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Abstract

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CHEMISTRY

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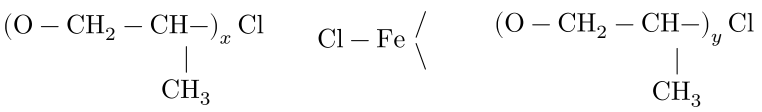
ON THE STRUCTURE OF THE $FeCl_3$ × PROPYLENE OXIDE CATALYST AND THE MECHANISM OF STEREOSPECIFIC POLYMERIZATION OF CERTAIN EPOXY COMPOUNDS

Iron-containing catalysts for the polymerization of organic oxides have been known only comparatively recently (^{1,2}). First, in the work of Price (^{3}), and subsequently in a number of studies (^{4,5}), it was noted that many organic oxides (ethylene, propylene, butylene, and others), when polymerized on a catalyst obtained from anhydrous ferric chloride and propylene or butylene oxide, form polymers of regular structure in high yield. It is noted that the polymerization reaction has two stages. The first—rapid—takes place at low temperature (0–10°) and ends with the addition of a small number of propylene oxide molecules to 1 mole of $FeCl_3$. The polymerization proper proceeds at a substantially different rate and at a higher temperature (80°). It is assumed (^{3}) that at the first stage a "complex compound" of ferric chloride with propylene oxide is formed, which in fact is the polymerization catalyst. In accordance with this, a coordination-complex mechanism of polymerization is proposed. The stereospecificity of the polymerization, as usual, is explained by the heterogeneity of the system (^{3}).

A detailed study of the product obtained in the first stage (^{4}) led to the conclusion that, in the ferric chloride molecule, only two chlorine atoms are replaced by propylene oxide, and that 5 moles of oxide interact with each mole of ferric chloride. The following catalyst structure is proposed:



$$(\mathrm{O-CH_2-}\underset{\displaystyle \mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{-})_x\,\mathrm{Cl} \qquad \mathrm{Cl-Fe}\begin{array}{l}/\\ \backslash\end{array} \qquad (\mathrm{O-CH_2-}\underset{\displaystyle \mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{-})_y\,\mathrm{Cl}$$

where $x+y=5$.

With regard to the mechanism of polymerization of propylene oxide on this catalyst, certain assumptions are put forward which, in the main, coincide with the hypothesis of coordination-complex polymerization advanced by Price.

When this same catalytic system was used for the polymerization of epichlorohydrin and divinyl monoxide, we showed that the monomer-catalyst system is completely homogeneous (^{6}). Nevertheless, polymerization proceeds with the formation of a polymer of regular structure, which is confirmed by data from X-ray and thermomechanical studies. In order to study the structure of the catalyst obtained by the interaction of anhydrous ferric chloride with propylene oxide, it was of interest: 1) to determine the nature of the bond (i.e., to show whether a compound of the complex type is formed or whether an alcoholate bond is formed); 2) to establish the formula of the compound formed; 3) to determine the order of opening of the oxygen-containing ring, if such opening takes place.

Experimental Part

Preparation of the catalyst. The catalyst was prepared according to the method (^{2}). To a suspension of 13.5 g (0.114 mole) of sublimed $FeCl_3$ in dry CCl_4, 27 g (0.465 mole) of propylene oxide in CCl_4 was added. The weight of the residue

after removal of the solvent and high vacuum treatment was 44 g (initially 45.5 g). Its elemental composition (in percent) was: Fe 15.06; C 37.33; H 6.56; Cl 21.26.

Isolation of the organic part. Forty grams of catalyst were dissolved in 25 ml of chemically pure acetone, 250 ml of water and 5 ml of saturated NaOH solution were added. At room temperature a thick precipitate of iron hydroxide formed. The suspension was diluted with water (to 500 ml), and the decomposition products were extracted with ether; the extract was washed with water, with 5% Na_2CO_3 solution, again with water, and dried over anhydrous Na_2SO_4. After removal of the ether, the residue was distilled on a rectification column of efficiency 20–30 theoretical plates (see Table 1).

Table 1

Fraction	P, mm Hg	Temp., °C	n_D^{20}	C	H	Cl	O (by difference)
I	1.5	45.5–46.5	1.4425*	46.86	8.50	23.04	21.6
I	1.5	45.5–46.5	1.4425*	46.99	8.38	23.21	21.42
II	1.5	46.5–47.5	1.4431	47.04	8.60	22.43	20.93

Fraction	P, mm Hg	Temp., °C	n_D^{20}	C	H	Cl	O (by difference)
II	1.5	46.5-47.5	1.4431	47.12	8.78	22.59	21.51
III	1.5	47.5-49.0	1.4431	46.98	8.61	22.71	21.7
III	1.5	47.5-49.0	1.4431	46.98	8.88	22.75	21.34
Residue	Non-distilling		1.4480	53.76	9.28	14.48	22.58
Residue	Non-distilling		1.4480	53.75	9.37	14.64	22.24

* Before distillation —1.4430.

Investigation of the catalyst. The molecular weight of the catalyst was determined by Rast' s method. A camphor sample was 0.05 g, the catalyst sample 0.0105 g. The depression of the melting point of camphor was 19°. The labile hydrogen of the isolated organic part of the catalyst was determined quantitatively by the method of Terevitinov with ethylmagnesium iodide. 0.01 mole of the organic part of the catalyst (calculated as the primary alcohol corresponding to the propylene oxide dimer) liberated ~0.01 mole of ethane. Chlorine was determined qualitatively by the Beilstein test and by means of IR spectra. Absorption spectra in the infrared region were recorded on an IKS-14 spectrophotometer with a NaCl prism in the frequency range 1800-640 cm^{-1}.

Discussion of Results

To elucidate the nature of the bond in the catalyst, the latter was decomposed under mild conditions with water and its organic part was studied. The liberation of alcohol in this process indicates the presence in the catalyst of a bond of the alcoholate type. Spectral studies of the catalyst lead to the same conclusion. If $FeCl_3$ were bound to propylene oxide by a coordination bond, an intense absorption band of the epoxy group in the range 1250-1260 cm^{-1} (7) should have been present in the catalyst spectrum. In the spectrum of the catalyst shown in Fig. 1, the absorption band of the epoxy group is absent, whereas the intense absorption band in the range 1150-1060 cm^{-1}, in contour and frequency values, corresponds to the C—O bond in aliphatic ethers. Evidently, during formation of the catalyst, opening of the oxygen-containing ring occurs with formation of a simple ether bond.

Data on the synthesis of the catalyst show that 4 moles of propylene oxide combine with 1 mole of anhydrous $FeCl_3$. Determination of the molecular weight of the catalyst (394 —calculated for $FeCl_3 \times 4$ moles of propylene oxide; 397

Fig. 1. Infrared absorption spectra. A—$FeCl_3 \times$ propylene oxide catalyst (film); B—organic part of the $FeCl_3 \times$ propylene oxide catalyst. Fraction I ($l = 0.009$ cm); V—organic part of the $FeCl_3 \times$ propylene oxide catalyst. Residue ($l = 0.009$ cm); G—organic part of the $FeCl_3 \times$ epichlorohydrin catalyst ($l = 0.009$ cm).

Figure 1: Fig. 1. Infrared absorption spectra. A—$FeCl_3 \times$ propylene oxide catalyst (film); B—organic part of the $FeCl_3 \times$ propylene oxide catalyst. Fraction I ($l = 0.009$ cm); V—organic part of the $FeCl_3 \times$ propylene oxide catalyst. Residue ($l = 0.009$ cm); G—organic part of the $FeCl_3 \times$ epichlorohydrin catalyst ($l = 0.009$ cm).

—found) agrees well with the data on the elemental composition of the organic part of the catalyst.

For a derivative of the propylene oxide dimer, the calculated percentages are C 47.3; H 8.56;

Cl 23.2; O 20.94; found: see Table 1, fractions I-III.

Analysis for the Cl ion shows that only two chlorine atoms in the $FeCl_3$ molecule are replaced by propylene oxide. The presence of chlorine in the organic part of the catalyst is shown qualitatively by the Beilstein test and by the presence of absorption bands at 744, 700, and 650 cm^{-1} in the IR spectrum. The empirical formula of the catalyst may be represented as

$$ClFe(C_6H_{12}O_2Cl)_2.$$

To elucidate the structure of the organic part of the catalyst, spectral studies were carried out. It was essential to determine the order of opening of the epoxy ring with subsequent formation of an ether bond.

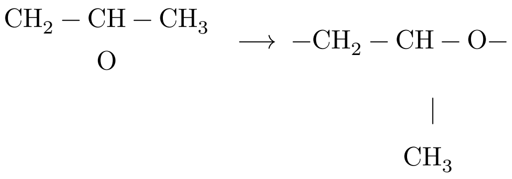
Fig. 1. Infrared absorption spectra.
A—$FeCl_3 \times$ propylene oxide catalyst (film);
B—organic part of the $FeCl_3 \times$ propylene oxide catalyst. Fraction I ($l = 0.009$ cm);
V—organic part of the $FeCl_3 \times$ propylene oxide catalyst. Residue ($l = 0.009$ cm);
G—organic part of the $FeCl_3 \times$ epichlorohydrin catalyst ($l = 0.009$ cm).

Theoretically, the formation of four structures of the organic part of the catalyst is possible:

I. $OH{-}CH(CH_3){-}CH_2{-}O{-}CH(CH_3){-}CH_2{-}Cl$ (opening of the oxirane ring occurred only at primary c
II. $OH{-}CH_2{-}CH(CH_3){-}O{-}CH_2{-}CH(CH_3){-}Cl$ (opening of the oxirane ring occurred only at secondary
III. $OH{-}CH(CH_3){-}CH_2{-}O{-}CH_2{-}CH(CH_3){-}Cl$ (the first molecule opens the oxirane ring at the primar
IV. $OH{-}CH_2{-}CH(CH_3){-}O{-}CH(CH_3){-}CH_2{-}Cl$ (the first molecule opens the oxirane ring at the seconda

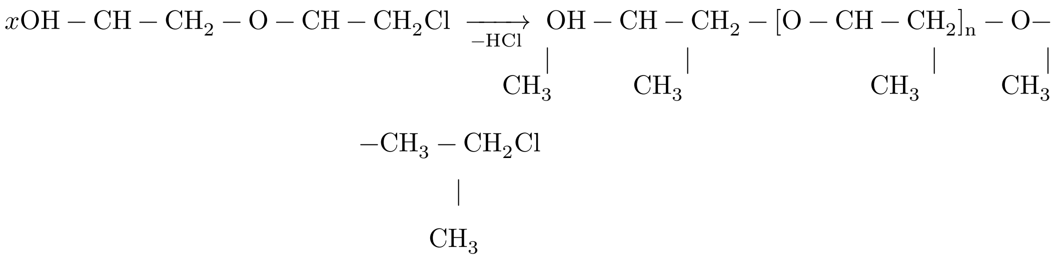
The character of the absorption of the C–O bond in the spectrum of the organic part of the catalyst makes it possible to exclude the fourth structure, since branching at the carbon atom forming the ether bond would lead to a considerable change in the contour and frequency of the absorption band of the C–O bond. Thus, for example, in the absorption spectrum of diisopropyl ether there is a distinct triplet in the region 1100-1070 cm^{-1} (7), which is not observed in our case (see Fig. 1B). The second and third structural variants may be excluded on the basis of consideration of the absorption bands of the C –Cl bond. In the spectrum no absorption band of secondary chlorine is found; on the contrary, the observed absorption bands at 743, 701, and 664 cm^{-1} are charac-

specific for the group CH_2—Cl (8). Consequently, when ferric chloride interacts with propylene oxide, opening of the epoxy ring occurs at the primary carbon atom with retention of the configuration at the secondary one



$$\underset{O}{CH_2 - CH - CH_3} \longrightarrow -CH_2 - \underset{\underset{CH_3}{|}}{CH} - O-$$

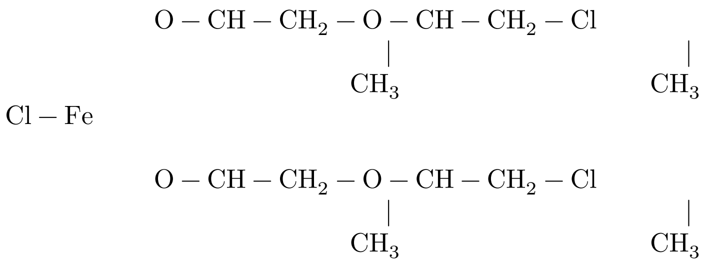
The elemental composition of the three distillation fractions and of the high-boiling residue showed the identity of these fractions and a certain difference between them and the high-boiling residue. Thus, the chlorine content in the residue decreased to 14% as compared with 23% for the fractions. The IR spectra of the three fractions are identical; see Fig. 1 B, while in the spectrum of the residue the same absorption bands are present, but the intensity of the bands corresponding to the chlorine bond (743, 701, and 664 cm^{-1}) decreases. At the same time, the absorption contour of the C–O bond (1150-1060 cm^{-1}) changes somewhat, with a small increase in intensity on going to the residue. The intensity of the absorption bands corresponding to the symmetric and asymmetric deformation vibrations of the CH_3 group (1458-1385 cm^{-1}) practically did not change. This can be explained by the fact that the distillation conditions (evacuation and heating) promote the course of a polycondensation reaction with formation of oligomeric products according to the equation:



$$x\mathrm{OH-CH-CH_2-O-CH-CH_2Cl} \xrightarrow[-\mathrm{HCl}]{} \mathrm{OH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-[O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2]_n-O-}$$

$$\mathrm{-\underset{\displaystyle CH_3}{\underset{|}{CH_3}}-CH_2Cl}$$

The results of the investigation carried out make it possible to propose the following structure for the catalyst:



$$\mathrm{Cl-Fe}\begin{array}{l}\mathrm{O-CH-CH_2-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Cl} \\ \\ \mathrm{O-CH-CH_2-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Cl}\end{array}$$

It is interesting to note that the order of formation of the ether bond in the organic part of the catalyst obtained from anhydrous $FeCl_3$ and epichlorohydrin has the same character (absorption bands of the C–O bond in the region 1150-1060 cm^{-1} and absence of secondary chlorine (see Fig. 1 G)).

The investigations carried out by us and the homogeneous character of the system proved earlier (6) make it possible to suppose that the reason for the formation of polymers of regular structure from α-olefin oxides is the mode of opening of the oxygen-containing ring at the primary carbon atom with retention of the configuration at the asymmetric carbon atom during polymerization. Consequently, in the present case preliminary orientation of the monomer is not obligatory.

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