Oxidation-reduction processes that take place in the Ziegler catalytic system lead to the formation of a complex mixture of products, consisting of titanium and aluminum halides and alkyl halides. In particular, in the reaction of TiCl₄ and AlEt₂Cl, compounds of trivalent titanium are formed, and AlEt₃Cl appears in place of AlEt₂Cl [1]. As the composition of the catalyst changes, the catalytic properties of the system change. A study of the kinetics of the polymerization of ethylene in the presence of TiCl₄ and AlEt₂Cl indicated that the nature of the dependence of the polymerization rate on the time varies complexly with increasing initial TiCl₄ concentration and constant diethylaluminum chloride concentration [2]. In order to understand these results, it was necessary to compare the kinetic curves of the polymerization and the curves of reduction of TiIV by diethylaluminum chloride. A comparison of the kinetics of the polymerization and reduction of TiCl₄ was conducted earlier with the catalytic system TiCl₄—Al(i-Bu)₂Cl as an example [3]. It was shown that the process of formation of active centers of polymerization is directly related to reductive reactions, which take place among the components of the catalyst.

In this work we studied the dependence of the rates of accumulation of reduced titanium and the rates of polymerization of ethylene in the presence of diethylaluminum chloride at 30°, molar ratios of AlEt₂Cl to TiCl₄ 0.6:1, 1.2:1, and 2.4:1, at a constant initial concentration of AlEt₂Cl equal to 7.4 × 10⁻³ M. To determine the influence of monoethylaluminum dichloride (which appears during the reduction) upon the catalytic properties of the system, we conducted experiments on the polymerization of ethylene on TiCl₄ and AlEt₂Cl with additions of AlEtCl₂.

**EXPERIMENTAL**

The methods of studying the kinetics of the polymerization of ethylene and the kinetics of the reduction of TiCl₄ by aluminum alkyls were described earlier [3, 4]. Ethylene, TiCl₄, AlEt₂Cl, and Al(i-Bu)₂Cl were the same as in [2, 3]. Monoethylaluminum dichloride was synthesized from AlEt₂Cl and AlCl₃. The weight ratio of La : Cl in the product obtained was 0.4 : 1. Polymerization was conducted in a medium of spectrally pure n-heptane. The volume of n-heptane in all experiments was 43 ml.

Comparison of the Kinetics of the Reduction of TiIV and the Kinetics of Polymerization of Ethylene.

For a proper comparison of the kinetic principles of the processes of reduction and polymerization, first of all it was necessary to establish whether the reduction of TiIV takes place in the same way in the presence of ethylene and without it. In view of this, experiments were conducted on the reduction of titanium, in which the reaction between TiCl₄ and AlEt₂Cl was carried out with and without ethylene. Figure 1 gives the kinetic curve of the reduction of TiCl₄ by trisobutylaluminum and disobutylaluminum chloride. The amount of FeCl₃ consumed for the titration is plotted along the Y-axis, and the time along the X-axis. From Fig. 1, it is evident that under the conditions studied (catalyst concentration ~1 g/liter, ethylene concentration 0.013 M), ethylene practically does not affect the course of the reduction. Consequently, the kinetic curves of the polymerization, obtained at a monomer pressure of 100 mm, can be compared with the curves of accumulation of reduced titanium, obtained in the absence of ethylene.

The kinetic results obtained in an investigation of the reduction of TiCl₄ by diethylaluminum chloride and in the polymerization of ethylene for various molar ratios of AlEt₂Cl to TiCl₄ are presented in Fig. 2. From a consideration of Fig. 2, it follows that with variation of the molar ratio of the reagents from 2.4 : 1,
FeCl₃ 10^5 M 

Fig. 1. Kinetic curve of the reduction of TiCl₄ in the presence of Al(i-Bu)₃ + Al(i-Bu)₂Cl. T. 30°, amount of TiCl₄ = 1.9 · 10⁻⁴ M; molar ratio Al: Ti = 2.5:1: 1) in the absence of ethylene; 2) ethylene pressure 100 mm.

Influence of Additions of AlEtCl₂ on the Kinetics of the Polymerization of Ethylene in the Presence of TiCl₄ and AlEt₂Cl. Experiments on the polymerization of ethylene with additions of AlEtCl₂ were conducted under conditions in which the polymerization rate varied with time and in which the process of polymerization was of a steady-state character. Figure 3 gives the kinetic curves of polymerization. Curve 1 was obtained without additions of AlEtCl₂, while curve 2 pertains to an experiment in which monoethylaluminum dichloride was introduced into the system 1 h after the beginning of polymerization. The amount of introduced AlEtCl₂ was approximately 30 times greater than the amount of monoethylaluminum dichloride that might be formed in the system in the reaction of TiCl₄ with AlEt₂Cl.

\[
\text{TiCl}_4 + \text{AlEt}_2\text{Cl} = \text{TiCl}_3 + \text{AlEtCl}_2 + \frac{1}{2}\text{C}_2\text{H}_4 + \frac{1}{2}\text{C}_2\text{H}_6 \quad (1)
\]

Comparing the rate curves 1 and 2 in Fig. 3, it is easy to note that an increase in the concentration of AlEtCl₂ in the system leads to a decrease in the catalyst activity. In the case cited, after the addition of monoethylaluminum dichloride, the steady-state rate of polymerization decreased 3.5-fold.

Experiments were also conducted with small additions of AlEtCl₂, in which the amount of monoethylaluminum dichloride introduced was comparable with the initial amount of diethylaluminum chloride. The kinetic curve of polymerization 2 in Fig. 4 was obtained in an experiment with additions of AlEtCl₂, in which the initial amount of AlEt₂Cl was equal to 2.76 · 10⁻⁴ M, while the amount of AlEtCl₂ introduced into the system 30 min after the beginning of the process was 2.8 · 10⁻⁴ M. As can be seen from Fig. 4, in the presence of AlEtCl₂, a sharper decrease in the rate with time is observed. Without the addition of AlEtCl₂, the polymerization rate becomes 3.7 times lower in comparison with the maximum rate 3 h after the time of mixing of the catalysts; in the case of introduction of AlEtCl₂, the system already possesses such activity after 1 h 40 min. It is characteristic that in both cases the systems reach a state at which their catalytic properties become very close. The rates of polymerization at the moment of time equal to 3 h possess the same values, 18.3 g of C₂H₄/h · liter · atm.

**DISCUSSION OF THE EXPERIMENTAL RESULTS**

As has been shown, after the introduction of AlEtCl₂ into the stable catalytic system formed in the interaction of TiCl₄ and and AlEt₂Cl, the activity of the catalyst is appreciably reduced. On the basis of