REACTIONS OF EPOXY WITH OTHER FUNCTIONAL GROUPS AND THE ARISING SEC-HYDROXYL GROUPS

By

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1. Introduction

The physical, chemical properties and processibility of the epoxy resins can be changed in a wide range — beside the resin frame structure — by subsequent modification, and by properly selecting the curing agent.

Both solvent-based and solvent-free epoxy systems are applied in the lacquer and paint industry. Through their hydroxyl-, ether-, amino-, carboxyl, carbonyl groups the epoxy resin systems give films strongly adhering to metal, wooden or other substrata. The process of curing may take place by homo- or heteropolymerization of the epoxy group, or in the presence of other curing compounds, by additive process accompanied by moderate shrinkage. In this work the uncatalyzed reaction of an aliphatic mono-epoxide has been investigated with a phenolic hydroxyl, aliphatic primary and secondary hydroxyl, aromatic and aliphatic mono-carboxyl, aromatic primary amino, aliphatic primary and secondary amino gropus as well as an aromatic monoepoxide with phenolic hydroxyl group in order to determine the reaction conditions of the epoxide and of the macromolecular systems modifying the epoxide (e.g. epoxy-polyester, epoxy-novolac etc.).

2. Literature

The curing of epoxy resins

The reactivity of the epoxy resins is based on that of the epoxy group in or at the end of the aliphatic chain or on the aromatic ring.

The high reactivity is due to the high tension in the three-membered epoxide ring as well as to the polarity caused by the oxygen atom.

For a three-membered aliphatic epoxy end group the energy of tension is 13 kcal/mol and the dipole moment is 2.9 Debye [1].

The highly tensioned three-membered epoxy end group is loosened by an electrophil or a nucleophil agent. The curing may proceed by the effect of

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* Budalakk Paint and Synthetic Resin Works

Lewis-bases or Lewis-acids or by compounds possessing active hydrogen. Curing with active hydrogen can also be catalyzed by Lewis-bases or Lewis-acids. The curing mechanism depends upon the presence or absence of a catalyst, the type of the curing compound and of the catalyst if any.

For some cases the reaction mechanisms have not yet been cleared [2—5].

The reaction of an aromatic diglycidyl ether with various functional groups has been investigated with especial regard to the selectivity and effect of the various catalysts on reactivity [6, 7]. The reactivity of aromatic diamines with aromatic mono- and diepoxide has also been studied [8].

Considerations in selecting model compounds for kinetic measurements

The model compounds for kinetic measurements should be possibly monofunctional, of well-known formulation, relatively easily synthetizable and long storable in normal conditions.

For this purpose only the mono epoxides (e.g. Cardura E,* phenyl, cresyl, butyl glycidyl ether etc.) can be taken into account, as applying diepoxides for the measurements, the subsequent reactions with the forming functional groups considerably encumbers the kinetic evaluations. The partner compounds have been selected so, that to have a structure analogous to the curing compounds or the epoxide-modifying resins. For our experiments we have therefore chosen monofunctional model compounds with long aliphatic chain or aromatic ring.

Methods for following the reactions

There are several physical and chemical methods for following the reactions.

The first stage of the reaction, i.e. from the beginning of reaction to the gelation phase, can be well followed qualitatively by a method of viscosimetry [1, 9].

The second phase of reaction, from the beginning of the caoutchouc-elastic phase to the firm stage can be well followed qualitatively by measuring the reversible deformation [1].

When the reaction is accompanied by the change of the refractive index, the first phase of reaction can also be followed qualitatively by measuring the refractive index of the medium.

Due to formation of hydroxyl groups during the reaction of the epoxy groups, the curing is accompanied by polarity change, which can be followed by measuring the capacity change of a condenser [10]. The method is also a qualitative one.

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* Shell Chemicals Ltd.

Both differential thermoanalysis (DTA), and differential scanning calorimetry (DSC) can be used for studying the process of cure [11], and the thermomechanical methods for examining the cured systems [1, 11].

The reaction of cure can be quantitatively followed by infrared spectroscopy (IR) [1, 9, 12—19]. The chemical methods are based on measuring the concentration of the reacting functional groups. The most frequent are the methods of measuring the epoxide equivalent weight, acid value, hydroxyl value, water content, anhydride content, free phenol content.

It is to be noted that a single method for characterizing the whole curing process of a system is usually not sufficient. Chemical methods can only follow the reaction of a monofunctional component, since the reaction of two- or polyfunctional compounds results in increased molecular weight and low solubility which inevitably necessitate the application of further methods.

3. Experiments

Model compounds, testing methods

The reaction of the Versatic 911 glicydyl ester (Cardura E) with phenol, palmitic acid, benzoic acid, normal- and iso-octanole, aniline, diethylamine, ethanolamine as well as the reaction of phenylglycidyl ether with phenol have been investigated in order to find the reaction conditions and determine the direction and relative rate of the reactions without applying a catalyst.

The model compounds used in our experiments were commercial technical products.

For our investigations we have made series of measurements with the stoichiometric ratio of two components at three different temperatures.

In addition to the stoichiometric ratios the components have been used in 100 per cent excess at the Cardura E—phenol reaction at each 3 different temperatures and in all other cases at a single temperature. By applying one or the other component in excess certain competing reactions had been overshadowed i.e. the part order of reaction for the component in excess had been adjusted to zero.

The preliminary experiments pointed out the temperature where the reaction had a rate measurable by the applied methods.

The reactions were followed in all cases by measuring the epoxide equivalent. To this aim the pyridinium hydrochloride method was used [20]. In addition to the epoxide equivalent determination at the Cardura E—phenol reaction the free phenol content was measured by using the iodometric method [21]. The Cardura E—palmitic acid, Cardura E—benzoic acid reactions were followed also by measuring the acid value [20].

Experimental results and discussion

The obtained kinetic diagrams enable in most cases to delimit certain simple reactions and to calculate their exact kinetic parameters.

Some competing reactions may be detected, from which the degree of activity of the forming functional groups can be concluded.

The reactivity of the initial and forming functional groups to the epoxy as well as to each other can be compared. At last the reactivity of the aliphatic and the aromatic epoxy groups can be compared in their reaction with phenol. The order of reaction was determined by the lgc—t plot, where *c* is the concentration of the "functional group", *t* the time where the concentration was measured [22]. The activation energy was calculated from the tangent-line of the log k—1/T plot on the basis of the Arrhenius equation where *k* is the reaction rate constant, and *T* the temperature [22].

a. Reaction of phenol with Cardura E

The reaction of the components in stoichiometric ratio at three different temperatures is presented by Fig. 1.

The reaction rate increasing with the temperatures and the higher conversions corresponding to the higher temperatures are well indicated by the curves. The reaction is exothermic and the effect of heat is the highest at the highest temperature. On all of the curves three parts can be distinguished.

The first steep part lasting for 20 to 30 minutes (increasing with increasing temperature), the intermediate, interim part and the third, slightly rising linear part.

At first it may be presumed that the first and last linear parts of the curves are due to two different reactions — the first part to the phenolic—OH—epoxide and the third to the formed sec—OH—epoxide reaction. The intermediate part may represent both the above reactions simultaneously proceeding at different and continuously changing rates.

The reaction carried out with 100 per cent excess of Cardura E (Fig. 2) was partly intended to prove this assumption.

The last, linear parts of the curves in Fig. 2 are the most interesting, since here it is doubtless that only the epoxy and the formed secondary hydroxyl groups may react. The same fact is affirmed by the last, linear parts of the Cardura E : phenol 1 : 1 and 2 : 1 plots in Fig. 3.

From the data in Fig. 2 it can be calculated that during the epoxide—phenolic hydroxyl reaction (at 133 °C) the conversion of the epoxide in the 510th minute is already 148 per cent, while that of the phenolic hydroxyl is only 57 per cent and after 300 minutes the latter is unchanged. It sufficiently proves the secondary reaction between the epoxy and the forming sec—hydrox-

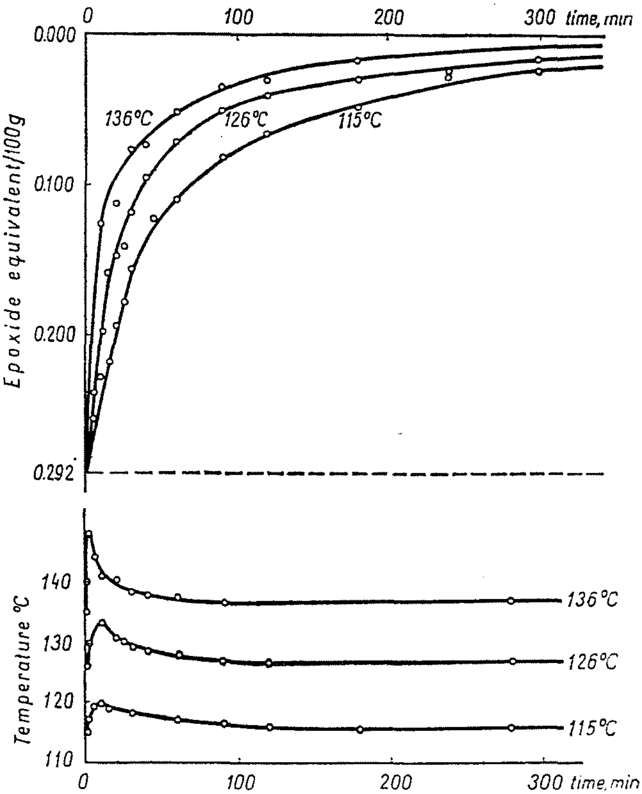

Fig. 1. Reaction of phenol with Cardura E at stoichiometric ratio at three different temperatures and the change of the temperatures

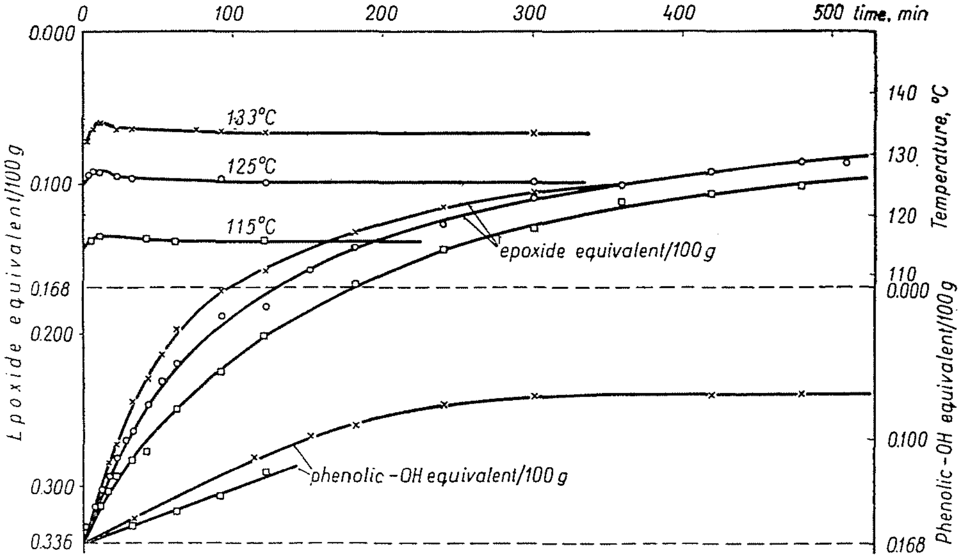

Fig. 2. Reaction of phenol with Cardura E of 100 per cent excess at three different temperatures and the change of the temperatures

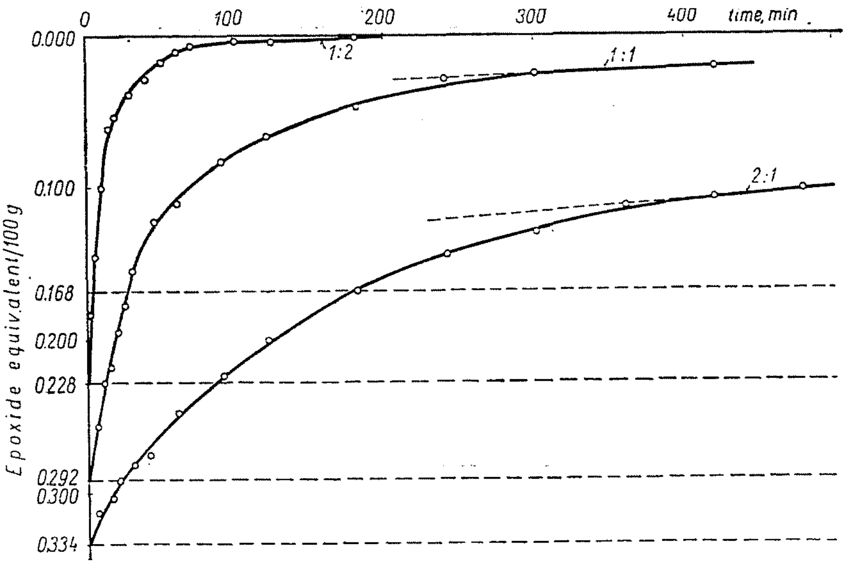

Fig. 3. Reaction of Cardura E with phenol at ratios of 1 : 2, 1 : 1 and 2 : 1 at 115 °C

yl groups. According to our measurements the reaction of the sec—hydroxyl group is very slow or absent at this temperature (see item d).

The conversion data of Fig. 2 and the third linear part of the plot show that the forming sec—OH groups consume the epoxide even at 133 °C and the rate of reaction surpasses that of the secondary and primary alcoholic hydroxyl groups (see Table 1).

According to these data the reaction of the ordinary secondary hydroxyl and the epoxy group would take place very slowly even at 133 °C, thence it follows that the secondary hydroxyl group formed by the epoxy—phenolic hydroxyl reaction is activated by the phenoxy group.

Let us consider now the first linear parts of the curves in Fig. 1. For the ease of understanding the phenol : Cardura E reaction was followed at 100 per cent excess of phenol at three different temperatures (Fig. 4).

Table 1

Kinetic data of the Cardura E—n-octanol and the Cardura E — newly formed sec — hydroxyl reaction

Reaction	Order of reaction n	Reaction rate constant k_{133} °C min^{-1}	Activation energy ΔE kcal/mol
Cardura E—n-octanol	1	$6.38 \cdot 10^{-4}$	10.90
Cardura E–sec-OH formed from phenolic reaction	1	$1.115 \cdot 10^{-3}$	7.02

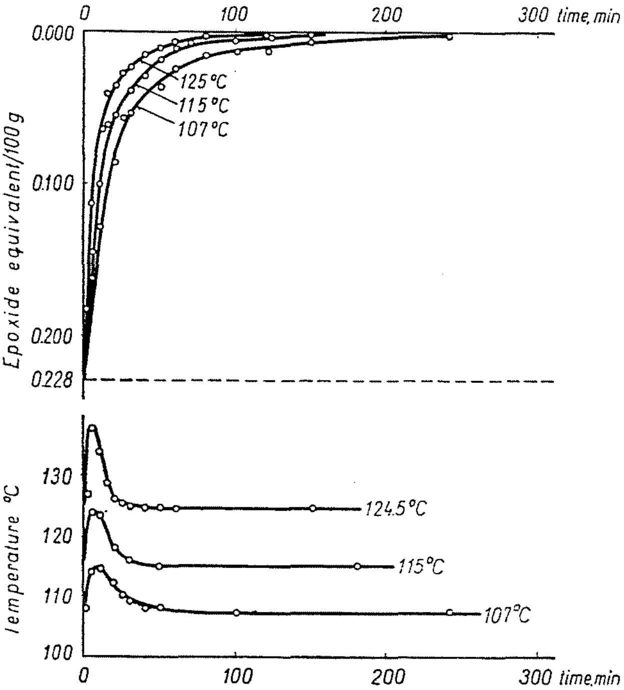

Fig. 4. Reaction of phenol with Cardura E at 100 per cent excess of phenol at three different temperatures, and the change of the temperatures

At all the three temperatures there was a quick epoxy consumption with large exothermic effect, as it was expected. The conversion was 100 per cent, however, only for the epoxy groups, for the phenolic hydroxyl groups it was only 65 and 57 per cent (Fig. 5).

It proves that according to the 100 per cent excess of the phenol the extent of the phenolic—OH—epoxy reaction is greater than that at the stoichiometric ratio, but contrary to the expectations it is not exclusive even at the beginning stage.

The diversity of the curves representing the epoxide consumption at both temperatures is unambiguous. Except for the higher conversion at the higher temperature this is only true with restriction for the curves representing the consumption of the phenolic hydroxyl groups.

At first it appears that the rise at the lower temperature is higher than that at the higher temperature. To clear this apparent contradiction both curves have been kinetically analyzed. It can give more information also for both the pure phenolic-OH—epoxy and the total reaction (see Table 2).

The activation energy of the phenolic-OH—epoxide reaction is smaller than that of the newly formed sec-OH—epoxide (see Table 1). At the very

Table 2

Kinetic data of the phenolic-OH—epoxide and the total phenol—Cardura E reaction
The order of reaction at the first stage in both cases is one

Reaction	Reaction rate constant min^{-1}			Activation energy ΔE kcal/mol
	k_{107}°C	k_{115}°C	k_{125}°C	
Phenolic-OH—epoxide	$8.83 \cdot 10^{-3}$	$9.56 \cdot 10^{-3}$	—	3.27
Total	$3.96 \cdot 10^{-2}$	$8.20 \cdot 10^{-2}$	$1.25 \cdot 10^{-1}$	22.00

beginning there is no chance of this secondary reaction, but with arising concentration of the sec-OH groups it is starting. At a higher temperature the competing reaction of higher activation energy may surpass the primary reaction — which is promoted also by the greater effect of heat (Fig. 4). Phenolic-OH—epoxide reaction is also proceeding, but there is less quantity of epoxide available for this reaction. This gives reason for the lower rise of the curve representing the phenolic-OH consumption at higher temperature. At the first minutes, when the secondary reaction is still excluded the rise is equal to that of the total reaction (see for 115 °C in Fig. 5). The data of Table 3, the higher rate of the epoxide consumption and the lower phenol conversion are proving that the phenolic-OH—epoxide reaction is unexclusive, the sec-OH—epoxide reaction appears already at the first stage with a rate about one order lower than that of the primary reaction.

The kinetic data calculated from the first parts of the curves in Fig. 1 are presented by Table 4.

Table 3

Rate constants of the phenolic-OH—epoxide and the newly formed sec-OH—epoxide reactions.
Order of reaction at the first stage is one

Reaction	k_{115}°C min^{-1}
Phenolic-OH—epoxide	$9.56 \cdot 10^{-3}$
Newly formed sec-OH—epoxide	$7.88 \cdot 10^{-4}$

Table 4

Kinetic data of the phenol—Cardura E reaction at stoichiometric ratio.
Order of reaction at the first stage is one

Temperature °C	115	126	136
Reaction rate constant min^{-1}	$2.00 \cdot 10^{-2}$	$3.99 \cdot 10^{-2}$	$8.32 \cdot 10^{-2}$
Activation energy ΔE kcal/mol		20.02	

The activation energy of the stoichiometric reaction is near to that of the reaction with 100 per cent phenol excess (see Table 2).

The slight difference in the rise of the curves corresponding to the stoichiometric and the phenol excess reaction at the first stage (see Fig. 3) is due to the great difference in the concentrations of the reacting partners (the phenolic and then the sec-OH groups). By this concordance of the above mentioned linear parts it is shown that during the first stage practically the same reactions take place with a gross rate constant, where the phenolic reaction is predominant, as the greater part of the reacted phenol is consumed at the first stage (Figs 5 and 6).

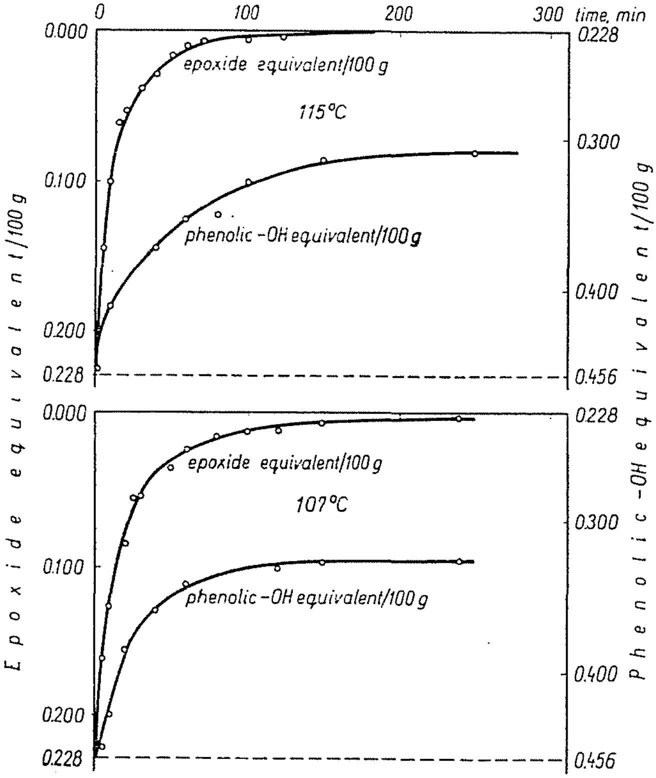

Fig. 5. The epoxide and the phenolic hydroxyl consumptions representing the reaction of phenol with Cardura E at 100 per cent excess of phenol at 115 and 107 °C

The rate and the reaction rate constant of the simultaneous reactions are changing with the proceeding reaction. The phenolic-OH—epoxide reaction is gradually overshadowed by that of the sec-OH—epoxide getting predominant and then exclusive.

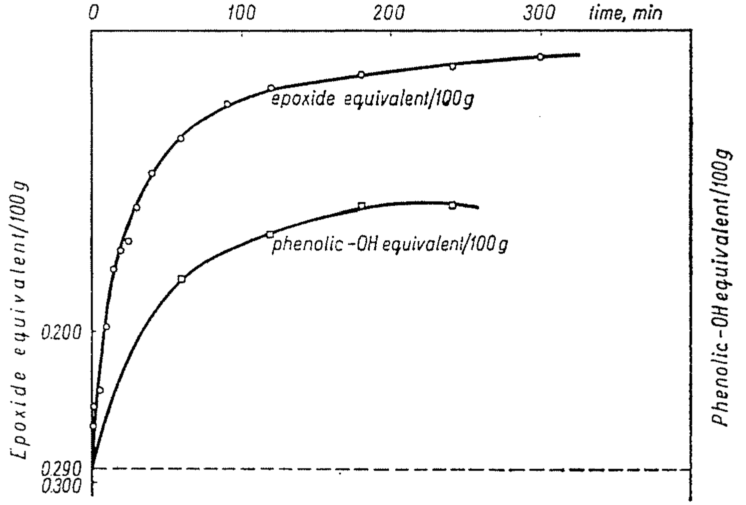

Fig. 6. The epoxide and the phenolic hydroxyl consumptions representing the reaction of phenol with Cardura E at stoichiometric ratio at 126 °C

b. Reaction of palmitic acid with Cardura E

The reaction is exothermic, the heat of reaction increases with the temperature. The order of reaction at the first stage is one. With increasing the temperature the curves are more sloping (Fig. 7).

Figure 8 shows the reaction with stoichiometric ratio and with 100 per cent excess of one and the other component.

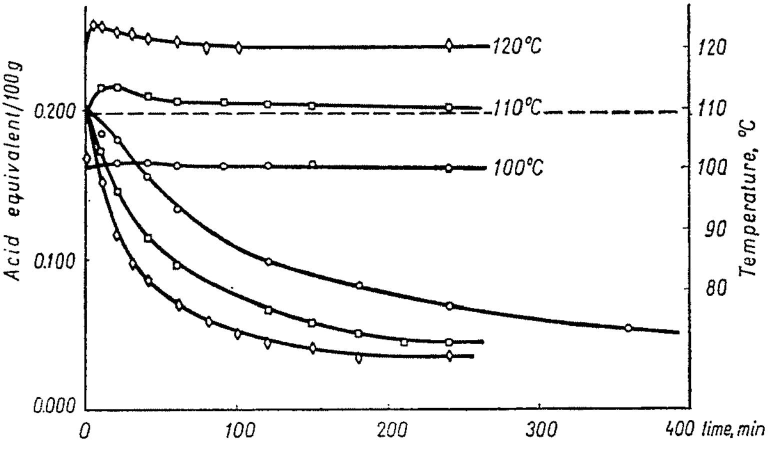

Fig. 7. Reaction of palmitic acid with Cardura E at stoichiometric ratio at three different temperatures, and the change of the temperatures

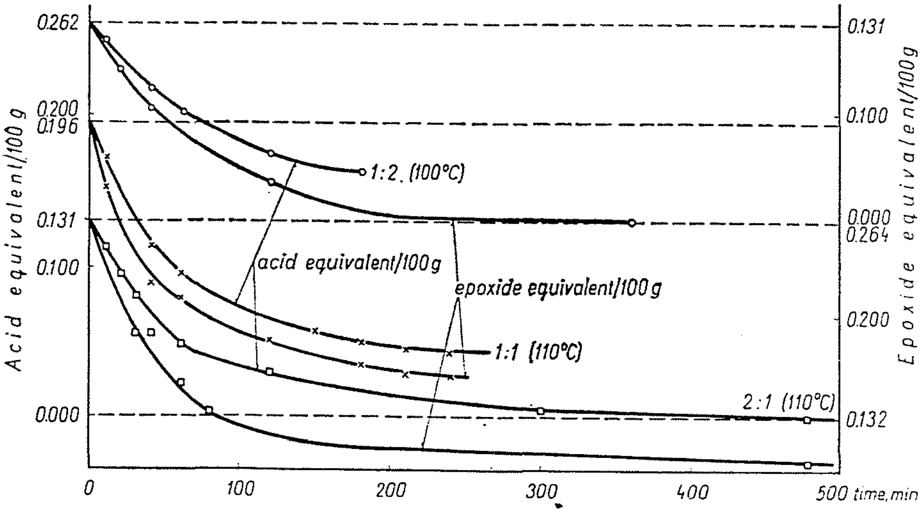

Fig. 8. Reaction of Cardura E with palmitic acid at ratios of 1 : 2, 1 : 1 and 2 : 1 at 100 and 110 °C

The slope of the corresponding curves is nearly equal for all the three ratios at the first reaction phase. The slightly lower slope of the curve corresponding to the acid excess reaction is due to the lower reaction temperature. It means that the preliminary reaction is that of the carboxyl to the epoxide with about equal rate in all the three cases. Comparing the acid consumption with that of the epoxide it can be stated that the carboxyl—epoxide reaction is not exclusive.

At the very beginning there is no simultaneous reaction. After the sec-OH groups formed by the carboxyl—epoxide reaction appeared, the secondary reaction immediately starts at a rate by one order less than that of the primary reaction (Table 5).

Let us consider the conversions at stoichiometric ratio in Fig. 8. At the 240th minute 77.5 per cent of the acid and 85.6 per cent of the epoxide have

Table 5

Kinetic data of the palmitic acid—Cardura E reaction. The order of reactions at the first stage is one

Reaction	Reaction rate constant min^{-1}			Activation energy ΔE kcal/mol
	k_{100}°C	k_{110}°C	k_{120}°C	
Carboxyl-epoxide	$6.58 \cdot 10^{-3}$	$1.39 \cdot 10^{-2}$	$2.62 \cdot 10^{-2}$	20.2
Total (carboxyl, sec-OH—epoxide)	—	$1.495 \cdot 10^{-2}$	—	—

been consumed. The difference of 8.1 per cent reacted with the sec-OH groups, amounting to only 9.5 per cent of the total acid. It means that on every ten carboxyl—epoxide reaction falls one sec-OH—epoxide reaction.

Considering the reaction with Cardura E excess in Fig. 8, the Cardura E conversion is 100 per cent at the 90th minute while at the same time only 72.5 per cent of the acid have been reacted. The existing 27.5 per cent of the acid are consumed at the 480th minute, while the further epoxide consumption is 28 per cent (epoxide conversion at the 480th minute is 128 per cent).

In this stage only 0.5 per cent of the epoxide reacted secondarily, and mainly during the 100 to 200 minute interval. Namely after 300 minutes the curves are parallel, that proves the absence of secondary reaction in this last stage.

The diverting lines of the acid and epoxide consumption curves as well as the fact of 128 per cent epoxide conversion (in the 480th min) relate to simultaneous, secondary reactions. The simultaneous reaction can take place only at the presence of the acid which presumably catalyses the secondary reaction.

c. *Reaction of benzoic acid with Cardura E*

The considerations for the palmitic acid—epoxide reaction apply to the benzoic acid—Cardura E reaction which is demonstrated by Figs 9 to 11. The reaction-kinetic data are presented in Table 6.

Table 6

Kinetic data of the benzoic acid—Cardura E reaction
Order of reaction at the first stage is one

Reaction	Reaction rate constant min^{-1}			Activation energy ΔE kcal/mol
	k_{90}°C	k_{100}°C	k_{110}°C	
Carboxyl–epoxide	$2.18 \cdot 10^{-2}$	$2.67 \cdot 10^{-2}$	$5.77 \cdot 10^{-2}$	15.70

The above data show that the reactivity of the aromatic carboxyl group to epoxide is greater than that of the aliphatic carboxyl group. Comparing the curves of epoxide and acid equivalent consumption at Cardura E : acid = = 2 : 1 ratio in Figs 8 and 11 it is clear that the curves slighter divert during the first stage of reaction in the case of the benzoic acid. It means the less extent of secondary reactions during the first reaction stage of benzoic acid—Cardura E, since the rate of the benzoic acid—epoxide reaction at 90 °C is nearly equal to the rate of palmitic acid—epoxide reaction at 115 °C and the sec-OH reaction at 90 °C is still undoubtedly slower.

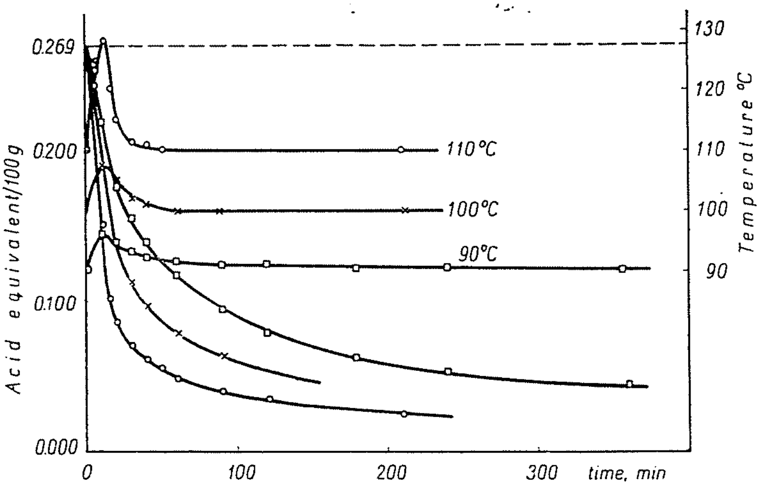

Fig. 9. Reaction of benzoic acid with Cardura E at stoichiometric ratio at three different temperatures and the change of the temperatures

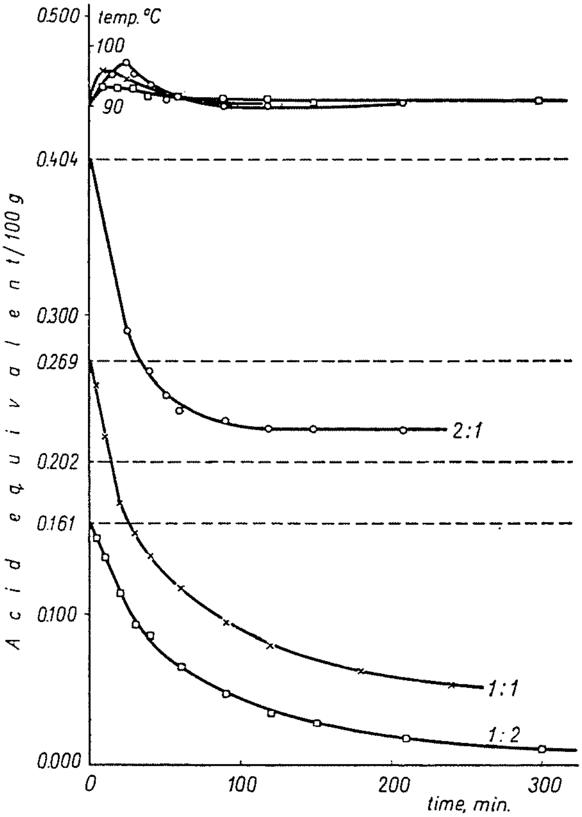

Fig. 10. Reaction of benzoic acid with Cardura E at ratios of 2 : 1, 1 : 1 and 1 : 2 at 90 °C, and the change of the temperature

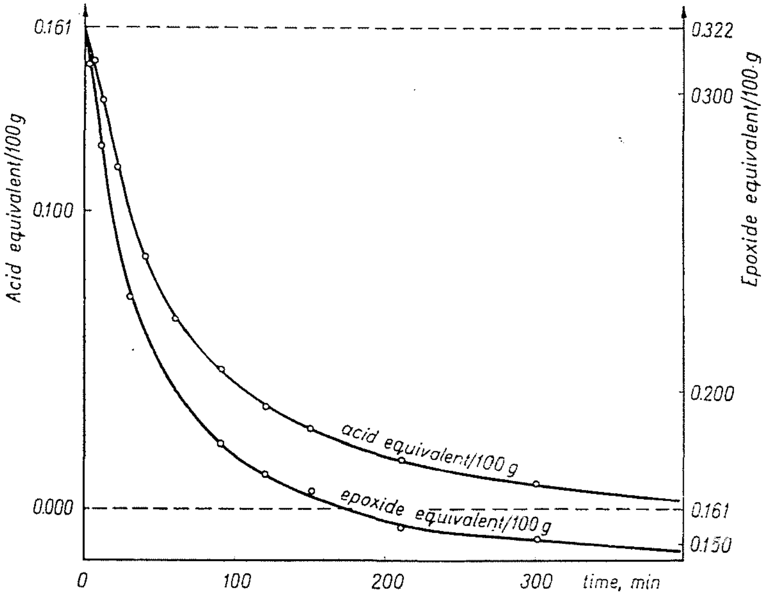

Fig. 11. The acid and epoxide consumption representing the reaction at 90 °C of benzoic acid with Cardura E at 100 per cent excess of Cardura E

For estimating the extent of secondary reactions let us consider the conversions in Fig. 11. In the 180th minute of reaction at 90 °C the Cardura E conversion is 100 per cent, while the benzoic acid consumption is only 86 per cent at the same time. (At 100 per cent Cardura E conversion the palmitic acid conversion was 72.5 per cent at 110 °C, Fig. 8.)

At the 300th minute the epoxy equivalent conversion is 115 per cent, the acid equivalent conversion is 96.3 per cent. The further acid reaction from the 180th minute was 10.3 per cent, while the further epoxide reaction 15 per cent. The difference of 4.7 per cent is due to the simultaneous sec-OH—epoxide reaction after 180 minutes. The total secondary reaction at the 300th minute is 15 per cent (115 per cent epoxide conversion). The rise of the curves in Fig. 11 show that up to the 180th minute the secondary reaction rate is about one order less than that of the carboxyl—epoxide reaction. From the 180th minute the carboxyl—epoxide reaction is only the double of the secondary reaction. After 300 minutes the curves of the epoxide and acid equivalent consumptions are parallel, showing the absence of secondary reactions in this last reaction stage. From this it can be concluded that similar to the palmitic acid, the benzoic acid also catalyzes the sec-OH—epoxide reaction. The numerical data seem to prove greater catalytic effect for the benzoic acid than for the palmitic acid. It must be proved, however, by numerical kinetic data of the reactions proceeding with both acids at the same temperature.

d. Reaction of normal- and iso-octanole with Cardura E

The results of the kinetic measures are presented by Figs 12—14.

The reaction comes to a rate measurable with our methods only at 150 °C. The obtained lines are the first part of the kinetic curves. The conversion is less than 50 per cent in all cases.

The reaction kinetic data are presented by Table 7.

Table 7

Kinetic data of n- and i-octanole—Cardura E reaction. The order of reaction is one

Reaction	Reaction rate constant min^{-1}			Activation energy ΔE kcal/mol
	k_{150}°C	$k_{155,5}$ °C	k_{163}°C	
n-octanole—Cardura E	$1.23 \cdot 10^{-3}$	$1.69 \cdot 10^{-3}$	$1.81 \cdot 10^{-3}$	10.9
i-octanole—Cardura E	$9.50 \cdot 10^{-4}$	—	—	—

By their reaction rate constants the reactivity of the normal- and iso-octanoles with Cardura E can be compared. The alcohol of a linear chain reacts a bit quicker (Fig. 12), that means the dependence of reactivity even on the extent of the unlinearity. Since the reactions were followed by measuring only the epoxide equivalent consumption, the secondary reactions could not be delimited. The simultaneous reaction of the forming sec-OH with epoxide may presumably proceed at a rate similar to that of the primary reaction in the case of the secondary alcohol, and at some lower rate in the case of the primary alcohol reaction. It is shown by Figs 13 and 14, where the line representing the Cardura E : octanole = 2 : 1 reaction is rising slightly lower than the 1 : 2, 1 : 1 lines while the corresponding line of the Cardura E : i-octanole = 2 : 1 reaction is parallel to the other two lines. The lower raise of the 2 : 1 line in Fig. 13 is due to the smaller reaction rate resulting from the lower concentration of the n-octanol. The decrease of reaction rate caused by the lower sec alcohol concentration in Fig. 14 is compensated by the simultaneous reactions

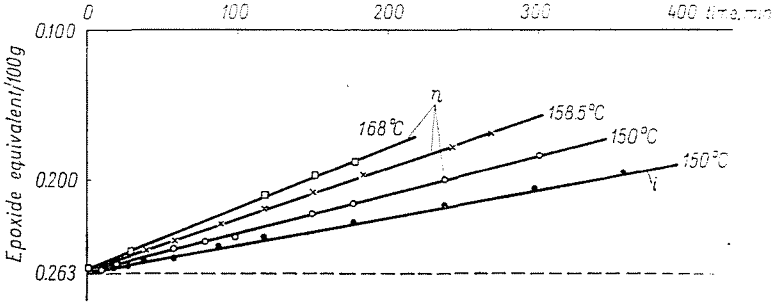

Fig. 12. Reaction of n- and i-octanole with Cardura E at stoichiometric ratio

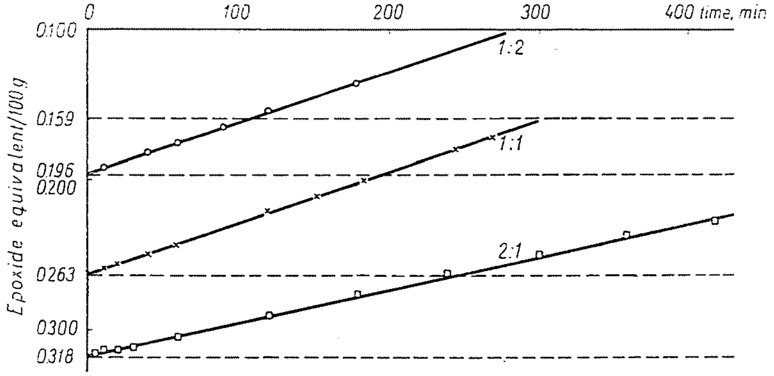

Fig. 13. Reaction of Cardura E with n-octanole at ratios of 1 : 2, 1 : 1 and 2 : 1 at 158.5 °C

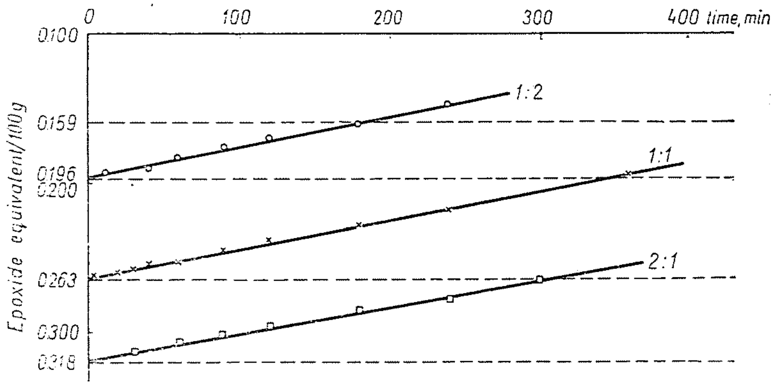

Fig. 14. Reaction of Cardura E with i-octanole at ratios of 1 : 2, 1 : 1 and 2 : 1 at 150 °C

of the formed sec-OH groups of similar reaction rate. Since the lines corresponding to the three different molar ratios are parallel, the formed sec-OH groups cannot be activated by the ether group.

e. *Reaction of aniline with Cardura E*

The lines representing the reactions are shown in Figs 15 and 16.

The reaction kinetic data are presented by Table 8. Since the reactions were followed by measuring only the epoxide consumption, the curves are showing the total reaction. Two different secondary reactions may be presumed, that of the forming sec-amino–epoxide and the sec-OH—epoxide. The measurements with excess components (Fig. 16) seem to prove the absence of simultaneous secondary reactions at the given reaction temperature. Hence the reaction of the primary and the secondary amino groups can be delimited at 80 °C, which is partly due to the steric hindrance.

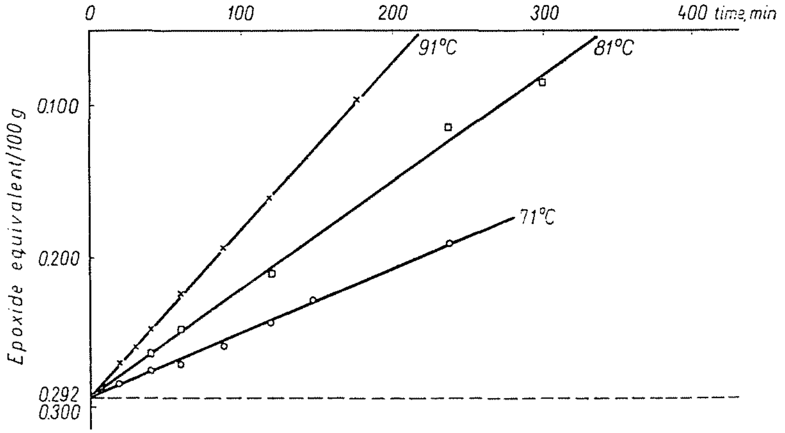

Fig. 15. Reaction of aniline with Cardura E at stoichiometric ratio at three different temperatures

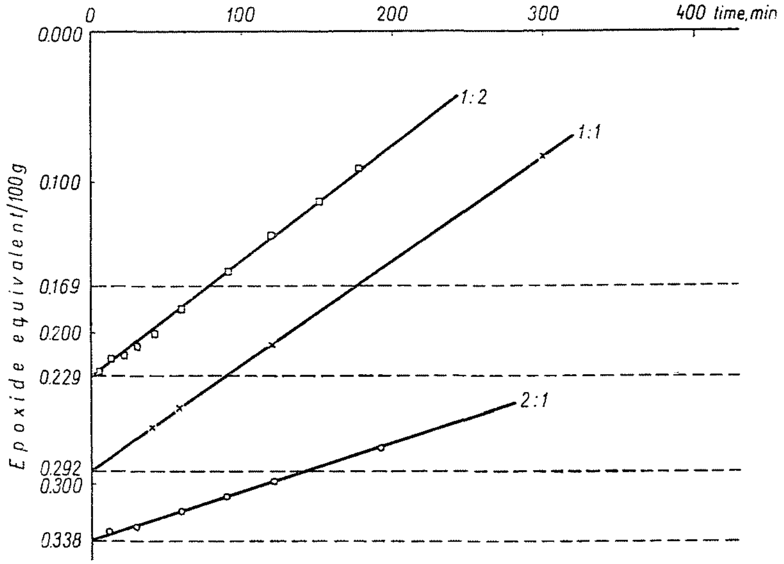

Fig. 16. Reaction of Cardura E with aniline at ratios of 1 : 2, 1 : 1 and 2 : 1 at 81 °C

Table 8

Kinetic data of the aniline—Cardura E reaction. The order of reaction is one at the first stage

Reaction	Reaction rate constant min^{-1}			Activation energy ΔE kcal/mol
	k_{71}°C	k_{81}°C	k_{91}°C	
Aniline-epoxide	$1.33 \cdot 10^{-3}$	$2.78 \cdot 10^{-3}$	$3.91 \cdot 10^{-3}$	11.70

f. Reaction of ethanolamine with Cardura E

The curves representing the reactions are presented by Figs 17 and 18.

As all the reactions were invariably followed by exothermic heat, there is no way of giving a quantitative evaluation. The high rate of reaction even at room temperature is due to the high reactivity of the primary amino group

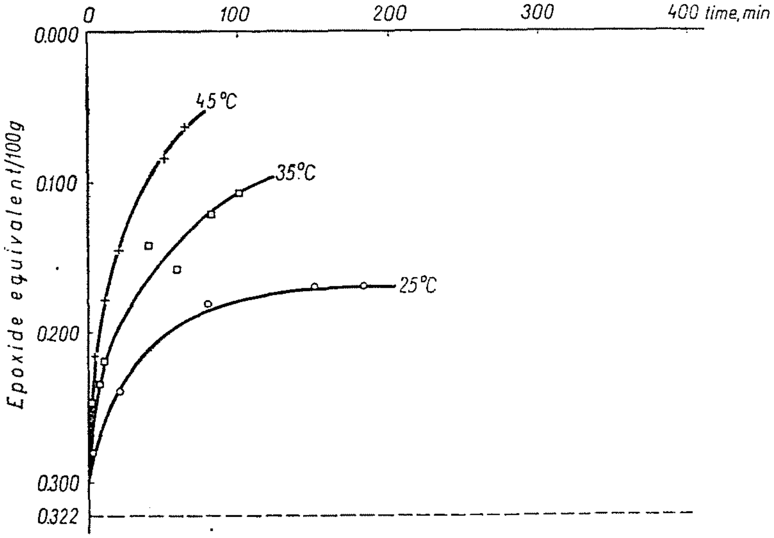

Fig. 17. Reaction of ethanolamine with Cardura E at stoichiometric ratio at three different temperatures

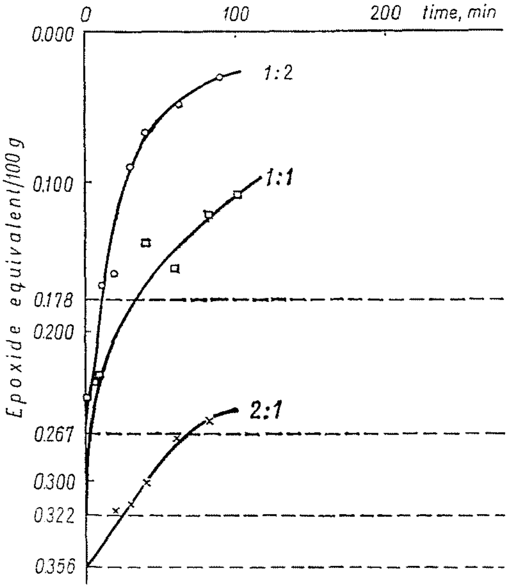

Fig. 18. Reaction of Cardura E with ethanolamine at ratios of 1 : 2, 1 : 1 and 2 : 1 at 35 °C

activated by the —OH group. In this case there are more chances for the simultaneous, competitive reactions. The forming sec-OH groups presumably cannot react at such low temperatures. The competitive reaction of the primary —OH group of the ethanolamine is possible. It was overshadowed by the excess of the ethanolamine, but the curve corresponding to the stoichiometric ratio is unambiguously showing secondary reaction, since not even its first part is linear (Fig. 18). The considerable increase of viscosity during the measurements may refer to simultaneous reactions, and the viscosity seems to be a measure for qualitatively following the gross reaction.

g. *Reaction of diethylamine with Cardura E*

The reactions are represented by the curves in Figs 19 and 20. The kinetic data are shown in Table 9.

At 72 and 80 °C the reaction takes place at a high rate up to high conversion (Fig. 19).

The raise of the curve at 91 °C has not yet been explained. Presumably at 91 °C an intermediate may form consuming sec-amine or an adduct-forming process may take place. For determining the reason of this phenomenon further measurements are required.

The curves in Fig. 20 show that at 80 °C the primary reaction can be made exclusive. Hence these kinetic data enable us to compare the reactivity of the aliphatic secondary amine to the epoxide with that of the other amines. It can be stated that in reactivity to epoxide the aliphatic secondary amine sur-

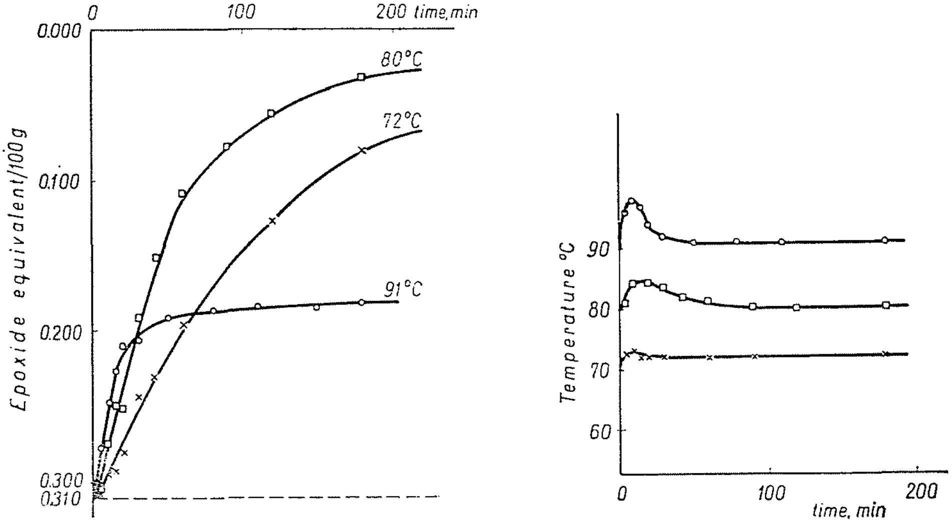

Fig. 19. Reaction of diethylamine with Cardura E at stoichiometric ratio at three different temperatures, and the change of the temperatures

passes the aromatic primary amine. Considering the great difference between the activation energies, it can be concluded that though the reactivity of a primary amine is higher than that of a secondary one, during the reaction of the latter the forming terciary amine acts as a catalyst. Therefore the secondary reactions come also more to the background. Also the steric hindrance of the aromatic ring must not be ignored.

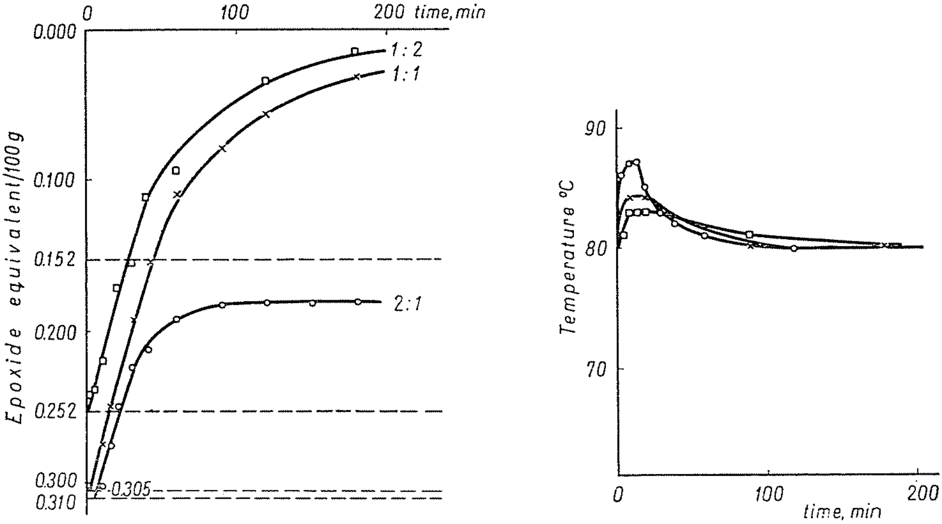

Fig. 20. Reaction of Cardura E with diethylamine at ratios of 1 : 2, 1 : 1 and 2 : 1 at 80 °C, and the change of the temperatures

Table 9

Kinetic data of the diethylamine—Cardura E reaction. The order of reaction up to 30 per cent conversion is one

Reaction	Reaction rate constant min^{-1}			Activation energy ΔE kcal/mol
	k_{72}°C	k_{80}°C	k_{91}°C	
Diethylamine-epoxide	$6.83 \cdot 10^{-3}$	$1.85 \cdot 10^{-2}$	$5.74 \cdot 10^{-2}$	27.3

h. Reaction of phenol with phenyl glycidyl ether

The lines representing the reactions are shown in Figs 21 and 22. The kinetic data are presented in Table 10.

Contrary to the expectation, the reactivity of phenylglycidyl ether to phenol is much less than that of Cardura E.

One of the reasons may be the steric hindrance caused by the aromatic ring. The plots in Fig. 21 correspond to the first part of the kinetic curves; Fig. 22 proves the absence of secondary reactions during the first stage.

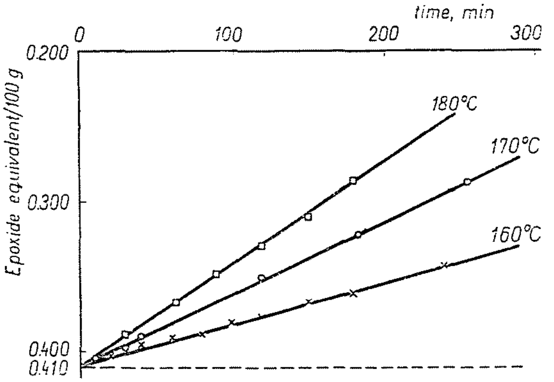

Fig. 21. Reaction of phenol with phenyl glycidyl ether at stoichiometric ratio at three different temperatures

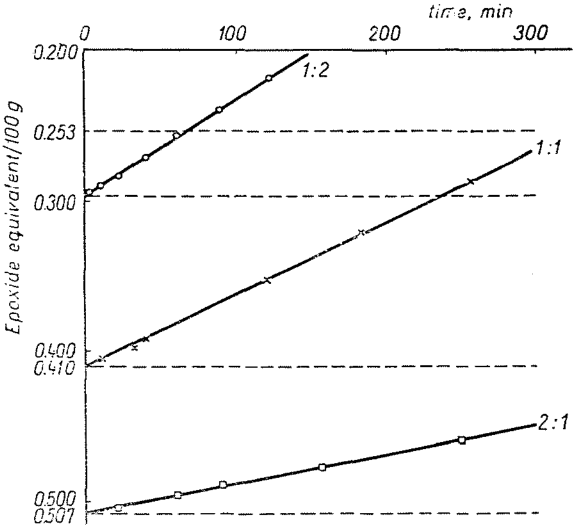

Fig. 22. Reaction of phenyl glycidyl ether with phenol at ratios of 1 : 2, 1 : 1 and 2 : 1 at 170 °C

Table 10

Kinetic data of the phenol-phenylglycidyl ether reaction. The order of reaction up to 50 per cent conversion is one

Reaction	Reaction rate constant min^{-1}			Activation energy ΔE kcal/mol
	k_{160}°C	k_{170}°C	k_{180}°C	
Phenol–phenyl glycidyl ether	$9.92 \cdot 10^{-4}$	$1.53 \cdot 10^{-3}$	$1.90 \cdot 10^{-3}$	13.80

4. Conclusions

The uncatalyzed reaction of the aliphatic monoepoxide (Cardura E) with the most characteristic functional groups has been investigated and the received data have been chemically and kinetically evaluated. The individual reactions could be in the most cases delimited, therefore the kinetic data could be unambiguously calculated.

Contrary to the literary data [2] the phenolic hydroxyl reacts with the epoxy group at a rate measurable even at 115 °C. The phenol comsumption is about 50 per cent, and most of this reaction is during the first stage, the further considerable epoxide consumption is due to the secondary reaction of the formed secondary hydroxyl groups. It indicates that the forming secondary —OH groups are activated by the phenoxy group which has also been quantitatively proven (see Part 3, item a). The aliphatic hydroxyl groups react with the epoxy groups at a much lower rate than does the phenolic hydroxyl. Even at 150 to 170 °C the reaction is very slow. The reaction rate of the aliphatic primary alcohol surpasses that of the aliphatic secondary alcohol as it was expected. Competitive reactions could not be delimited, as only the overall reaction was followed. The forming secondary hydroxyl groups are not activated by the alfa-ether group.

Both the aromatic and the aliphatic carboxyl groups have higher reaction rates to epoxy than the phenolic hydroxyl groups. The aromatic acid surpasses the aliphatic one in reactivity to the epoxy groups. There are secondary reactions in both cases and they proceed till the acid is present. It shows that the acid still present catalyzes the secondary hydroxyl–epoxide reaction. According to the conversion data during the last reaction phase the extent of the secondary reaction is greater in the case of the aromatic acid, that seems to show greater catalytic effect of the aromatic acid to the secondary—OH—epoxide reaction than that of the aliphatic acid. In spite of their high activation energy the aliphatic primary and secondary amines react already at 70 °C at a great rate. The reactivity of the aliphatic primary amine is greater than that of the aliphatic secondary amine even if the possible activating effect of the —OH group in the ethanolamine is taken into consideration. The aliphatic secondary amine reacts faster than the aromatic primary amine, which is due — according to the literature — to the catalytic effect of the forming tertiary amine as well as to the steric hindrance caused by the aromatic ring.

It can be presumed that the competitive reaction proceeding during the aniline to epoxide reaction comes from the secondary hydroxyl rather than from the secondary amino groups, which is sterically hindered. Also in this case, some activation of the secondary hydroxyl groups can be presumed. It is stated at last that the reactivity of the aromatic monoepoxide in phenol reaction is less than that of an aliphatic monoepoxide, which is presumably due to the steric hindrance caused by the aromatic ring.

The given kinetic results may be helpful in finding the proper reaction conditions for developing an epoxide—epoxide modifying high molecular resin system. For proving the presumptions not yet established by quantitative data some further measurements are needed.

Summary

The uncatalyzed reaction of the aliphatic monoepoxide (Cardura E) with phenolic hydroxyl, aliphatic primary and secondary hydroxyl, aliphatic and aromatic carboxyl, aliphatic primary and secondary amino, aromatic monoamino groups as well as the reaction of the aromatic monoepoxide (phenyl glycidyl ether) with phenolic hydroxyl group have been investigated. The phenolic hydroxyl reacts with the epoxy group at a rate well measurable even at 115 °C, and the competitive reaction of the forming secondary —OH groups activated by the phenoxy group takes place. The reaction rate of the aliphatic alcohols with the epoxy groups is very slow even at 150 to 160 °C. Competitive reaction could not be delimited, the forming secondary —OH groups are not activated by the alpha-ether groups. The aliphatic and aromatic carboxyl groups react faster with the epoxy than do the phenolic hydroxyl groups. The reactivity of the aromatic acid is higher than that of the aliphatic one. The catalyzing effect of the acid induces a secondary reaction. The aliphatic and aromatic primary and secondary amines react with the epoxy groups at a high rate. The aliphatic primary amine surpasses the aromatic in reactivity. The aliphatic secondary amine reacts faster than the aromatic primary amine. The aromatic monoepoxide is less reactive to the phenolic hydroxyl group than the aliphatic monoepoxide.

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