Epoxy Resins Based on Aromatic Glycidylamines. III. Kinetics of Intramolecular Cyclization of *N,N*-Bis(2-Hydroxy-3-Chloropropyl)aniline

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SYNOPSIS

The course of intramolecular cyclization of *N,N*-bis(2-hydroxy-3-chloropropyl)aniline (DCHA) was followed by HPLC. The rate constants (at 70, 85, 100, and 115°C) and the Arrhenius parameters for individual reaction steps were determined. The resulting product was isolated by semipreparative HPLC and its structure was confirmed by NMR spectroscopy. Attention was also paid to the different reactivity of DCHA diastereoisomers.

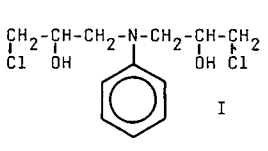
INTRODUCTION

The intramolecular attack of 2-hydroxy-3-chloropropyl group onto the ortho position of a benzene ring is an important side reaction during the synthesis of both *N,N*-diglycidylaniline (DGA)[1] and *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM).[2] This reaction has been previously mentioned in Ref 3. Intramolecular cyclization of DCHA proceeds in two steps according to the following scheme:

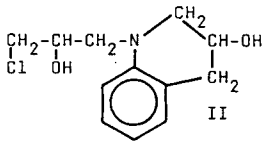
$$A \xrightarrow{k_1} B + HCl$$

$$B \xrightarrow{k_2} C + HCl$$

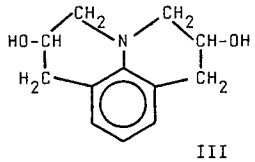
where A is DCHA (I), B is compound II, and C is compound III. The released hydrochloric acid then gives the corresponding hydrochlorides:



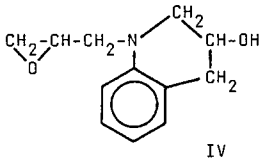
I



II



III



IV

Dehydrochlorination of compound II yields compound IV which represents one of several main impurities in technical DGA.[1] Similar 1,2,3,4-tetrahydro-3-hydroxyquinoline derivative has been identified in TGDDM-based epoxy resins.[2,4]

The aim of this work is the determination of rate constants and Arrhenius parameters of individual reaction steps.

EXPERIMENTAL

The instrumental equipment for HPLC and NMR and the synthesis of DCHA were described in our previous work.[1] Reversed-phase HPLC with gradient elution was carried out using Separon SGX C 18 columns (250 × 4 mm for analytical and 250 × 8 mm for semipreparative HPLC). A methanol–water gradient (35% methanol from 0 to 10 min; 68% methanol at 32 min; 100% methanol from 36 to 41 min) was used for the analyses of samples. Samples were prepared as 1.1% solutions in methanol.

The first derivatives of the experimental time–

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concentration dependences were approximated by the first derivatives of the corresponding Lagrange interpolation polynomials. The system of differential equations (1)–(3) was solved by the Euler method.

The cyclization reaction was carried out in bulk. The purity of the starting DCHA was 98.5% according to HPLC.

RESULTS AND DISCUSSION

Typical HPLC curve of reaction mixture is shown in Figure 1. The mixture of compounds I and II was isolated by semipreparative HPLC and analyzed by NMR. ^{13}C-NMR spectroscopy has confirmed that peaks 1 and 2 belong to diastereoisomers of compound III. The presence of a secondary hydroxyl group on a six-membered saturation ring is indicated by the signal at 63.6 ppm. The signal of a carbon atom with a chemical shift of 119.2 ppm indicates the orthosubstitution of the benzene ring. Peaks 3 and 4 belong to diastereoisomers of compound II.

Some oligomeric compounds were formed (mainly at 100 and 115°C) after long thermal treatment (Fig. 2). The structure of these oligomers has not yet been determined, but this reaction can be an important source of oligomeric compounds in DGA- and TGDDM-based epoxies. Experimental data where the content of these compounds exceeded 5% were not used for the calculation of rate constants.

The detector response was calibrated by pure DCHA and compounds II and III isolated by semipreparative HPLC. It was found that the response

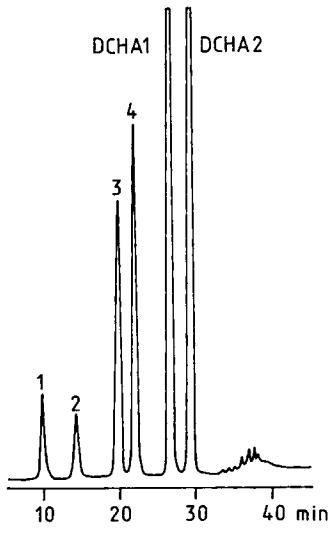

Figure 1 HPLC chromatogram of DCHA after 8 h at 100°C.

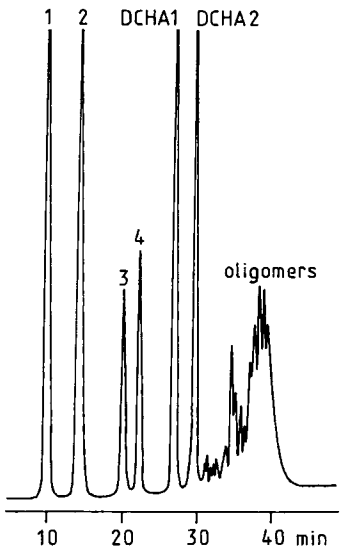

Figure 2 HPLC chromatogram of DCHA after 15 h at 115°C.

factors (expressed in area units per milligram) of compounds DCHA : II : III are in the ratio 1 : 1.19 : 2.56 (detection at 280 nm). These values were used as conversion factors for area % to wt % conversion. The actual concentrations of DCHA and compounds II and III were obtained by correcting for the amount of HCl formed.

A very important finding is that the hydrochloride of DCHA does not undergo cyclization. Within the investigated temperature range the cyclization is not reversible, as confirmed by thermal treatment of compound III in excess of HCl.

The reaction kinetics can be described by the following equations:

$$-\frac{dc_A}{dt} = k_1 \cdot m_A \tag{1}$$

$$\frac{dc_B}{dt} = k_1 \cdot m_A - k_2 \cdot m_B \tag{2}$$

$$\frac{dc_C}{dt} = k_2 \cdot m_B \tag{3}$$

where c_A, c_B, and c_C are the total concentrations of DCHA and of compounds II and III and m_A and m_B are the concentrations of free amines that undergo cyclization, and which govern the reaction rate.

The obtained data were evaluated under the following assumptions: (a) all released HCl forms hydrochlorides; (b) the basicity of all amines is the same and their hydrochlorides are formed in the ratio of their molar concentration. The concentration

Table I Rate Constants of Intramolecular Cyclization of DCHA

	t (°C)			
k (s^{-1})	70	85	100	115
k_1	6.27×10^{-7}	3.86×10^{-6}	1.31×10^{-5}	8.62×10^{-5}
k_2	5.40×10^{-7}	4.21×10^{-6}	1.31×10^{-5}	8.16×10^{-5}

of free amines can be then expressed by the equations

$$m_A = c_A - \frac{c_A}{c_A + c_B + c_C} c_{HCl} \quad (4)$$

$$m_B = c_B - \frac{c_B}{c_A + c_B + c_C} c_{HCl} \quad (5)$$

$$c_{HCl} = c_B + 2c_C$$

The total concentrations c of individual amines were determined by HPLC. The experimental data obtained for the concentration–time dependences were differentiated and the rate constants for the individual points were calculated from eqs. (1) and (3). The values were then averaged (relative standard deviations were 10–40%). The values of k_2 determined from eq. (2) were approximately the same as those calculated from eq. (3). The results are summarized in Table I. As a check, the system of differential equations (1), (2), and (3) was solved with the determined values of rate constants; the calculated time dependences of concentration are plotted in Figures 3 and 4 together with experimental values. The agreement of calculated and experimental dependences is very good and confirms that there is no gross error in the obtained values of rate constants and the reaction obeys the proposed kinetics scheme.

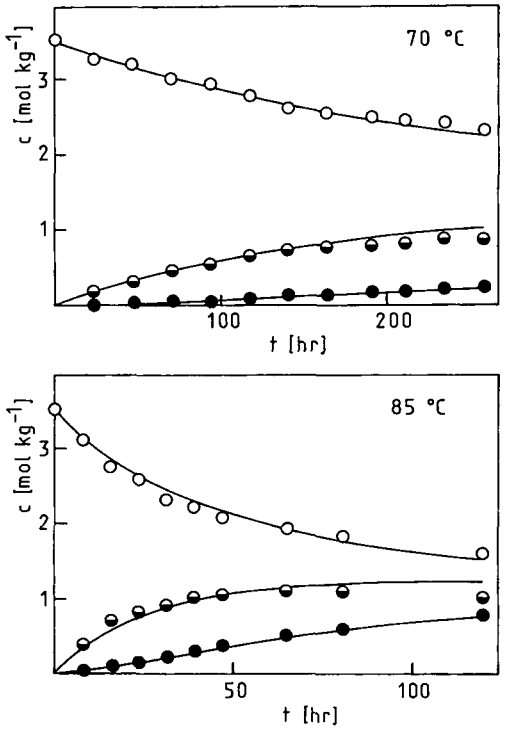

Figure 3 Kinetics of intramolecular cyclization of DCHA at 70 and 85°C: (—) calculated from eqs. (1)–(3). Experimental points: (○) DCHA; (◒) compounds II; (●) III.

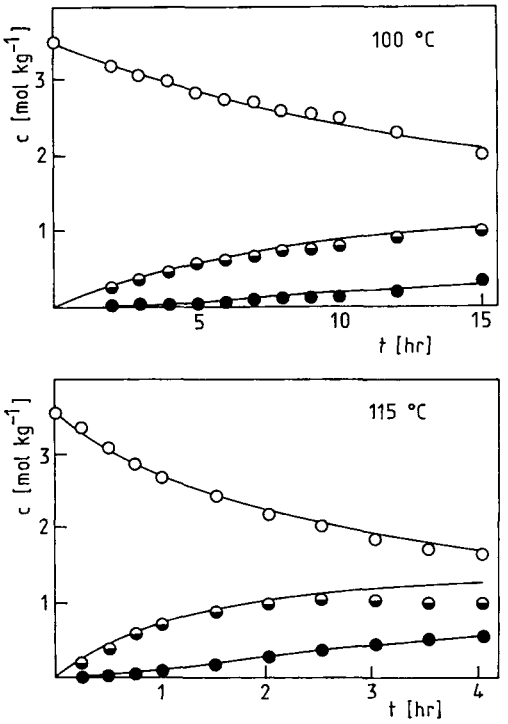

Figure 4 Kinetics of intramolecular cyclization of DCHA at 100 and 115°C: (—) calculated from eqs. (1)–(3). Experimental points: (○) DCHA; (◒) compounds II; (●) III.

The temperature dependences of rate constants conform to the Arrhenius equation (Fig. 5). The Arrhenius parameters determined from these dependences are $E_1 = 118$ kJ/mol, $A_1 = 5.5 \times 10^{11}$ s^{-1}, $E_2 = 120$ kJ/mol, and $A_2 = 9.1 \times 10^{11}$ s^{-1}.

The ratio of DCHA diastereoisomers depends on conversion (Fig. 6). It can be seen that diastereoisomer DCHA1 (RS configuration of asymmetric carbons[1]) reacts more rapidly than diastereoisomer DCHA2 [RR(SS) configuration of asymmetric carbons[1]]. Beyond the conversion of about 0.35, the ratio of DCHA diastereoisomers remains constant because the lower reactivity of DCHA2 is compensated by its higher concentration. The ratio of rate constants $k_{1,DCHA1}/k_{1,DCHA2} = 1.2$ was determined from the ratio of DCHA diastereoisomers beyond the conversion 0.35. The values of the rate constants k_1 and k_2, shown in Table I, are averages for the diastereoisomers of compounds I (DCHA) and II.

CONCLUSIONS

Intramolecular cyclization of 2-hydroxy-3-chloropropyl groups takes place during thermal treatment of DCHA leading to compounds II and III. The values of rate constants k_1 and k_2 are similar. The diastereoisomers of DCHA exhibit different reactivity,

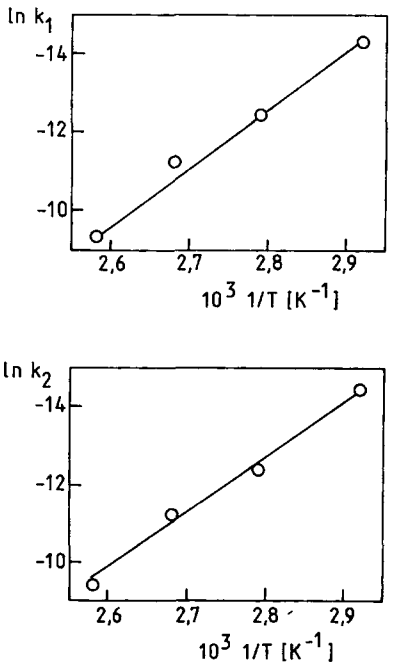

Figure 5 Temperature dependences of rate constants.

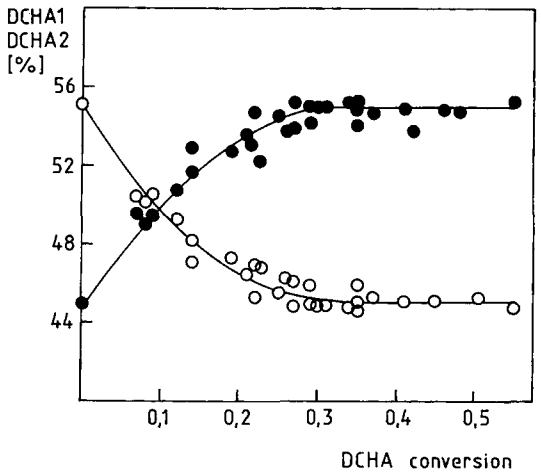

Figure 6 Mutual content of DCHA diastereoisomers: (○) DCHA1; (●) DCHA2.

the diastereoisomer with RS configuration being the more reactive.

REFERENCES

1. Š. Podzimek, I. Dobáš, Š. Švestka, J. Horálek, M. Tkaczyk, and M. Kubín, *J. Appl. Polym. Sci.*, Part I of this series, to appear.
2. Š. Podzimek, I. Dobáš, Š, Švestka, J. Horálek, M. Tkaczyk, and M. Kubín, *J. Appl. Polym. Sci.*, Part II of this series, to appear.
3. W. Davies and W. E. Savige, *J. Chem. Soc.*, 890 (1950).
4. A. J. Attias, J. Ancelle, B. Bloch, and F. Laupretre, *Polym. Bull.*, **18**, 217 (1987).

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APPENDIX

An ability of aromatic 2-hydroxy-3-chloropropyl ethers to undergo the intramolecular cyclization was proved by the HPLC following of the changes brought about during a thermal treatment of a model compound—2-hydroxy-3-chloropropyl phenyl ether. No peak of a cyclic product was found in chromatograms of 2-hydroxy-3-chloropropyl phenyl ether after 6 h at 100°C and even after additional 6 h at 130°C. Thus, the aromatic 2-hydroxy-3-chloropropyl ethers, unlike the aromatic 2-hydroxy-3-chloropropyl amines, do not intramolecular cyclize within the investigated temperature range.