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About Thallium Complexes of the Ziegler–Natta Type

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The reaction of $TiCl_4$ with various organo-metallic compounds has been thoroughly studied. According to Simon *et al.* [1–3] the composition of the solid complexes is not essentially affected by the various molar ratios of the initial components. In the formation of complexes, processes of reduction and alkylation of Ti^{+4} take place. $TlCl_3$ has been found to form with various organo-metallic compounds (R_nM) heterogeneous systems reminiscent of the $TiCl_4$ and R_nM systems. The aim of the present work is to establish some relationships in the reaction of $TlCl_3$ with R_nM. Mixtures of $TlCl_3$ with n-C_4H_9Li, C_2H_5MgBr, $(C_2H_5)Al$ and $(C_2H_5)_4Sn$ were studied at various temperatures and reaction times to determine the activating energy of the process. The Tl/M ratio in the solid complexes was determined at various $TlCl_3$ to R_nM molar ratios. Formation of the Tl–C bond was established by IR spectroscopy.

$TlCl_3$ was prepared from TlCl by known procedures and its ether solution was dried with anhydrous $CuSO_4$. n-C_4H_9Li was supplied by Merck and $(C_2H_5)_3Al$ by Fluka. $(C_2H_5)_4Sn$ and C_2H_5MgBr were obtained by known methods. The reaction of the initial component solutions was carried out in dry nitrogen at −18°, 0° and 20 °C. Determination of composition of the solid complexes was made by analysis accounting for mutual interference of the ions. The reduction of Tl^{+3} was determined iodometrically in the heterogeneous $TlCl_3$–R_nM mixtures.

The mixing of $TlCl_3$ with C_2H_5MgBr at 1:8 up to 6:1 molar ratios was found to yield compounds of approximately the same composition [4]. Analogous results were achieved using mixtures of $TlCl_3$ with other organo-metallic compounds. A sediment of Tl:Li = 1.7:1 composition was isolated from mixtures of $TlCl_3$ with n-C_4H_9Li at molar ratios up to 1:10. In the $TlCl_3/(C_2H_5)_3Al$ system this ratio was 1.5:1. These results show that complex compounds of nearly constant composition are formed by mixing of $TlCl_3$ with R_nM. The IR spectra of the solid complexes show typical maxima for the Tl–C bond, wich increase in intensity with increasing content of organo-metallic components of the $TlCl_3$–R_nM systems. The n-C_4H_9Li-containing system displays a broad maximum at 470 cm^{-1}, the C_2H_5MgBr-containing system shows maxima at 445, 470 and 515 cm^{-1}, the $(C_2H_5)_3Al$-containing system displays maxima at 430, 450 and 515 cm^{-1} and the $(C_2H_5)_4$-Sn-containing system has such maxima at 430, 568 and 588 cm^{-1}. These maxima are not found in the IR spectra of the initial components. According to Deacon and Green [5] the Tl–C bond has maxima in the 435–559 cm^{-1} range depending on the type of substituents. It can be assumed that in the reaction of $TlCl_3$ with R_nM processes of alkylation of Tl are taking place with formation of $TlR_{3-n}Cl_n$ compounds of varied concentration with time. This assumption is confirmed by the Tl^{+3} reduction data (Fig. 1).

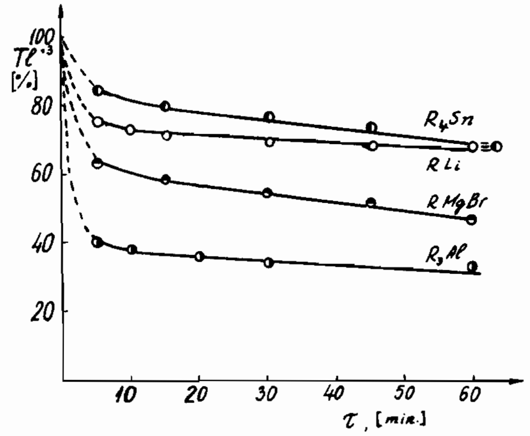

Fig. 1. Reduction of $TlCl_3$ at 0 °C with R_nM.

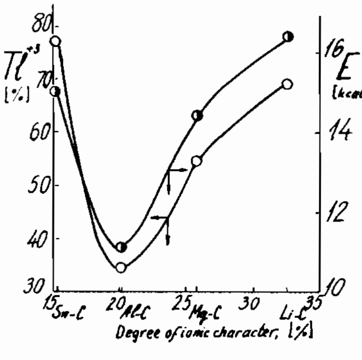

Fig. 2. Effect of the degree of ionic character of the M–C bond in organo-metallic compounds of the R_nMn–$TlCl_3$ systems on the activation energy of reduction of Tl^{+3} and on Tl^{+3} concentration after a 30 min reaction at 0 °C.

As can be seen from Fig. 1, the level of reduction of Tl^{+3} is higher in the order Sn < Li < Mg < Al. It is known that reduction ability of organo-metallic compounds is directly related to the degree of ionic character of the M–C bond of these compounds. The curves in Fig. 2 are obtained by arranging the activation energy values of the reaction of $TlCl_3$ with R_nM and the Tl^{+3} reduction values in an order depending on the degree of ionic character of the M–C bond calculated by the Polling equation [6].

The presence of a minimum in the relationships could be ascribed to the effect of alkylation and complex formation processes. The alkylating ability is increased and the complex formation ability is reduced when the degree of ionic character of the M–C bond is increased in the order R_n–M: C–Sn, C–Al, C–Mg, and C–Li. As is known, these two processes are determinant factors in the formation of the Ziegler–Natta complexes. The investigations carried out indicate the identity of the behaviour of $TlCl_3$ and that of $TiCl_4$ in the formation of complexes with organo-metallic compounds.

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