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In the oxidation of alkylaluminum compounds [1-5], the oxygen cleaves the A1-C bond with the formation of the corresponding peroxy derivative which, on reacting with the initial alkylmetal forms an ethoxy derivative which is the final oxidation product. In some papers [5, 6], mention is made of the isolation during the oxidation of organoaluminum compounds of small amounts of low-molecular-weight paraffinic and olefinic hydrocarbons, which shows the radical nature of the reaction of the organoaluminum peroxides with the alkylaluminums.

Only one paper on the oxidation of alkylaluminum dihalides is known, and in this it is stated that the reaction with  $O_2$  is accompanied by the formation of an organoaluminum peroxide with a yield of 9-10% (50-0°) [7]. The question of the oxidation of alkylaluminum dihalides RAlCl<sub>2</sub> is of great interest, since these compounds, and also the products of their reaction with  $O_2$ , may be components of catalytic systems for the polymerization of olefinic and dienic hydrocarbons [8, 9], the alkylation of benzene with ole-fins [10], and other processes.

In the present work we have studied the oxidation of ethylaluminum dichloride (EADC). The oxidation of EADC can be divided arbitrarily into two stages. The first stage takes place by the generally-accepted scheme of the oxidation of organoaluminum compounds [5] through a peroxy compound with the formation of the corresponding ethoxy compound:

 $\begin{array}{l} C_2H_5AlCl_2 + O_2 \rightarrow (C_2H_5AlCl_2 \cdot O_2) \rightarrow C_2H_5OOAlCl_2;\\ C_2H_5OOAlCl_2 + C_2H_5AlCl_2 \rightarrow 2C_2H_5OAlCl_2. \end{array}$ 

This process obeys the usual laws of the oxidation of organometallic compounds [10]. Thus, with a fall in the temperature and a reduction in the concentration of EADC the content of peroxide compounds formed as primary reaction products rises (Fig. 1a). The semilogarithmic anamorphosis of the curve (Fig. 1b) shows that the change in the concentration of peroxide compounds as a function of the temperature obeys the exponential law  $C = e^{kt}$ .

The main oxidation product – ethoxyaluminum dichloride (ethoxy-ADC) – was obtained with a yield of about 70% for the amount of EADC added (Table 1).

The formation of  $C_2$  and  $C_4$  hydrocarbons observed in the oxidation of EADC can be explained if it is assumed that this reaction takes place partially by a free-radical mechanism. The amount of gas liberated increases with a rise in the temperature (see Table 1).

The second stage, which is connected with the oligomerization of the ethoxy-ADC, takes place with the formation of an oily product which is insoluble in hydrocarbons and which has a ratio of the Cl and Al contents of 2:1. It has been established by chemical, elementary, and spectral methods of analysis that the oily product contains the Al-O-Al, C-O-Al, and  $C_2H_5O-Al-Cl$  groupings. The considerably greater width of the bands of the IR spectrum of this product as compared with the spectrum of ethoxy-ADC is caused by the presence of oligomeric molecules. The oily product is unstable to heating (40°, 0.5 mm Hg), decomposing with the evolution of  $C_2$  and  $C_4$  hydrocarbons and  $C_2H_5Cl$ , and with the formation of a product having the composition  $C_2H_5-(OAlCl)_4-OC_2H_5$ . The oligomerization of ethoxy-ADC probably takes place in

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Fig. 1. Dependence of the content of peroxide compounds in an oxidized solution of ethylaluminum dichloride on the temperature (a) and its semilogarithmic anamorphosis (b) at the following concentrations of  $C_2H_5AlCl_2$ : 1) 0.173; 2) 0.56; 3) 1.02 M.

a similar manner to that of diethoxyaluminum chloride:



Lowering the temperature of the oxidation of the EADC leads to an increase in the amount of oligomeric product: at 50°, the amount of oligomeric product is 17 mole % of the EADC charged, and at  $-70^{\circ}$  it is 25 mole % (see Table 1).

## EXPERIMENTAL METHOD

The gaseous products were analyzed by the GLC method using ETEGNMK as adsorbent (with argon as the carrier gas). The IR absorption spectra were taken on a UR-10 spectrophotometer in the 400-1300 cm<sup>-1</sup> region with KBr and NaCl prisms. The spectrum of the ethoxy-ADC was recorded in a 0.35 M solution in hexane in a cell with a KBr window; the thickness of the absorbing layer was 0.0119 cm. A liquid film was used to record the spectrum of the oily product. The ethylaluminum dichloride was obtained by a modified method [2]. The synthesis was performed in an atmosphere of Ar with constant stirring using the reaction of  $Al(C_2H_5)_3$  with  $AlCl_3$  in two stages at a temperature not higher than 40° for 25 h. Distillation at 50 mm Hg yielded a fraction with bp 114-116° corresponding to ethylaluminum dichloride – coarse transparent crystals with mp 32°. The Al content (trilonometrically) was 0.2611 g/ml and that of chlorine (Volhard) was 0.6975 g/ml, which corresponds to an Al: Cl ratio of 1:2. The content of exthoxy groups was determined by the hydrolytic decomposition of the alkoxide with subsequent determination of the amount of ethanol liberated spectrophotometrically.

The oxidation of the EADC was effected by air or molecular  $O_2$  dried to a dew point of  $-80^\circ$ , passed at a constant rate of 0.4-0.6 mole/mole of  $C_2H_5AlCl_2$  in heptane solution with a concentration of  $C_2H_5AlCl_2$  of 0.2-9 M in the temperature range from 50 to  $-80^\circ$ .

Amount, mole	т., °С			
		0	20	50
Oxygen absorbed Ethoxy~ADC C <sub>2</sub> fraction EADC converted into oligomeric product	0,53 0,71 0,034 0,25	0,50 0,58 0,044 0,246	0,50 0,65 0,055 0,212	0,43 0,64 0,098 0,163

TABLE 1. Conditions for the Oxidation of Ethylaluminum Dichloride and the Products Formed in the Oxidation (Calculated as g/mole of EADC)

In the oxidation of the EADC, gas was evolved and the reaction mixture separated into layers. The amounts of Al, Cl, alkoxy groups, and  $C_2H_5AlCl_2$  in the top layer – a solution of ethoxy-ADC in heptane – were determined. The ethoxy-ADC was isolated by the distillation of the heptane in vacuum (0.5 mm Hg, 20°). A viscous liquid was obtained which did not distil without decomposition in a vacuum of 0.5 mm on heating to 100°. Found:  $C_2H_5O$  31.46; Al 18.85; Cl 49.50%.  $C_2H_5OAlCl_2$ . Calculated:  $C_2H_5O$  31.46; Al 18.90; Cl 49.64%.

The structure of the ethoxy-ADC was confirmed by chemical methods [4, 5, 11-13], and also by IR and NMR spectroscopy. The NMR spectrum, taken in benzene, had two groups of lines: a triplet (J = 5.65 MHz relative to benzene) with a spin-spin coupling constant for  $CH_3CH_2$  of 7 Hz, relating to the protons of a  $CH_3$  group, and a quartet (J = 2.65 MHz relative to benzene) with the same constant, relating to the protons of a  $CH_2$  group attached to an oxygen atom. Thus, the NMR spectrum confirms the presence of an ethoxy group.

The IR spectrum of ethoxy-ADC has strong bands at 590 and 695 cm<sup>-1</sup> and peaks of medium intensity at 456, 565, and 830 cm<sup>-1</sup>. The bands at 490, 625, and 697 cm<sup>-1</sup> of pure EADC [12] have disappeared completely. The absorption bands at 695 and 830 cm<sup>-1</sup> are caused by the vibrations of the A1-O bond, and those at 930, 1100, and 1170 cm<sup>-1</sup> by the vibrations of the ethoxy group [14].

The oily layer was separated and analyzed for its contents of Al, Cl, and ethoxy groups. Found: Al 19.00; Cl 50;  $C_2H_5O$  31%; Cl:Al = 2:1. This corresponds to the composition of ethoxy-ADC but is characterized by a considerably greater width of the bands in the IR spectrum.

On heating (40°; 0.5 mm), the oily product decomposed with the evolution of gases containing  $C_2H_5Cl$ , a pulverulent product being formed. Found: C 13; H 2.62; Al 27.30; Cl 36.40; O 20.60%.  $C_2H_5(O-AlCl)_4 \cdot OC_2H_5$ . Calculated: C 12.50; H 2.60; Al 28.20; Cl 36.40; O 20.60%.

## CONCLUSIONS

The oxidation of ethylaluminum dichloride with molecular oxygen takes place in two stages: the formation of ethoxyaluminum dichloride and its oligomerization.

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