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Abstract

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INVESTIGATION OF THE COMPOSITION OF THE PRODUCTS OF THE REACTION OF VANADIUM OXYTRICHLORIDE WITH TRIETHYLALUMINUM

For the stereospecific polymerization of diolefin hydrocarbons, complex organometallic catalysts prepared on the basis of titanium salts and aluminum alkyls are used for the most part, since these systems make it possible to obtain cis-1,4-polyisoprene and cis-1,4-polybutadiene. Vanadium-containing catalysts are used, for example, for the copolymerization of ethylene with propylene. In the polymerization of diolefin hydrocarbons, polymers are obtained that contain 90–95% monomer units arranged in the trans-1,4 position, which opens routes to the synthesis of artificial gutta-percha. In addition, catalysts based on vanadium salts have a simpler and more stable composition than catalysts based on titanium salts, which makes them convenient for a detailed study of the mechanism of catalytic polymerization. The composition and catalytic properties of catalysts prepared on the basis of vanadium chlorides were studied by Natta et al. (1–6). They established that, upon reduction of vanadium oxytrichloride with aluminum alkyls, a precipitate is formed consisting mainly of complex compounds of vanadium chlorides with aluminum alkyls in a molar ratio of 1 : 1. The chlorine content in the precipitate decreases with an increase in the initial aluminum alkyl : vanadium oxytrichloride ratio.

The aim of the present investigation is to derive relationships that make it possible to determine by calculation the quantitative composition of the products of the reaction of vanadium oxytrichloride with triethylaluminum.

The reaction was carried out by adding a 0.1 M benzene solution of triethylaluminum to a 0.1 M solution of vanadium oxytrichloride at 20° under conditions excluding the presence of traces of moisture and oxygen. In one series of experiments, the precipitate that formed was filtered off and washed several times with benzene, then dissolved in 2% sulfuric acid, and the average valence of vanadium was determined by titration with a 0.1 N permanganate solution. The chlorine content was then determined by Volhard' s method, aluminum by Paulson' s method (8), and vanadium by reduction with sulfurous gas (7). The benzene solution obtained after filtration of the precipitate was subjected to analogous analysis. In another series of experiments, the gaseous hydrocarbons released during the reaction (ethane, ethylene, butane)* were collected. From the amount of carbon dioxide formed upon combustion of the gas mixture over copper oxide, the amount of ethyl groups of triethylaluminum that had reacted with formation of hydrocarbon gases was estimated. It was assumed that the intermediate unstable organovanadium compounds formed decompose practically completely (9), and that polymerization of ethylene does not play a significant role; consequently, the amount of such groups is equivalent to the amount of diethylaluminum chloride formed. After removal of the hydrocarbon gases, the reaction mixture was treated with 2% sulfuric acid, and the amount of ethyl groups not participating in the reaction was judged from the volume of ethane evolved. On the basis of the data obtained, the amounts of diethylethoxyaluminum formed and of unreacted triethylaluminum were calculated.

* The composition of the gas mixture was not investigated.

It turned out that the average valence of vanadium in the reaction products decreases with increasing molar ratio $[Al(C_2H_5)_3]/[VOCl_3] = n$ in the range of values $n < 2$ (Fig. 1); at the same time, the amount of diethylaluminum chloride and diethylethoxyaluminum formed increases (Fig. 2). At values $n \geq 2$, the valence of vanadium reaches a constant value. Consequently, the reduction reaction of vanadium proceeds simultaneously in two directions:

1) At the V—Cl bond, i.e., in accordance with the scheme proposed by Gilman, Jones, and Wood (^{10}):

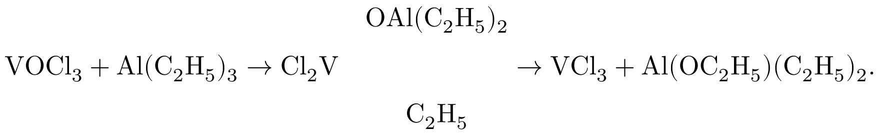
$$VOCl_3 + Al(C_2H_5)_3 \rightarrow C_2H_5VOCl_2 +$$

$$+AlCl(C_2H_5)_2;$$

$$C_2H_5VOCl_2 \rightarrow VOCl_2 + Et,$$

where Et denotes ethyl groups, taken into account as gaseous hydrocarbons.

2) At the V = O bond:



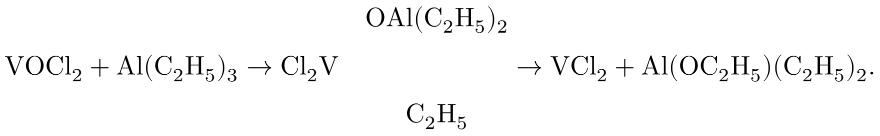
$$VOCl_3 + Al(C_2H_5)_3 \rightarrow Cl_2V\begin{matrix} OAl(C_2H_5)_2 \\ \\ C_2H_5 \end{matrix} \rightarrow VCl_3 + Al(OC_2H_5)(C_2H_5)_2.$$

Fig. 1. Dependence of the average valence of reduced vanadium (V_x) on the value $n = Al(C_2H_5)_3/VOCl_3$: 1—based on the results of titration with

permanganate, 2—based on determination of the content of diethylaluminum chloride and diethylethoxyaluminum in the reaction products.

The compounds of tri- and tetravalent vanadium that are formed are further reduced in the presence of an excess of triethylaluminum:

$$VCl_3 + Al(C_2H_5)_3 \rightarrow C_2H_5VCl_2 + AlCl(C_2H_5)_2 \rightarrow VCl_2 + AlCl(C_2H_5)_2 + Et;$$



$$VOCl_2 + Al(C_2H_5)_3 \rightarrow Cl_2V\begin{matrix}OAl(C_2H_5)_2\\ \\ C_2H_5\end{matrix} \rightarrow VCl_2 + Al(OC_2H_5)(C_2H_5)_2.$$

Thus, when one mole of diethylaluminum chloride is formed, the valence of vanadium decreases by one unit; when one mole of diethylethoxyaluminum is formed, it decreases by two units. The values of the average valence of vanadium calculated from the amount of diethylaluminum chloride and diethylethoxyaluminum formed satisfactorily coincided with the values found by direct titration (Fig. 1).

At values $n < 2$, owing to the high reactivity of vanadium oxytrichloride, it is also necessary to take into account the reduction reaction of the latter by chloro- and ethoxyaluminum alkyls.

In the present communication, the simplest system is considered, arising at values of n in the range $n > 2$. The insoluble complex compounds formed during the reduction reaction consist of equimolecular amounts of vanadium chlorides and aluminum alkyls. These compounds are evidently capable of equilibrium exchange with dissolved aluminum alkyls. At $n > 2$, as n increases, the chlorine content in the solution above the precipitate increases (Table 1). Since no further reduction of vanadium occurs in this case, the increase in the amount of chlorine is evidently due to the presence of the equilibrium:

$$VCl_2 \cdot AlCl(C_2H_5)_2 + Al(C_2H_5)_3 \rightleftarrows VCl_2 \cdot Al(C_2H_5)_3 + AlCl(C_2H_5)_2.$$

Table 1

Composition of the reaction products of vanadium oxytrichloride with triethylaluminum as a function of
n-$[Al(C_2H_5)_3]/[VOCl_3]$

n	V	Al	Cl	V	Al	Cl
	Composition of the insoluble precipitate, g-at/g-mol $VOCl_3$	**Composition of the insoluble precipitate, g-at/g-mol** $VOCl_3$	**Composition of the insoluble precipitate, g-at/g-mol** $VOCl_3$	**Composition of the solution above the precipitate, g-at/g-mol** $VOCl_3$	**Composition of the solution above the precipitate, g-at/g-mol** $VOCl_3$	**Composition of the solution above the precipitate, g-at/g-mol** $VOCl_3$
0.20	0.59	0.20	1.80	0.40	Not detected	1.20
0.25	0.73	0.25	2.20	0.24	»	0.69
0.33	0.96	0.33	2.78	Not detected	»	Not detected
0.50	1.00	0.50	2.84	»	»	»
1.00	0.97	1.00	2.89	»	»	»
1.64	1.05	1.02	2.60	»	0.62	0.28
2.00	0.98	1.06	2.48	»	0.94	0.49
2.35	1.02	1.01	2.23	»	1.34	0.58
3.00	0.99	1.10	2.22	»	1.90	0.65
3.50	0.89	1.05	2.19	»	2.45	0.70
4.00	0.94	0.86	2.12	»	3.14	0.76
5.00	0.96	1.10	2.14	»	3.90	0.81
5.80	1.06	1.09	2.09	»	4.71	0.85
7.00	0.88	1.13	2.04	»	5.87	0.87

An analogous reaction may also be assumed for diethoxyaluminum:

$$VCl_2{\cdot}Al(OC_2H_5)(C_2H_5)_2+Al(C_2H_5)_3 \rightleftarrows VCl_2{\cdot}Al(C_2H_5)_3+Al(OC_2H_5)(C_2H_5)_2.$$

Fig. 2. Dependence of the content of diethylaluminum chloride (m_0) and diethoxyaluminum (l_0) in the reaction products on the value $n = Al(C_2H_5)_3/VOCl_3$ (in mol/mol $VOCl_3$). 1 –content of diethylaluminum chloride; 2 –content of diethoxyaluminum.

Let us introduce the following designations: m_0, l_0 are the total contents, respectively, of diethylaluminum chloride and diethoxyaluminum in the reaction products; m, l are the same in the solution above the precipitate; m_1, l_1 are the same chemisorbed on the surface of the precipitate*. For small particle size of the precipitate, it may be assumed that:

$$m_0 = m + m_1; \qquad l_0 = l + l_1.$$

Then the expressions for the constants of the equilibrium reactions will have the following form:

$$K_1 = \frac{m}{m_1} \cdot \frac{1 - m_1 - l_1}{(n-1) - m - l};$$

$$K_2 = \frac{l}{l_1} \cdot \frac{1 - m_1 - l_1}{(n-1) - m - l}.$$

If the energies of formation of the complex compounds $VCl_2 \cdot AlCl(C_2H_5)_2$ and $VCl_2 \cdot Al(OC_2H_5)(C_2H_5)_2$ differ little from one another, then:

$$K_1 = K_2 = K.$$

Eliminating l, we obtain:

$$\left[\frac{m_0}{(m_0 + l_0)(m_0 + m)}\right] = K\left[\frac{m_0}{(m_0 + l_0)(m_0 + m)} \cdot \frac{(n-1)(m_0 - m)}{m}\right] + [1 - K].$$

To verify the correctness of the equation obtained over a wide range of values of m_0, a special series of experiments was carried out, in which—

* The values of the indicated quantities are expressed in moles per mole of initial vanadium oxytrichloride.

···after completion of the reaction of vanadium oxytrichloride with triethylaluminum, diethylaluminum chloride or triethylaluminum was added to the reaction mixture, and the change in the chlorine content in the solution above the precipitate was determined. The experimental points in the coordinates

$$Q = \left[\frac{m_0}{(m_0 + l_0)(m_0 + m)}\right] \quad \text{and} \quad S = \left[Q \cdot \frac{(n-1)(m_0 - m)}{m}\right]$$

fell satisfactorily around a straight line passing through the origin (Fig. 3); consequently, $K = 1$.

The results obtained make it possible to derive simple expressions determining the quantities of complex-bound diethylaluminum chloride and diethoxyaluminum. For $K_1 = K_2 = 1$, from the expressions for the equilibrium constants it follows that:

Fig. 3. Dependence of Q on S: 1 –at $l_0 = 1$, $m_0 = 1$; 2 –at $l_0 = 1$, $m_0 > 1$

Figure 1: Fig. 3. Dependence of Q on S: 1 –at $l_0 = 1$, $m_0 = 1$; 2 –at $l_0 = 1$, $m_0 > 1$

$$m_1 = \frac{m_0}{n}, \qquad l_1 = \frac{l_0}{n}.$$

Thus, the amount of diethylaluminum chloride chemisorbed on the surface of the reduced vanadium chlorides is inversely proportional to the amount of triethylaluminum introduced into the reaction. The decrease in catalytic activity of catalysts of this type with increasing $AlR_3/VOCl_3$ ratio, noted by a number of authors ($^{1-5}$), can be explained by a decrease in the content of complex-bound diethylaluminum chloride, if it is assumed that it is the active center initiating polymerization. A detailed study of the influence of the composition of such catalysts on the kinetics of polymerization of diolefin hydrocarbons will be the subject of subsequent communications.

Fig. 3. Dependence of Q on S: 1 –at $l_0 = 1$, $m_0 = 1$; 2 –at $l_0 = 1$, $m_0 > 1$

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