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Fig. 1. Conductometric titration with quinoline in cyclohexane solution: a $-Al(C_2H_5)_3$, b $-Al(C_2H_5)_2Br$, c $-Al(C_2H_5)_2H$. m/n (here and in the following figures) is the molar ratio of quinoline used for titration to aluminum contained in the sample being titrated.

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Abstract

Full Text

PHYSICAL CHEMISTRY

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PHYSICOCHEMICAL INVESTIGATION OF CERTAIN SYSTEMS CONTAINING TRIETHYLALUMINUM AND ITS DERIVATIVES

(Presented by Academician A. V. Topchiev, 5 VIII 1957)

For the polymerization of ethylene, propylene, and other alkenes at low pressure, a catalyst consisting of triethylaluminum and titanium tetrachloride may be used ([1,2]). The composition of triethylaluminum, depending on the method of its preparation ([3–5]), usually includes considerable amounts of the products of its oxidation and decomposition (hydride and ethoxide), as well as halo derivatives. In view of the different behavior of these compounds in the polymerization process, a quantitative study of the composition of triethylaluminum synthesized via ethyl bromide and used as a catalyst for the preparation of polyethylene and polypropylene was of interest. For this purpose, use was made of the ability of many organoaluminum compounds, owing to the electron unsaturation of the $3p$ level of the central aluminum atom, to form complexes with nucleophilic reagents containing nitrogen, oxygen, or fluorine atoms ([6–8]).

Fig. 1. Conductometric titration with quinoline in cyclohexane solution:
a $-Al(C_2H_5)_3$, *b* $-Al(C_2H_5)_2Br$, *c* $-Al(C_2H_5)_2H$.
m/n (here and in the following figures) is the molar ratio of quinoline used for titration to aluminum contained in the sample being titrated.

Pure triethylaluminum, diethylaluminum hydride, diethylaluminum bromide, and diethylaluminum ethoxide, synthesized by known procedures ([3,4,9]) and dissolved in cyclohexane, were titrated with quinoline potentiometrically in a cell with silver and platinum electrodes, or conductometrically in a cell with

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

unplatinized plate platinum electrodes. The titration was carried out in an inert-gas atmosphere. For measuring the e.m.f. in potentiometric titration, an LP-5 potentiometer was used; in conductometric titration, the cell was supplied with direct current* from a source with a voltage of 1.5 to 30 V; the current was measured with a microammeter or with a mirror galvanometer of the M-21 type.

* Because of the high internal resistance of the cell (0.1-1 MΩ), the current was small, and electrode polarization could be neglected.

The character of the conductometric titration curves of the individual substances (Fig. 1) shows that quinoline with triethylaluminum forms the electrically conducting complex $Al(C_2H_5)_3 \cdot C_9H_7N$, with diethylaluminum bromide—the electrically conducting complex $Al(C_2H_5)_2Br \cdot C_9H_7N$, and with diethylaluminum

Fig. 2. Conductometric titration of a mixture containing $Al(C_2H_5)_3$, $Al(C_2H_5)_2Br$, $Al(C_2H_5)_2H$, $Al(C_2H_5)_2OC_2H_5$

Fig. 3. Potentiometric titration of a mixture containing $Al(C_2H_5)_3$, $Al(C_2H_5)_2Br$, $Al(C_2H_5)_2H$, $Al(C_2H_5)_2OC_2H_5$

hydride—the complex $Al(C_2H_5)_2H \cdot C_9H_7N$, which is not electrically conducting, and the complex $Al(C_2H_5)_2H \cdot 2C_9H_7N$, which has considerable electrical conductivity. Diethylaluminum ethoxide does not form complexes with quinoline.

Fig. 4. Potentiometric titration of an equimolecular mixture $Al(C_2H_5)_2Cl + AlC_2H_5Cl_2$

In the course of the study, the complex compound $Al(C_2H_5)_2Br \cdot C_9H_7N$, not previously described, was isolated; it crystallizes from cyclohexane in the form of colorless needles with m.p. 45°.

Potentiometric titration confirms the results obtained conductometrically, and the jump in emf at the singular points is expressed much more sharply than the maxima of electrical conductivity.

Figures 2 and 3 show the curves for the conductometric and potentiometric titration of a mixture containing $Al(C_2H_5)_3$, $Al(C_2H_5)_2Br$, $Al(C_2H_5)_2H$, $Al(C_2H_5)_2OC_2H_5$. The character of these curves can be interpreted as follows.

Figure 4

Figure 4: Figure 4

The increase in electrical conductivity from the origin to the first maximum (Fig. 2) is explained by the formation of well-conducting complexes of quinoline with triethylaluminum and diethylaluminum bromide. At the point of the first maximum, $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Br$ have been completely titrated. The subsequent decrease in conductivity is associated with the formation of the nonconducting complex $Al(C_2H_5)_2H \cdot C_9H_7N$, which, upon addition of an excess of quinoline, is converted into the complex $Al(C_2H_5)_2H \cdot 2C_9H_7N$, and the electrical conductivity of the system increases again. The position of the second maximum corresponds to the complete conversion of the hydride into the bimolecular complex with quinoline. Upon further addition of quinoline, the conductivity of the mixture falls, since quinoline is nonconducting, and aluminum ethoxide does not form complexes with quinoline.

Interesting results were obtained in the titration of an equimolecular mixture of $Al(C_2H_5)_2Cl + AlC_2H_5Cl_2$ ("sesquichloride"). Conductometric investigation of this mixture could not be carried out, since, when titrated with quinoline in cyclohexane, a crystalline precipitate is formed, in all probability an insoluble complex of quinoline with ethylaluminum dichloride. The formation of this precipitate causes a sharp decrease in the current in the conductometric circuit as a result of a significant increase in the resistance between the electrodes. On the potentiometric titration curve (Fig. 4), at the point corresponding to a molar ratio of quinoline to aluminum equal to 0.5, a sharp potential jump is observed, which confirms the assumption that a complex is formed.

The present work is also of practical interest from the standpoint of the possibility of rapidly and reliably determining active triethylaluminum for evaluating the ratio between catalyst and cocatalyst in the production of polyalkenes.

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REFERENCES CITED

[1] K. Ziegler, U. Gellert, W. Lehmkuhl, Angew. Chem., **67**, 425 (1955).
[2] K. Ziegler, Angew. Chem., **67**, 541 (1955).
[3] A. Grosse, J. Mavity, J. Org. Chem., **5**, 106 (1940).
[4] K. Ziegler, Angew. Chem., **64**, 323 (1952).
[5] K. Ziegler, Angew. Chem., **68**, 721 (1956).
[6] K. Ziegler, H. Lehmkuhl, Zs. anorg. u. allgem. Chem., **283**, 414 (1956).
[7] E. Krause, B. Wendt, Ber., **56**, 466 (1923).
[8] E. Bonitz, Chem. Ber., **88**, 742 (1955).
[9] R. S. Brokaw, R. N. Pease, J. Am. Chem. Soc., **72**, 3237 (1950).

Note: Figure translations are in progress. See original paper for figures.