A SPECTROPHOTOMETRIC INVESTIGATION OF THE REACTION BETWEEN DIETHYLALUMINUM HALIDES AND TITANIUM TETRACHLORIDE IN CARBON TETRACHLORIDE

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(Received March 3rd, 1965)

Triethylaluminum and diethylaluminum halides reduce titanium tetrachloride to the lower titanium chlorides[1]; indeed this reaction is intimately connected with the formation of Ziegler catalysts for the polymerisation of α-olefines[2]. On the other hand, the lower titanium chlorides can be oxidised to titanium tetrachloride by carbon tetrachloride[3]. By a careful balance of these opposing tendencies, it should be possible to avoid precipitation of titanium trichloride in the reaction of alkylaluminum compounds with titanium tetrachloride in carbon tetrachloride.

By adding titanium tetrachloride to a solution of triethylaluminum in carbon tetrachloride a precipitate, presumably titanium trichloride, is formed. On standing, this precipitate re-dissolves and the resultant wine-red solution can catalyze the polymerization of ethylene[4]. If, instead of triethylaluminum, diethylaluminum bromide is used in carbon tetrachloride solution, the addition of titanium tetrachloride does not cause a precipitate to form[4]. The reaction can therefore be followed spectrophotometrically.

Triethylaluminum alone in carbon tetrachloride decomposes only slowly at 0° (ref. 5); diethylaluminum chloride alone does not decompose even in boiling carbon tetrachloride[5]. The addition of traces of titanium tetrachloride causes instantaneous decomposition of all the triethylaluminum to diethylaluminum chloride at 0° (ref. 5). The use of triethylaluminum in the ternary system with carbon tetrachloride and titanium tetrachloride is therefore equivalent to the use of diethylaluminum chloride in this study.

EXPERIMENTAL

Diethylaluminum bromide was prepared by the method of Von Grosse and Mavity[6].

Diethylaluminum chloride was prepared by subliming aluminum chloride *in vacuo* into a reaction vessel. Triethylaluminum was injected through a rubber gasket into the vessel and the mixture was heated to 90°. After distillation, the product was analyzed and found to contain some ethylaluminum dichloride. A calculated amount of triethylaluminum was added to convert ethylaluminum dichloride to diethylaluminum chloride.

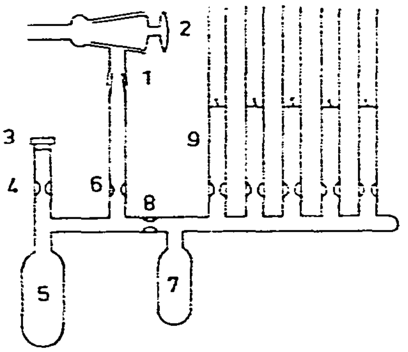
The triethylaluminum used was made by Texas Alkyls Inc.

Spectroscopic solutions in carbon tetrachloride were prepared in the apparatus shown in Fig. 1. After evacuation stopcock 2 was closed and about 100 ml of analytical grade carbon tetrachloride was injected through gasket 3. The carbon tetrachloride was frozen by liquid air and about 2 ml of the organoaluminum compound was injected followed by about 10 ml carbon tetrachloride for washing. The gasket was removed by sealing at 4, and the components were allowed to melt and to mix. After outgassing, the mixture was frozen in and the attachment was separated from the vacuum system by sealing off at 6. The solution at 5 was then allowed to melt and vessel 7 was cooled in liquid air, when a dilute solution of the organoaluminum compound, free from haziness, passed over. Relatively high concentrations could be achieved by allowing the distillation to proceed nearly to completion. When more dilute solutions were required only 20 to 50% of the mixture was distilled. After distillation, the manifold was sealed off at 8. On reaching room temperature the contents of 7 were distributed among the breakseals 9 which were then sealed off from the manifold at the constrictions. In order to determine the concentration, one or two breakseals were analyzed.

Spectroscopic solutions of titanium tetrachloride were prepared in an analogous manner. A further stage of distillation was added in this case in order to obtain sufficiently dilute solutions.

Aluminum was determined by the aluminon method[7a], halogens by Mohr's method[7b], and titanium colorimetrically[7c].

Spectrophotometric measurements, using a Beckmann DU spectrophotometer were carried out in 1 mm or 1 cm optical cells which were sealed to a mixing chamber connected with the breakseals containing the solutions. All measurements were carried out *in vacuo*.



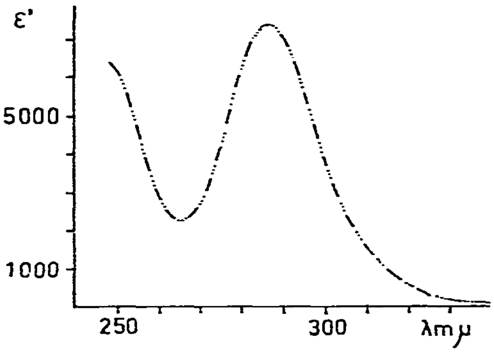
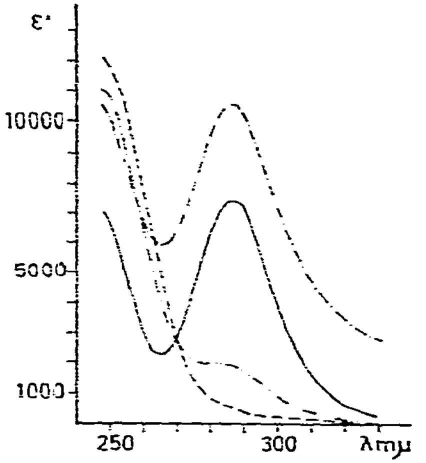


Fig. 1. Apparatus for the preparation of the spectroscopic solutions.

Fig. 2. Absorption spectrum of $TiCl_4$ in CCl_4; $TiCl_4$ conc. 0.8 mM.

RESULTS

In Fig. 2 the spectrum of titanium tetrachloride in carbon tetrachloride is shown; it is virtually the same as that in *n*-hexane[8], and shows a typical strong absorption at 285 mμ. Diethylaluminum chloride and bromide give no peak in the range under investigation, and the extinction coefficient for them is less than 70 over the whole range; so their absorption can be neglected. In Fig. 3, the change with time of the extinction coefficient of a mixture of diethylaluminum chloride and titanium tetrachloride in carbon tetrachloride is recorded. The extinction coefficient ε' is calculated on the basis of the titanium concentration. The solid line shows the calculated spectrum assuming that no reaction takes place on mixing. It will be noted that after 10 minutes the titanium tetrachloride peak has largely disappeared and after 70 minutes it has completely disappeared, and the disappearance is accompanied by a rise in absorption below 260 mμ. Carbon tetrachloride itself absorbs below this wavelength and causes cut-off at 247.5 mμ, but by a method described later it has been shown that the maximum of the new peak occurs at 230 mμ (Fig. 4). When the mixture is allowed to stand for a sufficient time, titanium tetrachloride reappears. This is demonstrated by the spectrum for 4300 minutes (Fig. 3) showing the typical absorption of titanium tetrachloride superimposed on a broad band caused by reaction products. With higher ratios of diethylaluminum chloride to titanium tetrachloride the same behavior is observed except that it is impossible to detect titanium tetrachloride as such after mixing.



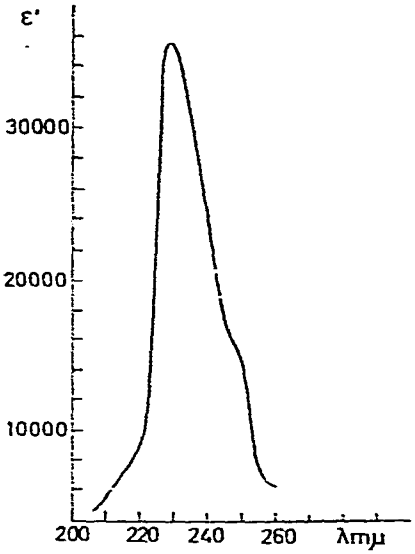
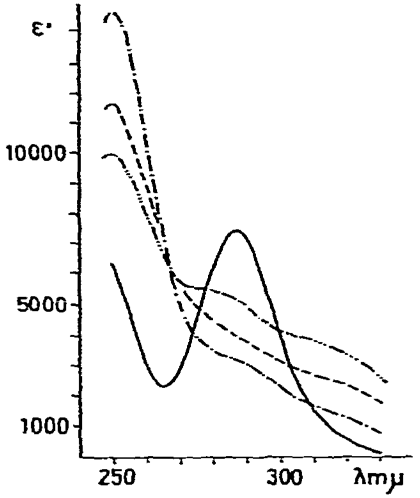


Fig. 3. Absorption spectra of $(C_2H_5)_2AlCl$ (16.0 m*M*) + $TiCl_4$ (1.1 m*M*) in CCl_4; —...—... 10 min after mixing; ---- 70 min after mixing; —·—·— 4300 min after mixing; ——— $\varepsilon_{Ti} + \varepsilon_{Al}$ calculated.

Fig. 4. Absorption spectrum of $(C_2H_5)_2AlCl$ (14 m*M*) + $TiCl_4$ (1 m*M*) in mixture of 6% CCl_4 in *n*-heptane.

In Figs. 5, 6 and 7 the absorption spectra for the system diethylaluminum bromide and titanium tetrachloride are given. It will be noted that at the higher ratios of diethylaluminum bromide to titanium tetrachloride, a peak forms at about 275 mμ and slowly increases in strength and moves towards shorter wavelengths. No similar peak is observed in the system containing diethylaluminum chloride. In Fig. 8 spectra are shown for a mixture of low Al:Ti ratio to which diethylaluminum bromide is later added. At the original low Al:Ti ratio only the peak due to the residue of the titanium



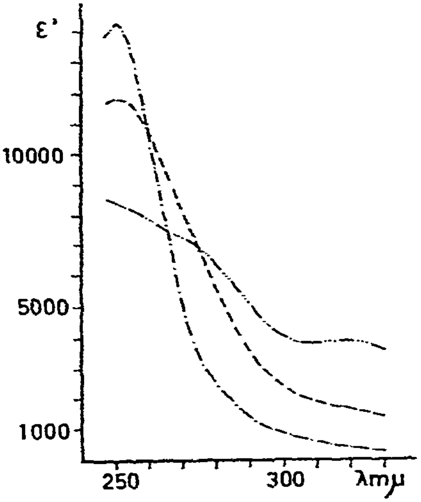


Fig. 5. Absorption spectra of $(C_2H_5)_2AlBr$ (2.5 m*M*) + $TiCl_4$ (0.7 m*M*) in CCl_4; -···- 5 min after mixing; ---- 25 min after mixing; -·-·- 180 min after mixing; ——— $\varepsilon_{Ti} + \varepsilon_{Al}$ calculated.

Fig. 6. Absorption spectra of $(C_2H_5)_2AlBr$ (5.5 m*M*) + $TiCl_4$ (0.9 m*M*) in CCl_4; -···- 10 min after mixing; ---- 120 min after mixing; -·-·- 390 min after mixing.

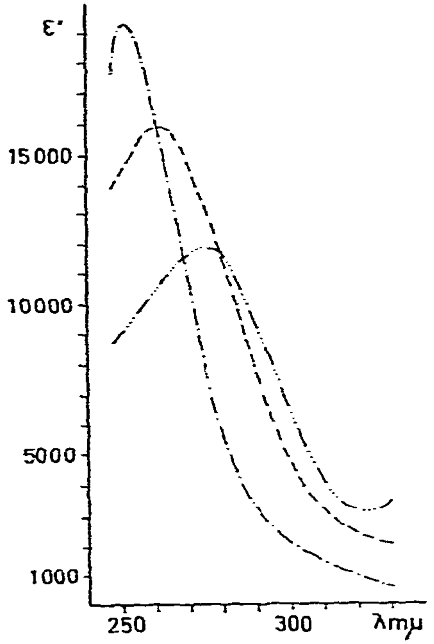


Fig. 7. Absorption spectra of $(C_2H_5)_2AlBr$ (19.5 m*M*) + $TiCl_4$ (0.9 m*M*) in CCl_4; -···- 15 min after mixing; ---- 300 min after mixing; -·-·- 1200 min after mixing.

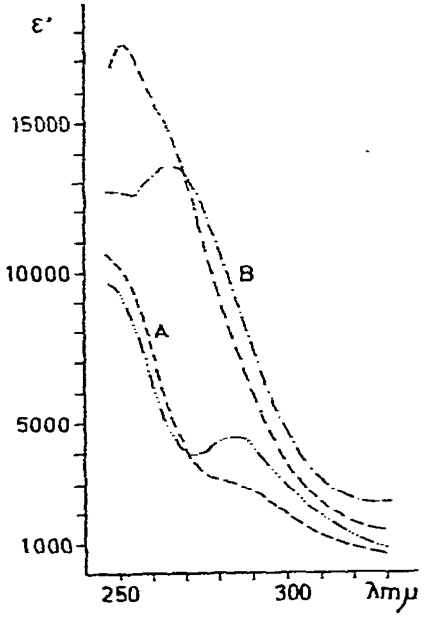


Fig. 8. Absorption spectra of $(C_2H_5)_2AlBr$ + $TiCl_4$ in CCl_4. Concentrations were changed during the reaction by adding $(C_2H_5)_2AlBr$ solutions 78 min after the first mixing. Resultant solutions: A. $(C_2H_5)_2AlBr$ (5.1 m*M*) + $TiCl_4$ (1.4 m*M*); -···- 15 min after the first mixing; ---- 55 min after the first mixing. B. $(C_2H_5)_2AlBr$ (19.3 m*M*) + $TiCl_4$ (0.7 m*M*); -·-·- 95 min after the first mixing; ---- 900 min after the first mixing.

tetrachloride can be distinguished; the 275 mμ peak is absent. On further addition of diethylaluminum bromide, the absorption at 275 mμ appears. When the reaction between the alkylaluminum compounds and titanium tetrachloride is carried out in *n*-heptane, titanium trichloride is precipitated instantly. When, however, *n*-heptane is added to a mixture of the alkylaluminum compound and titanium tetrachloride in carbon tetrachloride, no precipitate is formed. Since the cut-off of *n*-heptane is at a much shorter wavelength than that of carbon tetrachloride, dilution with *n*-heptane allows measurement of the absorption below 250 mμ (Fig. 4).

DISCUSSION

The spectra show that when a large excess of diethylaluminum halide is used the titanium tetrachloride disappears before the first measurements can be taken (Fig. 6). With a smaller excess, a residue of the titanium tetrachloride peak at 285 mμ can still be observed after 10 min. This is in accord with the hypothesis that fast ligand exchange[9] is the primary reaction:

$$(C_2H_5)_2AlX + TiCl_4 \rightleftharpoons C_2H_5AlClX + C_2H_5TiCl_3 \qquad (1)$$

When diethylaluminum bromide is used, the disappearance of the 285 mμ peak is accompanied by the appearance of a new peak at 275 mμ. With diethylaluminum chloride on the other hand, the peak at 275 mμ is absent; instead the absorption below 260 mμ increases and a new peak appears at 230 mμ (Fig. 4). Since the 275 mμ absorption occurs with the bromide but not with the chloride, it cannot be assigned to the ethyltitanium trichloride.

It is known that, in general, bromides yield more stable complexes than chlorides. The different behavior of the two halides can therefore be explained by assuming that a complex is formed by the bromide. By comparing Figs. 5, 6 and 7, in which the excess of diethylaluminum bromide is progressively increased it is seen that it takes a large excess of diethylaluminum bromide to develop a pronounced peak. This is borne out by the results in Fig. 8 in which no peak can be observed for the low Al:Ti ratio; on addition of an extra portion of diethylaluminum bromide, the intermediate peak at 275 mμ appears. This shows that even with the bromide, the complex is not stable and needs high concentrations of diethylaluminum bromide for stabilization. The equilibrium constant K for the equation

$$(C_2H_5)_2AlBr + C_2H_5TiCl_3 \rightleftharpoons (C_2H_5)_2AlBr \cdot C_2H_5TiCl_3 \qquad (2)$$

can be estimated from the data to be of the order of $K = 100$ liter/mole.

The peak at 275 mμ assigned to the complex becomes weaker with time and simultaneously the absorption below 260 mμ increases in strength. Apparently the complex passes over into the same compound which before has been prepared directly from diethylaluminum chloride and titanium tetrachloride. It is assumed therefore, that the absorption at 230 mμ is due to ethyltitanium trichloride.

It has been shown[10] that aluminum–alkyl bonds are destroyed in carbon tetrachloride in the presence of titanium chlorides. In particular dialkylaluminum halide is converted into alkylaluminum dihalide and eventually to aluminum chloride. Thus during each experiment of this study the concentration of diethylaluminum bromide is continually reduced and the equilibrium (2) shifted to the left. An additional factor causing reduction of the diethylaluminum bromide concentration is halogen exchange between the bromide and carbon tetrachloride. Both the degradation of the diethylaluminum bromide and the bromine–chlorine exchange decompose the complex and ethyltitanium trichloride appears.

The alkyltitanium trichlorides have been shown not to be very stable[9]. They decompose to titanium trichloride. With the 0.001 molar solutions in carbon tetrachloride used no precipitation occurs. Apparently titanium trichloride is oxidized by carbon tetrachloride to titanium tetrachloride[3] before saturation is reached. The newly formed titanium tetrachloride reacts as before by ligand exchange (1) so that substantially all the titanium present is held in the form of ethyltitanium trichloride either complexed or free. Indeed this is exactly the path by which titanium chlorides catalyze the decomposition of the Al–C bond by carbon tetrachloride. In hydrocarbons the oxidation cannot take place, and a precipitate of titanium trichloride builds up. When the alkylaluminum halide becomes exhausted ligand exchange (1) can no longer occur. The titanium tetrachloride from the oxidation of titanium trichloride can then not react any further. It will be seen from Fig. 3 that titanium tetrachloride eventually re-appears quantitatively.

SUMMARY

The reactions between diethylaluminum halides and titanium tetrachloride in carbon tetrachloride have been studied by UV absorption spectrophotometry. No titanium trichloride precipitates, though titanium tetrachloride disappears. Apparently ligand exchange takes place and ethyltitanium trichloride is formed. When excess of diethylaluminum bromide is present, a complex is formed. On standing, the ethyltitanium trichloride is eventually converted back into titanium tetrachloride.

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