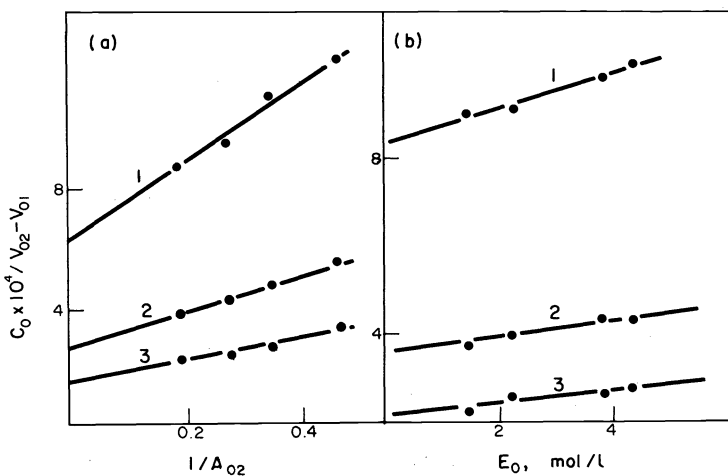
Fig. 8. Dependence of reaction rate for phenylglycidyl ether–N-ethylaniline in presence of cyclohexanol on reagents concentration in terms of equation, similar to (6.2).
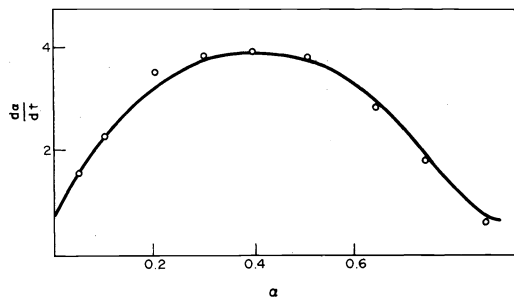
Fig. 9. Dependence of reaction rate for phenylglycidyl ether–N-ethylaniline on conversion. (The dots are experimental, solid line—calculated dependence.)
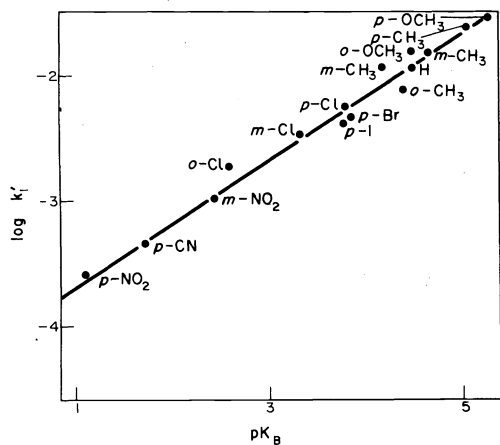
Fig. 10. Influence of pK_B of substituted anilines on rate constant k_1'.
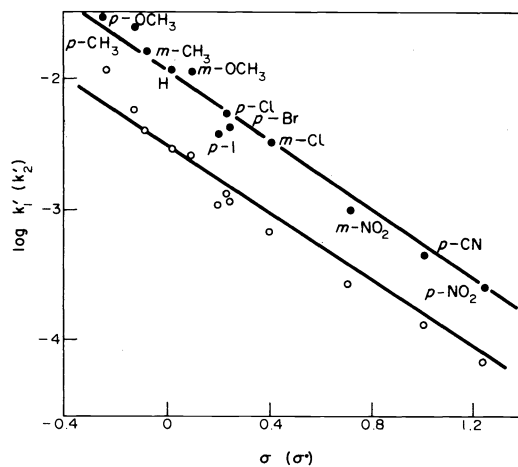
Fig. 11. Dependence of the logarith of rate constants k_1' and k_2' on Hammett constant, ●, k_1'; ○, k_2.

epoxide, with respect to the same epoxide. In diepoxide-diamine reactions of network formation the ratio of the rates of these reactions determines the ways in which the network is formed. Comparison of the rates of reactions of phenylglycidyl ether with aniline and the product of first addition of phenylglycidyl ether to aniline has shown that the reactivities of N–H groups of primary and secondary amines are near to each other: $K_2/K_1 = 0.8$. Such a ratio has been found for these reactions in butanol media. The similarity of the constants is not surprising since we have shown that the reacted group $C_6H_5OCH_2CH(OH)CH_2$—has an inductive donor effect,

which is verified from u.v.-spectra of azodyes synthesized from aniline and the products of the first and second additions. In this line the maximum of the $\pi - \pi^*$ adsorption band shifts to the near u.v.-region. This positive effect compensates for steric hindrance made by this group at the N-atom.

The above consideration can be used in the investigation of the interaction between epoxydiane oligomers and an aromatic diamine (m-phenylenediamine).[10,11] To eliminate the reaction retardation due to the formation of complexes between amine and hydroxyl groups and widen the kinetic region of reaction, the curing process was made adiabatic. In adiabatic regime, providing heat capacity (c), density (ρ) and heat of reaction (Q) do not change with conversion, the temperature of the reaction media (T) can be related to the concentration of reacted groups (x) by the following equation:

$$X = \frac{C\rho}{Q}(T - T_0) \tag{8}$$

where T_0 is the initial curing temperature.

Typical kinetic curves are presented in Fig. 12, the dependence of limiting temperatures in cured system on initial epoxy groups concentration (E_0) (Fig. 13) being

described by the following equation:

$$T_\infty = \frac{Q}{c\rho} E_0 + T_0 \tag{9}$$

which gives evidence of the truly adiabatic character of the process. The determined values of parameters were: $Q/cp = 25.7$ deg/mol, $C = 0.162$ kcal/mol deg, $\rho = 5.81$ mol/l and $Q = 24.21$. kcal/mol which is in accordance with similar values for the model reaction.

From Scheme 4 without the last three reactions of complex formation between amine and hydroxyl groups, the following kinetic equations can be written for the adiabatic regime, that can be used for experimental verification and determination of kinetic parameters of the process:

1. $V_0 \equiv \left(\dfrac{d\alpha}{dt}\right)_{t\to 0} = \dfrac{Q}{c\rho} k_{10} \exp\left(-\dfrac{E_1}{RT}\right) A_{10}E$

2. $\log V_{01} = \log \dfrac{Q}{c\rho} k_{10}A_{10}E_0 - \dfrac{E_1}{2,3RT_0}$

3. $\dfrac{Q/cpA_{10}E_0}{V_{02}} = \dfrac{1}{k'_{10}k_p \exp\left(\dfrac{-E'_1+\Delta H}{RT}\right)C_0}$
$\qquad\qquad + \dfrac{1}{k'_{10}\exp\left(-\dfrac{E'}{RT}\right)}$

4.
$\log \beta \equiv \log \left\{ \dfrac{dT/dt\left[1+\dfrac{1}{k_p \exp(-\Delta H/RT)(T-T_0)cp/Q}\right]}{[E_0 - cp/Q(T-T_0)](T-T_0)} \right.$

$\qquad \left. - \dfrac{k'_{10}\exp(-E'_1/RT)[A_{10}-(T-T_0)cp/Q]}{(T-T_0)cp/Q} \right\} = \log k'_{20}$

$\qquad - \dfrac{E'_2}{2,3RT}. \tag{10}$

The notations are the same as before. However, one remark should be made. For diamine-epoxide reaction, in general six reactions should be written, namely:

$H_2N\text{---}R\text{---}NH_2 + R'X \xrightarrow{K_1} (R'\text{---}Y)NH\text{---}R\text{---}NH_2$

$(R'\text{---}Y)NH\text{---}R\text{---}NH_2$
$\qquad + R'X \xrightarrow{K_2} (R'\text{---}Y)NH\text{---}R\text{---}NH(Y\text{---}R')$

$(R'\text{---}Y)NH\text{---}R\text{---}NH(Y\text{---}R') + R'X \xrightarrow{K_3}$
$\qquad\qquad (R'\text{---}Y)_2\text{---}N\text{---}R\text{---}NH(Y\text{---}R')$

$(R'\text{---}Y)_2N\text{---}R\text{---}NH(Y\text{---}R') + R'X \xrightarrow{K_4}$
$\qquad\qquad (R'\text{---}Y)_2\text{---}N\text{---}R\text{---}N(Y\text{---}R')_2$

$(R'\text{---}Y)N\text{---}R\text{---}NH_2 + R'X \xrightarrow{K_5} (R'\text{---}Y)_2\text{---}N\text{---}R\text{---}NH_2$

$(R'\text{---}Y)_2N\text{---}R\text{---}NH_2 + R'X \xrightarrow{K_6}$
$\qquad\qquad (R'\text{---}Y)_2N\text{---}R\text{---}NH(Y\text{---}R')$

$X = \text{---}\underline{C}H\text{---}O\text{---}\underline{C}H_2$

$Y = \text{---}CH(OH)\text{---}CH_2\text{---}$

Taking into account that the reactivity of primary amines is several times higher than that of secondary amines, the last two reactions may be neglected. Eichler and Dobaš[12] have shown for the reaction of some aromatic
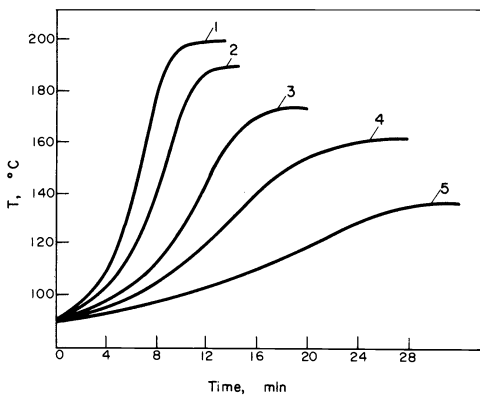

Fig. 12. Kinetic curves of temperature change for interaction of m-phenylenediamine ($A_{10} = 5.74$ mol/l) with ED-5 (mol/l): 1—4.77; 2—3.86; 3—3.26; 4—2.77; 5—1.91 at 90°C.
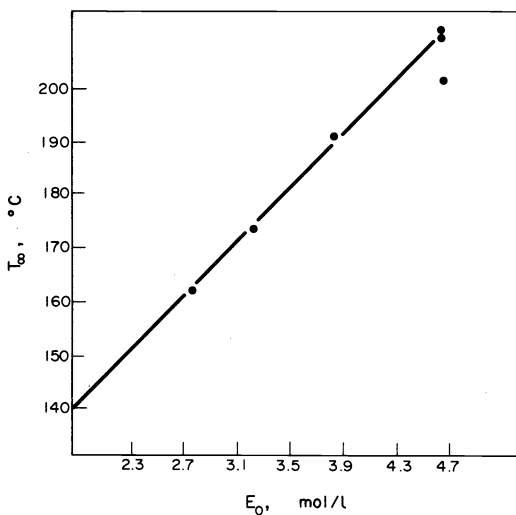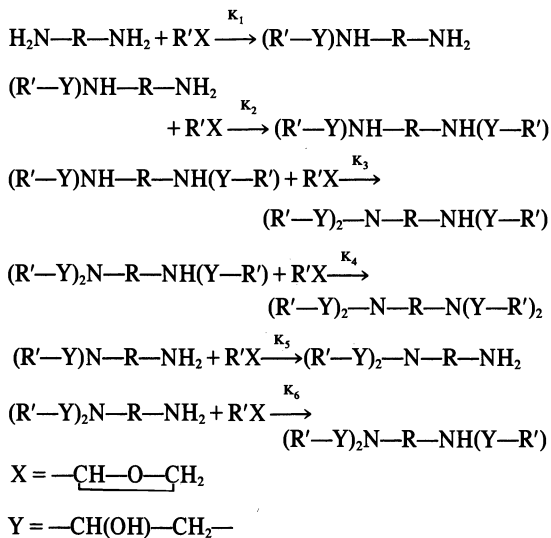

Fig. 13. Dependence of T_∞ on E_0.

amines with p-tolylglycidyl ether in ethanol, that $k_1' \cong k_2'$ and $k_3' \cong k_4'$, i.e. the inductive effect is negligible (see Table 4).

From these data, instead of using the 6 rate constants of Scheme 11, for non-catalytic and catalytic reactions we used only two constants to describe the curing process: k_1 and k_2 (in absence of proton-donors) and k_1' and k_2' (in presence of hydroxyl groups).

Kinetic parameters of the curing process can be found from eqns (10) (Table 5). Experimental results are in fair agreement with these equations (see, for example, Figs. 14, 15).

Comparison of curing rates of epoxydiane oligomers ED-5, ED-6, ED-16 and E-41, differing in molecular

weight, have shown, that the curing rate for these oligomers differs and increases with increase of the molecular weight of initial oligomer 11 (Fig. 16). This fact is naturally explained by the increasing role of the catalytic process of curing due to the increased initial concentration of hydroxyl groups in epoxide-oligomer molecules with the increase of chain length of an oligomer.

Quantitatively the influence of hydroxyl group concentration in initial oligomers can be estimated by relating their concentration to the concentration of epoxy groups in the initial oligomer through the proportionality coefficient β. Evidently, this coefficient should increase with increasing chain length.

Taking into account the initial concentration of hydroxyl groups in the oligomer, equal to $C_0' = C_0 + \beta E_0$, where C_0 is the concentration of added alcohol, βE_0 is the concentration of hydroxyl groups in the reacting oligomer, equations similar to 10 can be obtained. Comparing them with experimental data, it is possible to obtain kinetic and thermodynamic parameters of the curing of epoxydiane oligomers of various molecular weights (Table 5).
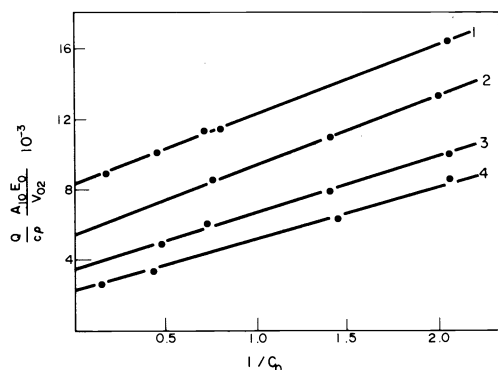

Fig. 14. Dependence of $(Q/cp) \cdot (A_{10} \cdot E_0/V_{02})$ on $1/C_0$ at 1—80°C; 2—90°C; 3—100°C for ED-5 curing with m-phenylenediamine.
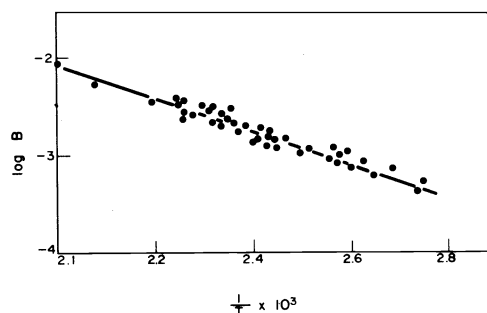

Fig. 15. Dependence obtained from 10.4.
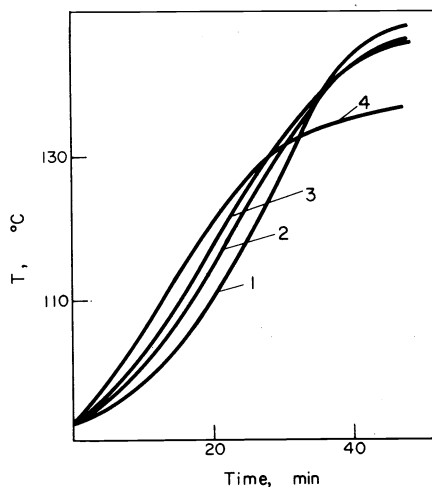
Fig. 16. Influence of molecular weight of epoxy oligomer on curing kinetics at 93°C; $A_{10} = 4.63$ mol/l; $E_0 = 1.64$ mol/l. 1—ED-5; 2—ED-6; 3—ED-16; 4—E-41.

Table 4

Diamine	k_1'	k_2'	k_3'	k_4'
4,4'-diamino-diphenylmethane	43.7	37.8	14.8	12.9
phenylenediamine	151.5	12.5	53.7	44.3
benzidine	38.5	30.7	11.0	8.76
4,4'-diamino-diphenylsulfone	1.24	0.844	0.637	0.434

Table 5. Kinetic and thermodynamic parameters of epoxydiane oligomer curing with m-phenylenediamine[11]

Oligomer	$K_{10}' \times 10^3$ (l/mol sec)	E_1', $\dfrac{kcal}{mol}$	$K_{20}' \times 10^3$, l/mol sec	E_2', $\dfrac{kcal}{mol}$	$-\Delta H$, $\dfrac{kcal}{mol}$	$-\Delta S$, $\dfrac{cal}{mol°K}$
ED-5	1.1 ± 0.2	9.4 ± 0.5	5.5 ± 0.2	9.8 ± 0.5	4.6	13.0
ED-6	1.6 ∓ 0.3	10 ± 0.5	5.3 ± 0.2	10.4 ± 0.5	4.7	12.5
ED-16	1.2 ± 0.2	9.5 ± 0.5	5.3 ± 0.2	10.3 ± 0.5	4.6	12.3
E-41	1.1 ± 0.2	9.7 ± 0.5	5.4 ± 0.2	10.5 ± 0.5	4.8	13.0

As was expected, all epoxydiane oligomers are described, within experimental error, by the same values of the kinetic parameters. The values obtained β were 0.26; 0.28 and 0.98 for ED-6, ED-16 and E-41, and are in accordance with hydroxyl groups concentrations in these oligomers determined from chemical analysis.

Thus, the results speak in favour of the correctness of the proposed curing mechanism of epoxy oligomers with aromatic amines (Scheme 4).
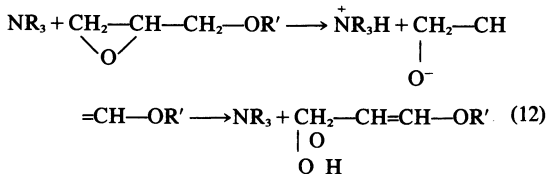
As we pointed out earlier, tertiary amine groups formed in reactions of primary or secondary aromatic amines with epoxides are not capable of catalyzing epoxide polymerization. However, if aliphatic primary or secondary amines are used, in many cases polymerization of epoxides catalyzed by the forming tertiary amine group is an important part of the curing process as a whole. Tertiary amines can also be used by themselves as catalysts of epoxide polymerization and curing agents.

An important contribution to the studies of the mechanism of this interesting reaction was made by M. F. Sorokin et al.[13-16] Recently the mechanism of this reaction has been intensely studied at the Inst. Chem. Phys. Ac. Sci. USSR.

We shall deal shortly with the kinetics and main features of this interesting and rather complex reaction.

Typical kinetic curves are presented in Fig. 17. The curves are of a pronounced S-shape, the induction periods decreasing with the increase of alcohol content. Polymerization proceeds up to complete monomer conversion both in presence and absence of alcohol (Fig. 17).

In the latter case polymerization is characterized by a large induction period during which alcohol accumulates as a result of isomerization of the α-substituted epoxide under the action of tertiary amine.

$$NR_3 + CH_2\text{—}CH\text{—}CH_2\text{—}OR' \longrightarrow \overset{+}{N}R_3H + CH_2\text{—}CH$$
$$\underset{O}{\diagdown\diagup} \qquad\qquad\qquad\qquad\qquad | $$
$$O^-$$

$$=CH\text{—}OR' \longrightarrow NR_3 + CH_2\text{—}CH=CH\text{—}OR' \quad (12)$$
$$\underset{O\ H}{|\ O}$$

As follows from the figure, introduction of equimolecular amounts of alcohol leads to a high reaction rate, and the polymerization is completed sooner than reaction can begin in the absence of alcohol. This fact means, that in these conditions a quantitative description can be given without taking into account the accumulation of phenoxypropyl alcohol in the course of the reaction.

If a new portion of phenylglycidyl ether is added into the reaction system after complete monomer conversion reaction begins with approximately the same rate, i.e. the system has a "living" character. It also turned out that tertiary amine is practically not consumed. These facts mean that the active centre termination proceeds with the regeneration of tertiary amine, and the active centre concentration at any time is a negligible part of the introduced tertiary amine. This is also confirmed (see later) by direct determination of the concentration of active growing centres.

The reaction rate depends on reagent concentrations in a complex way. Figure 18 presents kinetic curves of phenylglycidyl ether polymerization with the same initial concentration and different alcohol and amine concentrations, the product of reagent concentrations being constant. It turned out that a ten-fold excess of alcohol with respect to amine accelerates monomer polymerization much more effectively than the reverse ratio of these reagents. This fact indicates high reaction order with respect to alcohol and is probably related to alcohol solvation of the active growing species (alkoxyl anions).

Simultaneous investigations of reaction kinetics and change of conductivity of reaction system has shown the ionic character of the active growing species. Time dependence of the reduced reaction rate: $(d\alpha/dt(1-\alpha)) = k_pR^*$ (where α is the conversion, k_p is the effective polymerization rate constant, and R^* is the total concentration of active growing centres) reflecting the change of concentration of active growing centres during the reaction, turned out to be similar to the time dependence of the viscosity-corrected conductivity (χ') of the reaction system (Fig. 19). It is essential that the maximum of χ' corresponds to the moment of maximum reduced polymerization rate. It also turned out that any binary mixture of phenylglycidyl ether, isopropyl alcohol and dimethylbenzylamine has χ almost two orders lower than that of a ternary system. This latter fact shows that in the formation of active growing centres (quarternary ammonium bases) all the three components take part—monomer, tertiary amine and alcohol. Decrease of
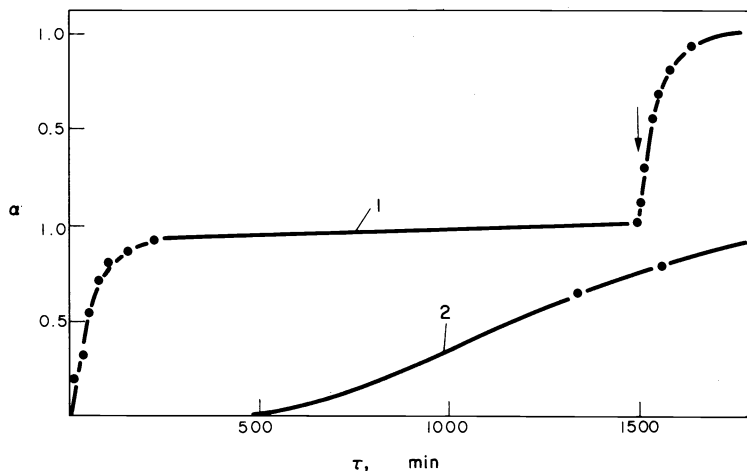

Fig. 17. Kinetic curves of phenylglycidyl ether polymerization by dimethylbenzylamine (A_3) in presence of isopropyl alcohol C_0 at 70°C. 1—$E_0 = A_{30} = C_0 = 1.75$ mol/l; 2—$C_0 = 0$.

Fig. 18. Kinetic curves of phenylglycidyl ether polymerization by dimethylbenzylamine at 70°C. $E_0 = 0.5$ mol/l. 1—$C_0 = 5$ mol/l; $A_{30} = 0.5$ mol/l; 2—$C_0 = 0.5$ mol/l; $A_{30} = 5$ mol/l.

Fig. 19. Kinetic curve for phenylglycidyl ether polymerization 70°C (1) ($E_0 = C_0 = 1.75$ mol/l; $A_{30} = 0.25$ mol/l) and change of reduced rate (2) and conductivity of the system (3) during the reaction.

the reduced polymerization rate and conductivity after the point of maximum naturally relates to monomer consumption.

The molecular weight distribution of polymerization products, from sedimentation and ebulliometry, turned out to be $\bar{M}_z : \bar{M}_w : \bar{M}_n = 2.5 : 1.8 : 1$, which is quite near the statistical Flory distribution ($\bar{M}_z : \bar{M}_w : \bar{M}_n = 3 : 2 : 1$).

From the above facts and literature data as a first approximation we may write the following mechanism of epoxide polymerization by tertiary amines:

initiation

1. $CH_2{-}CH{-}R'' + NR_3 \longrightarrow R_3\overset{+}{N}CH_2{-}CH{-}R''$
   $\underset{O}{\diagdown\diagup}$ $\underset{O^-}{}$ (I)

2. $(I) + R'OH \longrightarrow R_3\overset{+}{N}CH_2{-}CH{-}R'' + R'O^-$
   $\phantom{(I) + R'OH \longrightarrow R_3\overset{+}{N}CH_2{-}CH{-}}OH$ (13)

3. $R'O^- + CH_2{-}CH{-}R'' \longrightarrow R'OCH_2{-}CH{-}R''$
   $\underset{O}{\diagdown\diagup}$ $\underset{O^-}{}$

chain growth

$R'OCH_2{-}CH{-}R'' + (n)CH_2{-}CH{-}R'' \longrightarrow$
$\phantom{R'OCH_2{-}CH}\underset{O^-}{|}\phantom{{-}R'' + (n)CH_2}\underset{O}{\diagdown\diagup}$

$R'(OCH_2{-}CH)_n{-}O{-}CH_2{-}CH{-}O^-$
$\phantom{R'(OCH_2{-}CH)_n{-}O{-}CH_2}\underset{R''}{|}\phantom{{-}CH{-}}\underset{R''}{|}$

chain transfer

$R'(OCH_2{-}CH)_n{-}O{-}CH_2{-}CH{-}O^- + R'OH \rightleftharpoons$
$\phantom{R'(OCH_2{-}CH)_n{-}O{-}CH_2}\underset{R''}{|}\phantom{{-}CH{-}}\underset{R''}{|}$

$R'(OCH_2{-}CH)_n{-}O{-}CH_2{-}CH{-}OH + R'O^-$
$\phantom{R'(OCH_2{-}CH)_n{-}O{-}CH_2}\underset{R''}{|}\phantom{{-}CH{-}}\underset{R''}{|}$

regeneration of catalyst

$R'O^- + R_3\overset{+}{N}CH_2{-}CH{-}R'' \longrightarrow R_3N + R'OCH_2{-}CH{-}R''$
$\phantom{R'O^- + R_3\overset{+}{N}CH_2}\underset{OH}{|}\underset{OH}{|}$

$R'(OCH_2{-}CH)_n{-}OCH_2{-}CH{-}O^- + R_3\overset{+}{N}CH_2{-}CH{-}R'' \longrightarrow$
$\phantom{R'(OCH_2{-}CH)_n{-}OCH_2}\underset{R''}{|}\phantom{{-}CH{-}O^- + R_3}\underset{R''}{|}\underset{OH}{|}$

$R'(OCH_2{-}CH)_n{-}OCH_2{-}CH{-}OCH_2{-}CH{-}R'' + R_3N$
$\phantom{R'(OCH_2{-}CH)_n{-}O}\underset{R''}{|}\underset{R''}{|}\phantom{{-}OCH_2}\underset{OH}{|}$

To these monomer isomerization reactions should be added (Scheme 12). For simplicity the reactions of free ions only are shown. Similar reactions can be written for ion pairs. The mechanisms of the above reactions have not yet been proved rigorously. For this reason the above scheme should be treated as preliminary.

Analysis of the scheme makes it possible to obtain equation relating the rate of polymerization to the change of conductivity in the process.

$$\frac{k_p R}{\kappa'} = k_p^- \cdot \frac{10^3}{\lambda_\infty} + k_p^\pm \cdot \frac{10^6}{K_d(\lambda_\infty)^2}\,\kappa' \qquad (14)$$

where $R = \sum\limits_1^\infty R_j^- + \sum\limits_1^\infty R_j^\pm$—concentration of active growing centres in the form of free ions and ion pairs, κ'-viscosity corrected conductivity of the solution ($\kappa' = \eta\kappa$), k_p^- and $k_p^\pm$—rate constants of free ions and ion pairs, respectively, K_d and λ_∞—dissociation constant and equivalent conductance at infinite dilution. The dependence of $(k_p R/\kappa') = [(d\alpha/dt\,1/(1-\alpha)\kappa']$ on κ', presented in Fig. 20 according to eqn (14), is linear. From the slope and intercept, combinations of the constants $k_p^\pm \cdot k_p^- \cdot \lambda_\infty$ and K_d can be determined. The last two constants can be determined independently from conductivity measurements of a model ammonium salt—tetrabutylammonium-hexafluoroantimoniate. They turned out to be at 70° ($\epsilon = 7.24$) $K_d = 4.36 \times 10^{-5}$ mol/l and $\lambda_\infty = 51$ cm^2/Ω mol. From this $k_p^- = 0.3$ mol/l and $k_p^\pm = 0.04$ mol/sec.

From the obtained K_d and λ_∞ values the concentration of active growing centres R can be estimated.

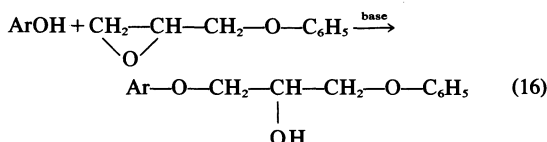$$R = \frac{10^6(\kappa')^2}{K_d(\lambda_\infty)^2} + \frac{10^3\kappa'}{\lambda_\infty}. \qquad (15)$$

Thus at maximum $R_{max} = 8.2 \times 10^{-4}$ mol/l, i.e. the effective concentration of active growing centres, as was determined earlier, is far less than the tertiary amine concentration.

REACTIONS OF EPOXIDES WITH PHENOLS

From the data on amine–epoxide reactions catalyzed by hydroxyl-containing substances many questions arise on reactions of phenols with epoxides with base catalysis. It is yet to be found out whether the base, for example tertiary amine, reacts with epoxide by itself, independently of phenol, or whether aliphatic hydroxyl groups,

formed through addition of phenol to epoxide, react with the epoxide. The answer to these questions would help investigation of the kinetics of phenol—epoxide reactions, which is of considerable practical value in epoxy-resin formation and their curing with phenols.

By thin-layer chromatography we investigated the reaction of mono- and diphenols with phenylglycidyl ether and various initiators: alkali-metal hydroxides, quarternary ammonium bases, triethylamine, alkali metal salts, with or without solvents, in the temperature range 60–160°, reactions of products of oxidation being totally excluded. We have shown that this reaction proceeds exclusively through the attachment of phenol to epoxide:

$$\text{ArOH} + \text{CH}_2\text{—CH—CH}_2\text{—O—C}_6\text{H}_5 \xrightarrow{\text{base}}$$

$$\text{Ar—O—CH}_2\text{—CH—CH}_2\text{—O—C}_6\text{H}_5 \qquad (16)$$
$$|$$
$$\text{OH}$$

By applying various identification reactions we can show with high sensitivity that general scheme of the reaction is independent of phenol-epoxide ratio.

By column chromatography the reaction products have been isolated in chromatographically pure form; their structures were proved chemically and spectroscopically, molecular weights of the products corresponding to their structures.

KINETICS OF EPOXIDE- CRESOL REACTION IN PRESENCE OF AN ALKALI

Formation of epoxydiane resins proceeds through interaction of phenol and epoxy end groups of oligomers. The reaction has been investigated on model substances—p-cresol and phenylglycidyl ether in solvents water-alcohol and water-acetone in presence of alkali (NaOH) in homogeneous conditions. From chromatography and titration of epoxy groups the rate of the reaction is directly proportional to alkali and epoxide concentrations and independent of solvent.

In aqueous solvents, the formation of epoxide-hydrolysis products is possible; alcoholysis may occur in alcohols.[17]

Indeed, hydrolysis of epoxides in the solvent water-alcohol yields products both of hydrolysis and alcoholysis. Thus, for example, in the reaction of epichlorohydrin (ECH) with alkali in water–ethanol solvent,
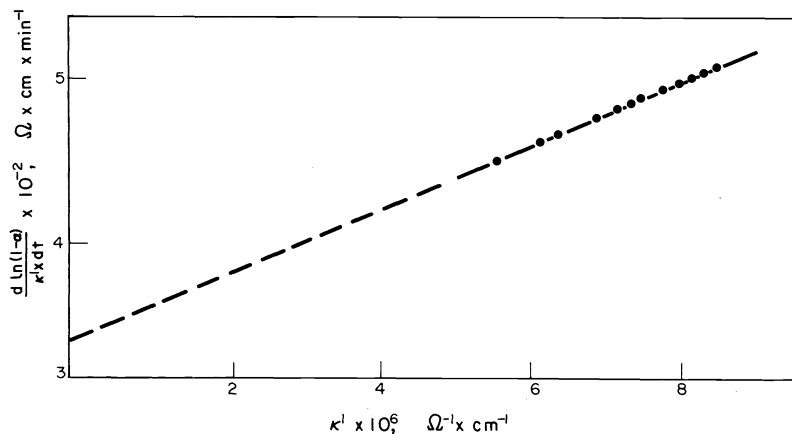

Fig. 20. Kinetic curve for phenylglycidyl ether polymerization in terms of eqn (14).

Table 6

| | K × 10^2 l/mol min | | | |
Solvent	ECH p-cresol	ECH hydrolysis	PGE p-cresol	PGE hydrolysis
Water-acetone	9.2 (1:2)	8.6 (1:1)	6.3 (1:2)	2.3 (1:1)
Water-alcohol	12.5 (1:2)	30.0 (1:2)	8.0 (1:2)	14† (1:1)

†Hydrolysis of ethylglycidyl ether (brackets indicate volume composition of mixed solvent).

ethylglycidyl ether has been isolated as a result of interaction of sodium ethylate with ECH:
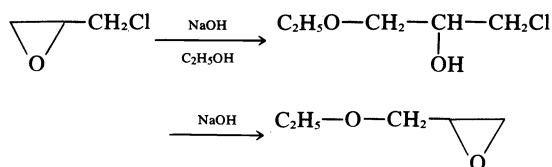
The rate of this reaction depends on alcohol content in the system and at high alcohol concentrations the reaction prevails. The rates of hydrolysis and alcoholysis of epoxides are directly proportional to epoxide and alkali concentrations. Rate constants of ECH, glycidol and glycidyl other consumption in water-alcohol solvent and in presence of alkali (NaOH) are, respectively $10^{9.7}$ exp $(-15600/RT)$; $10^{9.7}$ exp $(-15800/RT)$ and $10^{9.5}$ exp $(-15900/RT)$ 1/mol min. Both the enthropy factor and activation energy values of these reactions are similar, confirming the resemblance to the mechanism of opening of epoxide rings.

In water-acetone solvent, increasing acetone concentration increases rates of epoxide hydrolysis reactions due both to the destruction of solvation complexes of epoxide rings with water molecules and to the elimination of alcoholysis reactions.

Solvent influences on rate constants of epoxide reaction with p-cresol and hydrolysis rate constants at 60° are presented in Table 6.

Data in the table show that the rate constants of hydrolysis of epoxides in water-alcohol are greater than rate constants of their attachment to p-cresol, while in water-acetone these rate constants are comparable.

The rate of hydrolysis of epoxides has been found to decrease on introduction of sodium chloride into the system. The dissociation equilibrium of sodium hydroxide seems to shift to undissociated forms, thus decelerating hydrolysis reaction.[18]

From calorimetry, the heat of PGE with p-cresol was found to be 18.0 kcal/mol.

Thus, the use of water-organic solvents always causes side-reactions such as hydrolysis and alcoholysis of epoxides. To suppress these reactions water (alcohol) should be excluded from the solvents used. A change from aqueous to non-aqueous organic solvents requires a change of catalyst, for example, a change from alkali to a similar organic base. An example of such a strong base is a quarternary ammonium hydroxide. Rate constants of PGE and ECH reactions with cresol have been measured in acetone. Though these rate constants turned out to be lower (2–3 times) than those obtained in the presence of alkali, such a system totally excludes the side-reaction of hydrolysis, as was verified by thin-layer chromatography.

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