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Abstract

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KINETICS AND MECHANISM OF THE INITIATION OF ETHYLENE POLYMERIZATION ON A SOLUBLE COMPLEX CATALYST OF THE ZIEGLER TYPE

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In the interaction of $(\pi\text{-}C_5H_5)_2TiCl_2$ with certain aluminum alkyls, complexes soluble in hydrocarbons are formed which are capable of catalyzing the polymerization of ethylene (^{1,2}). The most convenient system for investigation is the complex formed by the interaction of $(C_5H_5)_2TiCl_2$ with dimethylaluminum chloride. In this case, in the absence of olefins, reduction does not take place and the solution does not change over a long period of time. The interaction of the catalyst components ends with the formation of an alkylated titanium derivative, which is bound by a donor-acceptor bond to the aluminum alkyl (^{3})

$$(C_5H_5)_2TiCl_2 + Al(CH_3)_2Cl \to (C_5H_5)_2Ti(CH_3)Cl \cdot AlCH_3Cl_2. \qquad \text{(A)}$$

In the presence of ethylene, its polymerization occurs and, at the same time, titanium is reduced; in the presence of other α-olefins, titanium is reduced to the trivalent state according to the reaction

$$2(C_5H_5)_2Ti(CH_3)Cl \cdot Al(CH_3)Cl_2 + RCH{=}CH_2 \to$$

$$\to R(CH_3)C{=}CH_2 + 2(C_5H_5)_2TiCl \cdot Al(CH_3)Cl_2 + CH_4.$$

Studying the kinetics of the reduction of titanium under the action of heptene-1, we came to the conclusion (^{3}) that the reaction rate is determined by the interaction of the olefin with ions formed upon dissociation of complex A. In this process the olefin molecule is “inserted” into the Ti–CH_3 bond. Immediately after this reaction, disproportionation of the alkyl group formed with the methyl group occurs, with titanium being reduced and losing its activity

$$A \rightleftarrows (C_5H_5)_2TiCH_3^+ + Al(CH_3)Cl_3^-,$$

$$(C_5H_5)_2TiCH_3^+ + RCH{=}CH_2 \to (C_2H_5)_2TiCH_2CH(R)CH_3^+,$$

$$(C_5H_5)_2TiCH_2CH(R)CH_3^{+}+AlCH_3Cl_3^{-} \rightleftarrows (C_5H_5)_2TiCH_2CH(R)CH_3Cl\cdot Al(CH_3)Cl_2,$$

$$(C_5H_5)_2TiCH_2CH(R)CH_3Cl\cdot Al(CH_3)Cl_2 \xrightarrow{A} (C_5H_5)_2TiCl\cdot AlCH_3Cl_2. \quad \text{(C)}$$

We assumed that the reaction of ethylene polymerization has a similar mechanism, but, in contrast to the other olefins, after the first reaction of ethylene insertion there follows a multitude of other similar reactions. Direct evidence for this mechanism has not existed up to now. Moreover, Carrick (^{4}), who investigated this system, came to the conclusion that its activity is associated with profound changes, in particular with the detachment of cyclopentadienyl groups from titanium.

In the present work we set ourselves the aim of obtaining direct evidence for the proposed mechanism of initiation of ethylene polymerization. For this purpose we studied changes in the spectra of the catalytic system in the presence of polymerizing ethylene. The catalyst solution was introduced directly in the spectrometer into a cuvette into which a definite amount of ethylene had previously been admitted on a vacuum apparatus. The amount of ethylene (pressure in the cuvette 200-600 mm Hg) was sufficiently small that, during its polymerization, no precipitation of polyethylene occurred that would interfere with the spectroscopic determination. If the initiation of polymerization does indeed proceed by insertion of ethylene into the Ti—CH_3 bond, a complex in which a propyl group is bound to titanium must initially be formed.

$$(C_5H_5)_2Ti(CH_3)Cl\cdot Al(CH_3)Cl_2 \xrightarrow{C_2H_4} (C_5H_5)_2Ti(C_3H_7)Cl\cdot Al(CH_3)Cl_2. \quad \text{(B)}$$

To test this assumption, we determined the spectrum of a complex analogous to B, obtained by the interaction of dipropylaluminum chloride with $(C_5H_5)_2TiCl_2$. In this case the reaction proceeds

$$\mathrm{(C_5H_5)_2TiCl_2 + Al(C_3H_7)_2Cl \rightarrow (C_5H_5)_2Ti(C_3H_7)Cl\cdot AlC_3H_7Cl_2}, \quad \text{(B')}$$

followed by reduction of titanium. The spectrum in the visible region of the compound B′ formed should be similar to the spectrum of B, since the electronic transitions corresponding to the spectrum are determined by the groups directly bonded to the titanium atom, and differences in the alkyl groups bonded to the aluminum atom have only a slight effect.

Fig. 1. Optical absorption spectra in benzene. 1 —complex A, 2 —complex B, 3 —complex C. [A] = [B] = [C] = $4.18 \cdot 10^{-3}$ mol/l

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Fig. 2. Kinetics of the change in the concentration of complexes A, B, and C in the reaction of complex A with ethylene. Experimental conditions: $[(C_5H_5)_2TiCl_2] = 8.36 \cdot 10^{-3}$ mol/l, $[Al(CH_3)_2Cl] = 3.50 \cdot 10^{-2}$ mol/l, $[C_2H_4] = 2.2 \cdot 10^{-2}$ mol/l; $t = 22^\circ$, solvent —benzene.

Figure 1 shows the spectrum of complex B′, as well as that of the initial complex A and the final complex C, formed during the reduction of titanium in the presence of olefins. If only complexes A, B, and C are present in the system, then the concentration of each of them can be determined from the optical density of the solution at three wavelengths by solving a system of three equations with three unknowns of the type

$$l(\varepsilon_A c_A + \varepsilon_B c_B + \varepsilon_C c_C) = D,$$

where D is the optical density of the solution, l is the cuvette thickness, and ε and c are the extinction coefficients and concentrations of complexes A, B, and C. We chose the optical density D at 660 and 610 mμ, where the change in D, as follows from Fig. 1, is proportional to the change in the concentration of A and B, respectively, for determining the concentrations of these complexes. The concentration of complex C was measured from the change in optical density at 720 mμ, and also at 520 mμ, where the change in D is proportional to the concentration of complex C. We also measured the concentration of the paramagnetic complex C by the method of electron paramagnetic resonance, carrying out the reaction in parallel in a vessel placed directly in the resonator of the EPR spectrometer.

Figure 2 presents the results of measurements of the concentrations of the three complexes during the interaction of ethylene with the catalytic system under study. It can be seen that the changes in the concentrations of complexes A, B, and C with time correspond to the consecutive reaction A→B→C. The results for complex C obtained from optical spectra (circles) and EPR spectra (triangles) coincide completely. The curve corresponding to the sum of the concentrations of all three complexes is drawn in Fig. 2 as a dashed line. As can be seen, throughout the entire reaction the balance relation is fulfilled, which confirms the correctness of the assumption made about the chemistry of the reaction. These data are the first direct proof of the insertion of an olefin molecule into the Ti–C bond in the polymerization process. It should be noted that this conclusion could be called into question if rapid exchange of alkyl groups between aluminum and titanium existed, as was found for some similar systems. However, special experiments showed that, for the system under study, exchange is insignificant at the selected component concentrations.

From the kinetic curves for the increase in the concentration of complex B, the dependence of the rate of its formation on various factors was determined. It was found that the initial rate of this reaction is proportional to the concentration of ethylene in the solution and is practically independent of the concentration of aluminum alkyl over the range of variation of the Al/Ti ratio from 2 to 10. When the initial concentration of $(C_5H_5)_2TiCl_2$, and consequently of catalytic complex A, is varied, the initial rate of formation of complex B changes in proportion to the square root of the concentration of A. Thus, the kinetic equation for complex B has the form:

$$(d[\mathrm{B}]/dt)_0 = k[\mathrm{A}]^{1/2}[\mathrm{C_2H_4}].$$

The same kinetic equation was obtained by us earlier for the reduction reaction of complex A under the action of heptene-1 (^{3}). This confirms the conclusion that in both cases a similar mechanism is involved. The dependence of the rate on the concentration of complex A is consistent with the assumption of equilibrium dissociation of this complex into ions, one of which $(C_5H_5)_2TiCH_3^+$ is the catalytically active particle. As in work (^{3}), a strong dependence of the reaction rate on the purity of the solvent was noted, and relatively good reproducibility of the results was obtained only with one and the same portion of specially purified solvent. The results of a series of experiments for olefins carried out with this condition observed are given below.

Fig. 3. Decrease in the concentration of ethylene upon interaction with complex A. Experimental conditions: $[(C_5H_5)_2TiCl_2] = 6.69 \cdot 10^{-3}$ mol/l, $[Al(CH_3)_2Cl] = 3.50 \cdot 10^{-2}$ mol/l, $[C_2H_4] = 2.2 \cdot 10^{-2}$ mol/l; $t = 22^\circ$, solvent—benzene.

Olefin	C_2H_4	C_3H_6	C_7H_{14}	C_2H_3Cl
$k_{22^\circ} \cdot 10^3$, $l^{1/2} \cdot mol^{-1/2} \cdot sec^{-1}$	4.9 ± 0.2	1.7 ± 0.1	0.51 ± 0.04	0.037

For ethylene the rate of formation of complex B was measured directly; for the other olefins, the rate of reduction of Ti was measured, but in all cases this in fact corresponds to the rates of insertion of the olefin into the Ti—CH_3 bond. As with other Ziegler-type catalysts, propylene, and especially heptene, reacts more slowly than ethylene. This is apparently associated with steric factors. Vinyl chloride reacts considerably more slowly than the other α-olefins. In this case, evidently, the role of chlorine is manifested, hindering the reaction of the α-olefin with the positive ion.

It is clear that differences in insertion rates are insufficient to explain the qualitative difference in the behavior of ethylene from other α-olefins, especially propylene. The main role is played by the difference in the stability of the intermediate compounds in the case of ethylene, on the one hand, and the other α-olefins, on the other. This is due to the fact that, upon insertion of ethylene, a linear propyl group is formed, whereas upon insertion of other α-olefins of the formula $RCH = CH_2$, a branched group $-CH_2—CH(CH_3)R-$is formed, containing a tertiary H atom, which evidently leads to its easy conversion into the isoolefin $CH_2 = C(CH_3)R$ by abstraction of H in an intramolecular disproportionation. In this process titanium is reduced, which in the given case proves to be chain termination, since Ti^{3+} is not reactive. In our opinion, this explanation is of a general nature and applies to those Ziegler-type catalytic systems in which

in which ethylene polymerizes and other α-olefins do not polymerize. If this is so, then such a property of systems of this kind means that the transition element entering into the catalytic complex must be in a state of high valence.

The sharp slowing of the reaction of complex A several minutes after the start of the reaction (Fig. 2) is associated with the disappearance of ethylene in the catalyst solution as a result of polymerization. Figure 3 shows the change in the concentration of C_2H_4 during the experiment. The experimental points were obtained by chromatographic analysis of the ethylene concentration. The curve was calculated from the rate of change of the concentration of A, on the assumption that

$$[C_2H_4] = -d[A]/dt\,/\,k[A]^{1/2}.$$

It can be seen that the experimental points agree well with the calculated curve. The first insertion of C_2H_4 into the $Ti-CH_3$ bond in this case is the initiation process. Subsequently, chain-growth reactions proceed by the same mechanism, and in the course of elongation of the alkyl group at the Ti atom after formation of the propyl group:

$$Ti-C_3H_7 \to Ti-C_5H_{11} \to Ti-C_7H_{15} \quad \text{etc.}$$

in the visible region the spectrum of complex B probably changes only insignificantly.

If the reduction of complex B is neglected up to the point of its maximum concentration, where practically all dissolved ethylene has disappeared, then the ratio of the rate constants for chain growth and initiation of polymerization can be calculated, assuming that

$$-d[A]/dt = d[B]/dt = k_1[A]^{1/2}[\mathrm{C_2H_4}],$$

$$-d[\mathrm{C_2H_4}]/dt = k_1[A]^{1/2}[\mathrm{C_2H_4}] + k_2[B]^{1/2}[\mathrm{C_2H_4}].$$

Hence

$$\frac{k_2}{k_1} = \frac{d-b}{[b(a-b)]^{1/2} - a\arcsin(b/a)^{1/2}},$$

where k_2 and k_1 are the constants of chain growth and initiation, a and d are the initial concentrations of complex A and ethylene, respectively, and b is the maximum concentration of complex B.

Table 1 gives the values of k_2/k_1 obtained in this way from a series of experiments. At the same time, we can obtain this ratio by comparing the maximum rate of polymerization as measured by ethylene absorption at its constant pressure with the initial rate of formation of complex B at the same ethylene concentration. Such a comparison gave, for k_2/k_1, the value 19, which is in close agreement with the value obtained analytically. Thus, the polymerization mechanism receives quantitative confirmation.

Table 1*

$a \cdot 10^3$, mol/l	$b \cdot 10^3$, mol/l	$d \cdot 10^2$, mol/l	k_2/k_1
4.18	0.80	6.30	22.0
4.18	1.25	12.5	23.4
4.18	2.00	25.0	20.9
6.69	3.64	27.6	12.8
6.69	3.04	27.6	14.7
7.90	2.30	22.0	21.6
8.36	2.51	22.0	19.5
8.36	2.80	22.0	20.6
18.7	4.00	22.0	13.5
		Average	18.9

* At a temperature of 22°.

It should be noted that our data to a significant extent contradict the scheme of Chien[2], who previously studied polymerization on the same system. In particular, Chien assumes a pathway of polymerization initiation independent of ethylene. Our results leave no doubt that the active complex B is obtained only in the presence of ethylene.

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