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# New aspects in acceleration of glycidyl ether oligomerization by imidazole compounds

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Summary

Using simple model compounds the oligomerization of glycidyl ethers accelerated by imidazole and imidazole derivatives was investigated. The formation of oligomers depending on 1,3-diphenoxy-2-hydroxypropane as their starting compound was predominant.

In the case of imidazole 1,2-dihydroxy-3-phenoxypropane and the resulting oligomers are further formed. It seems to be obvious that this reaction also occurs in the absence of water.

An over-all reaction mechanism including both the main products of the glycidyl ether oligomerization formed and the different imidazole compounds investigated is proposed.

## Introduction

Imidazole compounds play an important role in the acceleration of epoxy resin curing reactions. Imidazole-cured resins show good adhesiveness, improved heat and water resistance as well as good electrical and mechanical properties.

In the patent literature imidazoles are one of the most frequently mentioned accelerators for the curing of epoxy resins. On the other hand, less information exists about the actual mechanism of imidazoles as accelerators in curing systems.

Farkas and Strohm (1) investigated the model system consisting of phenyl glycidyl ether and 2-ethyl-4(5)-methylimidazole. They suggested that the true catalytic species is an addition product formed from equimolar quantities of these two reactants (1:1 adduct). A second mole of phenyl glycidyl ether then reacts with the N-atom in the 3rd position of the imidazole nucleus of the 1:1 adduct leading to an 1:2 adduct which is the starting compound for further addition steps. Dearlove (2) proved that imidazoles unsubstituted in the 2nd position deactivate by conversion into a dihydroimidazole compound.

Kinetical investigations by Barton and Shepherd (3) showed a first order reaction of the 1:1 adduct and 1:2 adduct formation.

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Kamon et.al. (4) discussed a relation between the basicity of an imidazole compound and its reactivity. Investigating the reaction of glycidyl ether with 2-methylimidazole Ricciardi et.al. (5) discussed the polymerization of the glycidyl ether and a chain termination by Hoffmann elimination. Other reactions of the 1:1 adduct such as β-elimination forming phenoxyacetone, elimination of water and dealkylation of imidazole via a substitution process are also covered (6). Analyzing a mixture of p-cresyl glycidyl ether and 1-methylimidazole reaction Berger and Lohse (7), (8) found 1,3-diphenoxy-2-hydroxypropane. Jones, Poncipe, Barton and Wright (9) observed an accelerating effect by adding various alcohols such as 1:1 adduct, 1,3-diphenoxy-2-hydroxypropane and phenol.

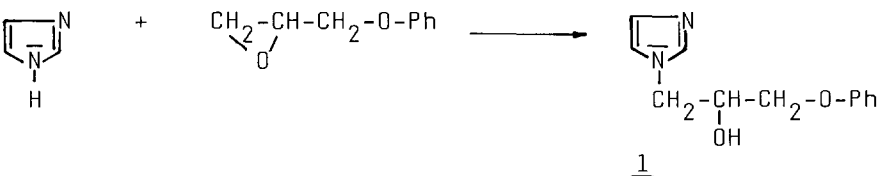
It can be seen that some hypotheses concerning the curing of epoxy resins by imidazoles are not in every case fully described, but the high effectivity of imidazoles in curing processes is not yet fully understandable.

## Experimental

The chemicals, the identification of reaction products, and the experimental conditions for oligomerization, high liquid chromatography (HPLC), coupled gas chromatography- mass spectroscopy (GC-MS), infrared spectroscopy (IR), gas chromatography (GC) and UV spectroscopy were described in detail in another publication (10). The absence of remaining water was determined by IR spectroscopy.

## Results and Discussion

The first reaction step of N-unsubstituted imidazole derivatives with glycidyl ether is the formation of the 1:1 adduct.




(1)

1

Some details about this reaction and further reactions of imidazole are described in (10). But there is no significant difference between products formed using imidazole or the 1:1 adduct if the conversion is the same.

Analysing a reaction mixture of imidazole and PGE (31% PGE conversion) it was found that the 1:1 adduct formation is the first step of the imidazole PGE reaction. The main products of PGE (71% PGE conversion) are shown in Fig.1. Phenol, 1,3-diphenoxy-2-hydroxypropane 1,2-dihydroxy-3-phenoxypropane and oligomers were identified using an excess of glycidyl ether. Using equimolar amounts of imidazole and glycidyl ether mainly the 1:1 adduct is formed.

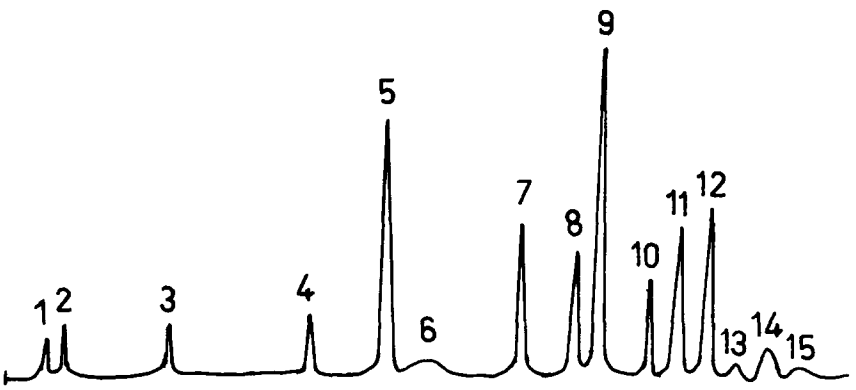



Fig.1: Reaction products of PGE with imidazole bulk oligomerization (concentration of imidazole = 1mole·l$^{-1}$, temperature = 70°C, conversion of PGE = 71%)
HPLC-conditions: $CH_3CN$ : $H_2O$ = 30 :70 to 100 : 0 in 24,5min sample concentration = 3 % in $CH_3CN$, sample volume = 6 µl reaction products : 1 ≙ 1,2-dihydroxy-3-phenoxypropane; 2 ≙ phenol; 3 ≙ PGE; 4,7,10,13 = oligomers originating from 1 and PGE; 5 ≙ 1,3-diphenoxy-2-hydroxypropane 6,8,11,14 ≙ unknown; 9,12,15 ≙ oligomers originating from 5 and PGE

The identification of the distilled products of the imidazole/MGE reaction (Table 1) led to a product distribution which was similer to the results of the imidazole/PGE system. Additionally, an oligomer containing a double bond was found, which could not be identified due to its low concentration in the reaction mixture.

In the case of 1-methylimidazole no adduct formation occurs. The distilled main products of MGE/1-methylimidazole/reaction (table 1) are the same as those using imidazole. By products are methoxy acetaldehyde and methoxy propionaldehyde (For more mechanistic details see (10)).

All the identified products of the glycidyl ether imidazole reaction show that the reaction mechanism is extremly complicated. The following scheme 1 demonstrates the main reactions of the imidazole glycidyl ether system taking into account the fact that 1-methylimidazole only possesses one reaction centre, whereas in the case of imidazole and the corresponding 1:1 adduct two reaction centres have to be considered.

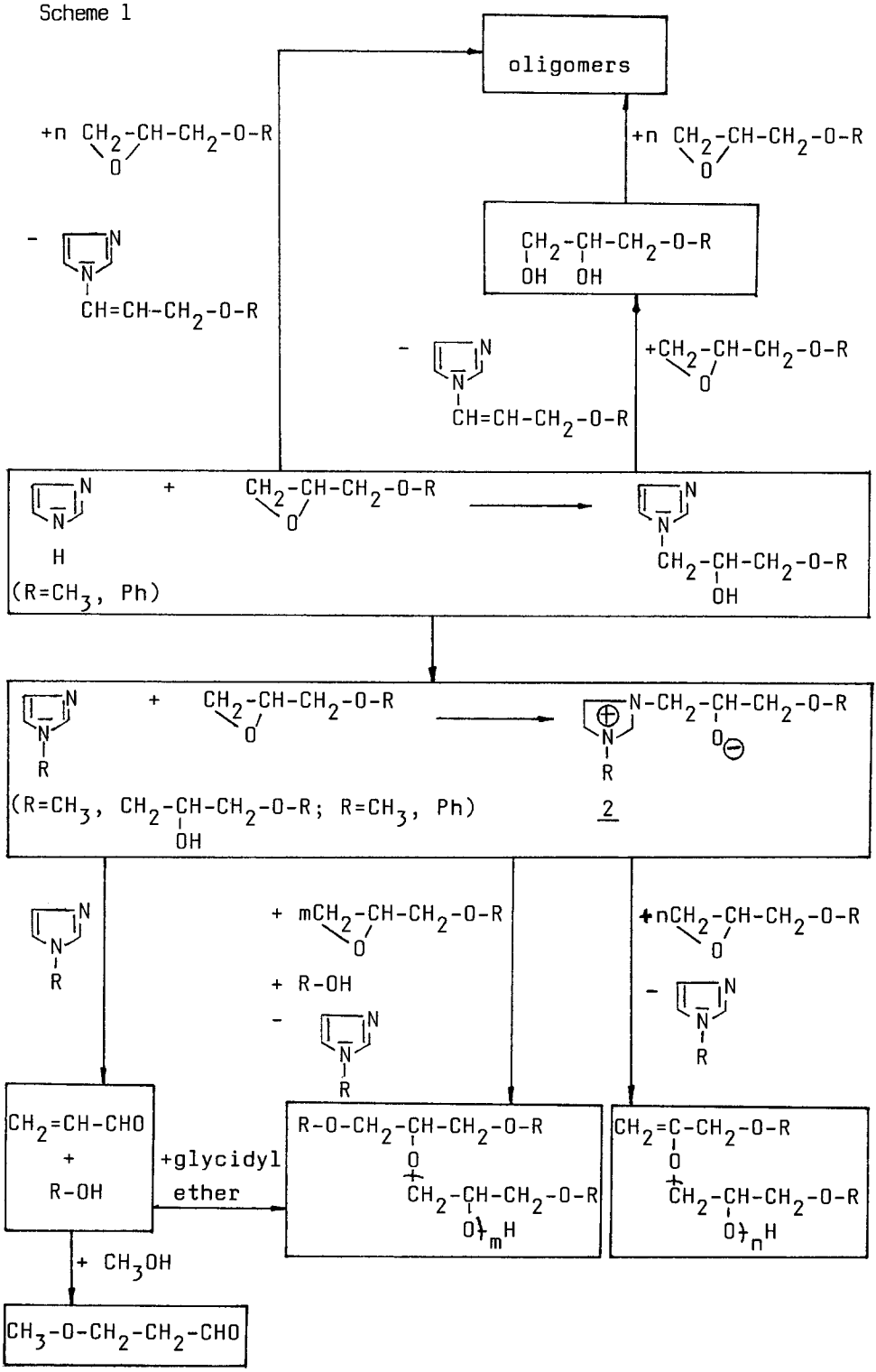
The dual ion 2 has four possibilities for stabilization. Three possibilities are shown in the scheme 1. The splitting reaction of the heterocyclic system is described in (10). The formation of acrolein and phenol or methanol is well known with other aminic accelerators (11). In our system acrolein was not found due to the high catalytic effectivity of imid-

Table 1: Distilled products of MGE identified by GC-MS and IR spectroscopy

2,5 mole MGE, 0,25 mole imidazole (T=70°C, t=7h) or 1-methylimidazole (T=30°C, t=20d)

| | MGE + imidazole 35% distillate | MGE + 1-methylimidazole 22% distillate |
|---|---|---|
| main products of distillate | $CH_3OH$<br>$CH_3-O-CH_2-CH(OH)-CH_2-O-CH_3$<br>$CH_2(OH)-CH(OH)-CH_2-O-CH_3$ | |
| | $CH_3-O-CH_2-CH(OH)-CH_2-O-CH_2-CH(OH)-CH_2-O-CH_3$ | ——— |
| | ——— | $CH_2=C(O-CH_2-CH(OH)-CH_2-O-CH_3)-CH_2-O-CH_3$ |
| byproducts of distillate | $CH_2=C(O-CH_2-CH(OH)-CH_2-O-CH_3)-CH_2-O-CH_3$ | ——— |
| | ——— | $CH_3-O-CH_2-CH_2-CHO$<br>$CH_3-O-CH_2-CHO$ |

Scheme 1


oligomers
+n CH2-CH-CH2-O-R
O
- N
N
CH=CH-CH2-O-R
CH2-CH-CH2-O-R
OH OH
+CH2-CH-CH2-O-R
O
H
(R=CH3, Ph)
CH2-CH-CH2-O-R
OH
N-CH2-CH-CH2-O-R
O⊖
R
2
(R=CH3, CH2-CH-CH2-O-R; R=CH3, Ph)
OH
+ mCH2-CH-CH2-O-R
+ R-OH
+nCH2-CH-CH2-O-R
CH2=CH-CHO
+
R-OH
+glycidyl
ether
R-O-CH2-CH-CH2-O-R
O
CH2-CH-CH2-O-R
O}mH
CH2=C-CH2-O-R
O
CH2-CH-CH2-O-R
O}nH
+ CH3OH
CH3-O-CH2-CH2-CHO

azole compounds as catalysts for acrolein polymerization (12).

Only 3-methoxy propionaldehyde, resulting from the reaction of acrolein with methanol , was identified. It seems to be clear that many of these products influence the reaction rate of the imidazole glycidyl ether system.

## Conclusions

1:1 Adduct formation is the first step in the imidazole glycidyl ether reaction. This product is the basis for further reactions.

The main oligomeric products resulting from the reaction of imidazole or 1-methylimidazole with glycidyl ether are based on 1,3-diphenoxy-2-hydroxypropane. Oligomers depending on 1,2-dihydroxy-3-phenoxypropane are only important in the case of imidazole. These products are formed in the absence of water. This fact is due to the active hydrogen atom of imidazole.

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