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# Reactions of cyclic carbonates with amines: Model studies for curing process

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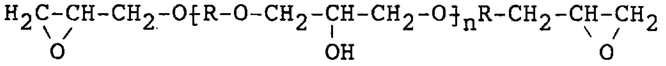
## Summary

The reaction of 4-phenoxymethyl-1.3-dioxolan-2-one with primary amines was studied as a model for $CO_2$-modified epoxy resins. Reaction products were characterized by HPLC, spectroscopic methods and titration. A time law was suggested.

## Introduction

The most important types of epoxy resin intermediates derive from the diglycidyl ether of bisphenol A and its advancement products:

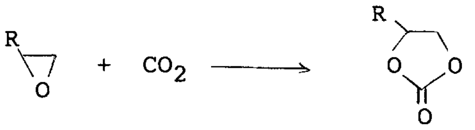


$$\underbrace{H_2C-CH}_{O}-CH_2-O\!\left[R-O-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-O\right]_n\!R-CH_2-\underbrace{CH-CH_2}_{O}$$

R = $-C_6H_4-C(CH_3)_2-C_6H_4-$

Commonly used curing agents are polyamines, dicarboxylic acids or their anhydrides. Furthermore it is possible to cross-link the resin by catalytically acting tertiary amines or complexes LEWIS-acids.

In recent years the modification of epoxy resins by the addition of carbon dioxide to the functional oxirane group was investigated. This reaction gives rise to cyclic carbonates or 1.3-dioxolan-2-ones (Eq. (1)).



(1)

Curing epoxy resins containing cyclic carbonate groups with polyamines ROKICKI et al. /1/ gave interesting effects:

- gel time decreases during raising moiety of carbonate
- reaction rate of the carbonate has a lower energy of activation than the corresponding oxirane
- the reaction of these modified resins is less exothermic than the reaction of commonly used epoxy resins.

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The application of such fully or partially modified epoxies for the build-up of networks requires the study of the reaction mechanism in more detail.

Due to the cross-linking of polyfunctional systems it is difficult to characterize the products formed. Therefore, it is necessary and common practice to carry out investigations using monofunctional models. We selected 4-phenoxymethyl-1.3-dioxolan-2-one (PMD) as a model. The reactions of PMD with several amines were investigated in the melt and in solution. The products were analysed by high performance liquid chromatography (HPLC) and spectroscopic methods.

## Experimental

Amines were dried with KOH pellets, N,N-dimethyl benzyl amine (DMBA) was purified by the reaction with phenyl isocyanate. All amines were distilled (aniline: b.p. 82 - 83 °C / 2.6 kPa; n-butyl amine: b.p. 75 - 76 °C; benzyl amine: b.p. 66 - 67 °C / 2 kPa; DMBA: 91 - 98 °C / 2,7 kPa). 4-Anisidine was provided from Laborchemie Apolda in "for analysis" quality.

4-Phenoxymethyl-1.3-dioxolan-2-one was prepared according to /15/ from phenyl glycidyl ether and carbon dioxide and purified by recristallization from ethanol; m.p. 97 °C.

Benzyl carbamic acid (2-hydroxy-3-phenoxyprop-1-yl)ester: A solution of 15 g PMD and 9 g benzyl amine in 50 ml propane-2-ol was refluxed for 15 hours. Solvent and excess of amine were separated by distillation in vacuum. The product was purified twice by recrystallization from carbon tetrachloride (m.p.: 55 °C; yield: 68 %; N (calc.): 4.65 %, N (found): 4.85 %).

Phenyl carbamic acid (2-hydroxy-3-phenoxyprop-1-yl)ester: A solution of 2 g phenoxypropan-2.3-diol and 1,4 g phenyl isocyanate in 25 ml acetonitrile was refluxed for 20 h. After evaporation the product was dissolved in carbon tetrachloride to separate diphenyl urea. The evaporated product was solved in propan-2-ol and the bisurethane precipitated by water. From the residual solution phenyl carbamic acid (2-hydroxy-3-phenoxyprop-1-yl)ester slowly crystallizes (m.p. 70 °C; yield: 39 %; N (calc.) 4.88 %, N (found) 4.93 %).

N.N'-Diphenyl urea was synthesized according to /2/ from aniline and phenyl isocyanate (m.p. 246.5 °C; yield: 98 %).

Kinetic measurements were carried out in a thermostated three necked flask equipped with a thermometer, magnetic stirrer and reflux condenser.

HPLC samples were run with apparatures from KNAUER (Wiss. Gerätebau KG, F.R.G.); column 250 x 4 mm LiChrosorb RP-18, 7.8 µm; eluent: acetonitrile-water 30 : 70 to 100 : 0 linear; flow: 1.8 ml/min; detection: UV 263 nm; samples: 5 % solution in acetonitrile.

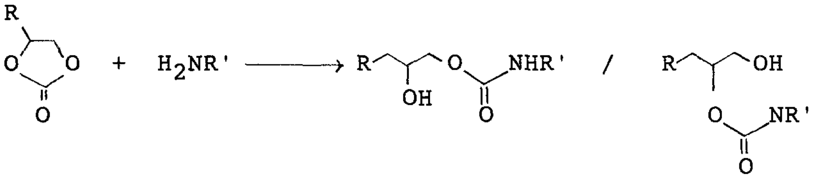
IR spectra were measured with a NICOLET FTIR spectrometer 205. Samples were prepared as solution in chloroform.

$^{13}$C-NMR spectra were performed on a VARIAN 300 XL spectrometer at 75,4 MHz using acetone as a solvent and tetramethyl silane (TMS) as internal standard.

The conversion was followed by evaluation of the relations of infrared absorption of the carbonyl groups at 1805 (carbonate) and 1720 cm$^{-1}$ (urethane). Furthermore the content of amine was followed by titration with $HClO_4$. Partially the relation between carbonate and urethane was observed by HPLC.

## Results and Discussion

The reaction of 1.3-dioxolan-2-ones with primary aliphatic amines gives rise to ß-hydroxy urethanes (/3/, /4/) with two isomeric structures in the position of the hydroxyl group (1 and 2).



(2)

1 2

Studies about the distribution of isomers are rarely published; usually isomer 1 is stated. BAIZER et al. /5/ investigated the reaction of propylene carbonate with monoethyl amine. The product was found to consist of 70 % isomer 1 and 30 % of isomer 2. COUVRET et al. /8/ found a dependence of ring-opening upon the substituent on the dioxolanone ring. We reacted n-butyl amine and benzyl amine with 4-phenoxymethyl-1.3-dioxolan-2-one (PMD). The chromatogram (Fig. 1) shows that ß-hydroxy alkyl urethane is the only product. The existence of isomers could not be observed by this method.

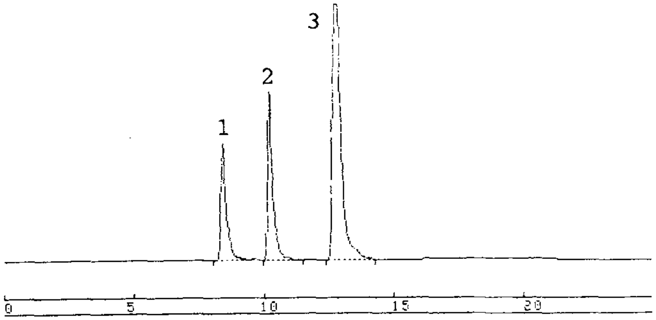


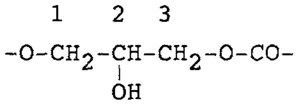
Fig. 1. Chromatogram PMD : $BzNH_2$ = 1 : 1
(100 min, 80 °C in toluene)
1 - PMD, 2 - ß-hydroxy urethane, 3 - toluene

Tab. 1: Shift and relalive intensities

| isomer | C-atom | shift | rel. intensiv |
|---|---|---|---|
| 1 | 1 | 69.2 | 1 |
| | 2 | 70.3 | 0.97 |
| | 3 | 66.7 | 0.97 |
| 2 | 1 | 67.4 | 0.285 |
| | 2 | 74.6 | 0.285 |
| | 3 | 61.9 | 0.30 |

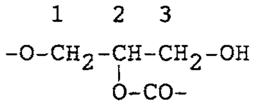
Using $^{13}$C-NMR spectroscopy could be shown that about 75 % isomer 1 is formed in this reaction (Fig. 2, Tab. 1). This isomer is isolated during recrystallisation from carbon tetrachloride.

The same distribution of isomers was found in the reaction of PMD with n-butyl amine and iso-pentyl amine.



$-O-CH_2-\underset{OH}{CH}-CH_2-O-CO-$

1



$-O-CH_2-\underset{O-CO-}{CH}-CH_2-OH$

2

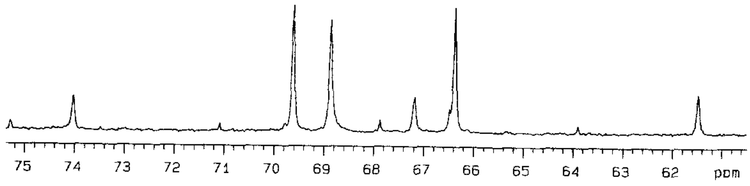


Fig. 2. $^{13}$C-NMR spectrum of the mixed isomeric β-hydroxyurethanes (range)

Kinetics

Investigations of the velocity of the reaction between cyclic carbonates and amines from NEMIROVSKY and SKOROKHODOV /9/, STROGANOV et al. /6/, MICHEEV et al. /7/ and TABUSHI and ODA /10/ show that it depends from solvent and initial concentrations of the amine. As described in the reaction of propylene carbonate with butyl amine in dimethyl formamide (/9/) we found, that the course depends from initial concentrations in the reaction of PMD with aliphatic amines in toluene (Fig. 3).

This may be described by a time law (3) containing an uncatalysed and an autocatalysed reaction. Such a time law is known for the reaction of epoxies with amines (/11/ - /14/).

$$-d[c]/dt = k_1[c][a]^p + k_2[c][a]^q[OH] \qquad (3)$$

[c] = concentration of cyclic carbonate
[a] = concentration of amine
[OH] = concentration of the product + initial conc. of OH

The exponents are ascertained to be p = 2.5 and q = 2 in our system.

$k_2$ is much larger than $k_2$ (Tab. 2).

Tab. 2: Kinetic constants at 65 °C

| | $k_1$ ($l^{2.5}/mol^{2.5}min$) | $k_2$ ($l^3/mol^3min$) |
|---|---|---|
| n-BuNH$_2$ | 0,0065 | 0,11 |
| BzNH$_2$ | 0,0006 | 0,035 |

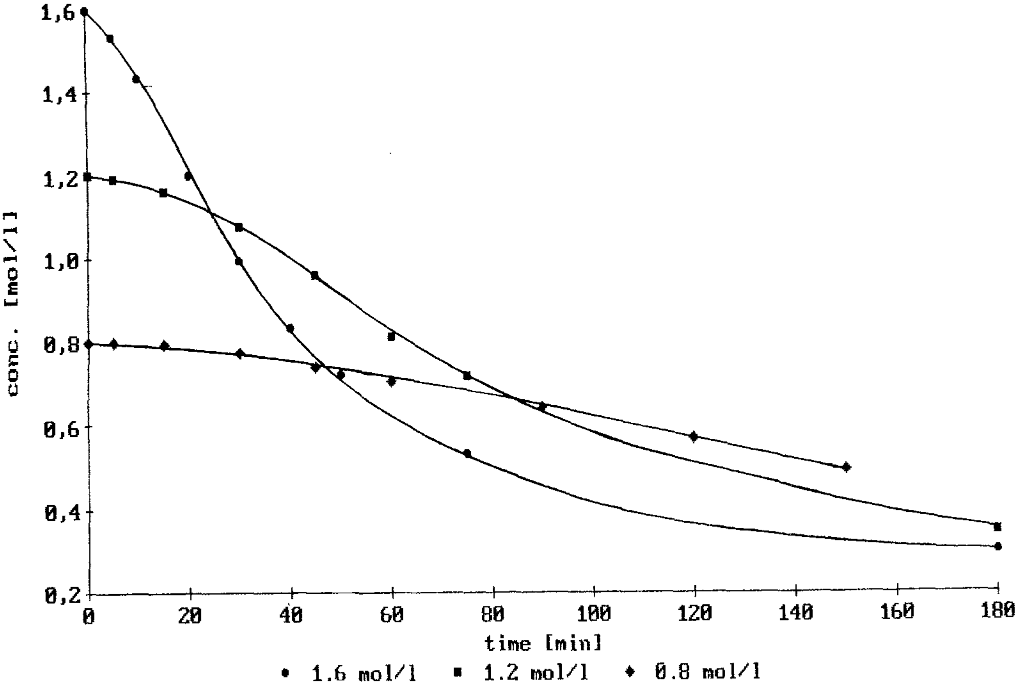


Fig. 3. Course of the reaction of
PMD : benzyl amine = 1 : 1
80 °C in toluene at several initial concentrations

A reaction of aromatic amines with cyclic carbonates is not described yet in literature. It does not take place in our results up to 100 °C.

Adding a tertiary amine (dimethyl benzyl amine) to a mixture of PMD and aniline and raising the temperature to about 120 °C a lot of products is to be hold after a short time. Fig. 4 shows the chromatogram. Main product is N,N'-diphenyl urea (peak 4). Furthermore, the expected ß-hydroxy urethane and phenoxy propan-2.3-diol could be detected. Other products could not be identified yet.

At temperatures beyond 120 °C the reaction of PMD and aromatic amines takes place also without a catalyst . This reaction may be accelerated by substituents causing +M-effect to the amine (4-anisidine, 4-chloroaniline). In absence of tertiary amines less urea in comparison to urethane is formed (Fig. 5).

With 4-anisidine a double peak in the chromatogram was observed. Whether that means separation of both isomers could not be proved.

At temperatures > 100 °C the results found apply to aliphatic amines too. Furthermore it could be shown that urea is formed from ß-hydroxy urethanes and amines using these conditions. It is possible to formulate a simplified mechanism of the reaction between 4-phenoxymethyl-1.3-dioxolan-2-one and primary aliphatic and aromatic amines (Eq. 4 and 5).

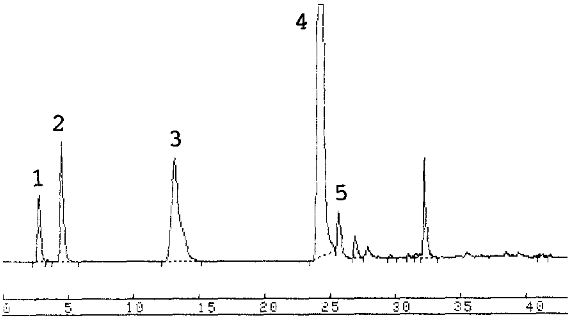


Fig. 4. Chromatogram of the system PMD/aniline/DMBA = 1 : 1 : 0,05
1 - phenoxy propan-2.3-diol, 2 - aniline, 3 - PMD,
4 - N.N'-diphenyl urea, 5 - urethane 3a

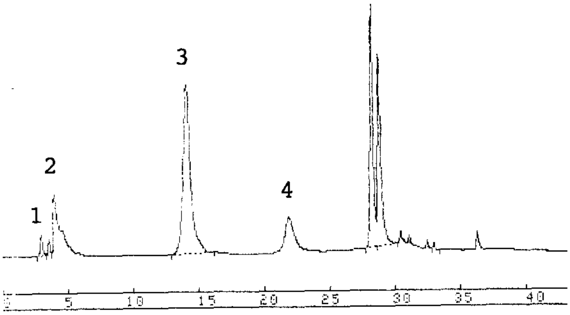
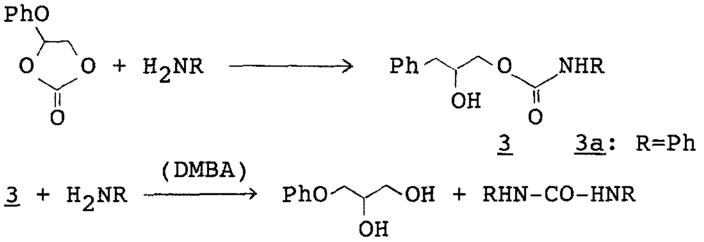


Fig. 5. Chromatogram of the system PMD/4-anisidine = 1 : 1
1 - phenoxy propan-2.3-diol, 2 - 4-anisidine, 3 - PMD,
4 - N.N'-bis (4-methoxyphenyl)urea,



(4)

(5)

In a first step cyclic carbonate reacts with amine to form ß-hydroxy urethane (3); in a second step the urethane is able to react at temperatures > 100 °C with another molecule of the amine to form substituted urea. Especially the second step may be accelerated by tertiary amines.

Further reactions of cyclic carbonates with amines, especially with aminoalcohols and in polyfunctional systems and the influence of cyclic carbonates to epoxy-amine reactions are under investigation. The results will be described elsewhere.

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