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Abstract

Full Text

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INFRARED SPECTRA OF THE PRODUCTS OF THE INTERACTION OF $(C_5H_5)_2TiCl_2$ WITH ALUMINUM ALKYLS

(Presented by Academician V. N. Kondrat' ev on February 19, 1962)

The systems $(C_5H_5)_2TiCl_2$—$Al(C_2H_5)_3$ and $(C_5H_5)_2TiCl_2$—$Al(C_2H_5)_2Cl$ have recently been widely used as soluble catalysts for the polymerization of ethylene at low pressure. It has been established ([1]) that the final product of the interaction of these systems in toluene and in heptane is a "blue complex," in the molecules of which the titanium atom is trivalent. X-ray structural analysis showed ([2]) the presence in the "blue complex" of two three-center bonds forming "bridges" between titanium and aluminum atoms. The same bridging bond also exists in the dimer of diethylaluminum chloride. In the formation of the "blue complex" from $(C_5H_5)_2TiCl_2$ and $Al(C_2H_5)_3$, two ethyl groups are attached to the Al atom in the complex; if one starts from $(C_5H_5)_2TiCl_2$ and $Al(C_2H_5)_2Cl$, then C_2H_5 and Cl are attached.

$C_5H_5\backslash$ Cl C_2H_5
Ti Al
$C_5H_5/$ Cl C_2H_5

$C_5H_5\backslash$ Cl C_2H_5
Ti Al
$C_5H_5/$ Cl Cl

$C_2H_5\backslash$ Cl C_2H_5
Al Al
$C_2H_5/$ Cl C_2H_5

We have obtained IR spectra of the "blue complexes" of both types.

Fig. 1. IR spectra of organometallic compounds:
1 –$(C_5H_5)_2TiCl_2$ (KBr tablet),
2 – "blue complex" $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$,

3 $-Al(C_2H_5)_3$, dimer,
4 – "blue complex" $(C_2H_5)_2TiCl_2Al(C_2H_5)Cl$,
5 $-Al(C_2H_5)_2Cl$, dimer.

The procedure for preparing samples for the measurements was as follows: in an argon atmosphere, 0.3 M solutions of $Al(C_2H_5)_3$ or $Al(C_2H_5)_2Cl$ in heptane were added to crystals of $(C_5H_5)_2TiCl_2$. After the disappearance of the red precipitate of $(C_5H_5)_2TiCl_2$, blue crystals slowly precipitated from the solution, having respectively the compositions $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ and

$(C_5H_5)_2TiCl_2Al(C_2H_5)Cl$. Then the mother liquor over the crystals was removed, and they were dissolved in heptane. The concentration of the solutions was $\sim$ 0.3 mole/liter. This solution was poured into cells of constant thickness, analogous to those described in the literature ([3]). The spectra were recorded on an IKS-14 instrument in the range 2000–400 cm^{-1} (NaCl, KCl, and KBr prisms).

The spectra of the starting substances and of the "blue complexes" are shown in Fig. 1. In the range 1200–700 cm^{-1} the spectra of the "blue complexes" practically coincide with the sum of the spectra of $(C_5H_5)_2TiCl_2$ and the corresponding aluminum alkyl. Only two main differences should be noted:

1. The intense band at 870 cm^{-1}, present in the spectrum of $(C_5H_5)_2TiCl_2$, disappears in the spectra of the "blue complexes."

2. The band at 820 cm^{-1}, belonging to $(C_5H_5)_2TiCl_2$, in the spectra of the "blue complexes" is shifted into the long-wavelength region to 812 –810 cm^{-1} and coincides with the absorption band of the aluminum alkyl. The intensity of this band increases more than would have been expected from addition of the optical densities of these bands in $(C_5H_5)_2TiCl_2$ and the aluminum alkyls.

Analysis of the causes of these changes is at present made difficult by the absence of an assignment of the bands of $(C_5H_5)_2TiCl_2$. Comparison of the spectra of $(C_5H_5)_2TiCl_2$ and $(C_2H_5)_2Fe$ makes it possible to assign a number of bands in the spectrum of $(C_5H_5)_2TiCl_2$, but does not permit any conclusions concerning the 870 cm^{-1} band. The spectrum of the complex $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ in the region of the stretching vibrations Al–C and Al–Cl, 700–400 cm^{-1}, may be compared with the spectrum of the dimer $Al(C_2H_5)_2Cl$ ([4]), which makes it possible to assign the bands at 638 and 543 cm^{-1} in the spectrum of the "blue complex"

to the asymmetric and symmetric stretching vibrations of the group $Al\langle{}^{C}_{C}$.

In the spectrum of the complex $(C_5H_5)_2TiCl_2Al(C_2H_5)Cl$, the bands at 640–650 and 550 cm^{-1} are absent, since the group $Al\langle{}^{C}_{C}$ in it has been replaced by the group $Al\langle{}^{C}_{Cl}$. The band at 620 cm^{-1}, as in the complex $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$, belongs to one of the deformation vibrations of the CH_2 group bonded to an Al atom. In addition, in the spectrum of $(C_5H_5)_2TiCl_2Al(C_2H_5)Cl$ there appear intense bands at 493 and 476 cm^{-1}, characterizing the group $Al\langle^{C}_{Cl}$.

A more detailed description of these bands is possible by comparing the spectrum of $(C_5H_5)_2TiCl_2Al(C_2H_5)Cl$ with the spectrum of the dimer of ethylaluminum dichloride. However, we have not yet succeeded in obtaining the spectrum of this compound, since it interacts with the material of the cell windows.

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