

## DEUTERON MAGNETIC RESONANCE STUDY OF THE MECHANISM OF METHYL GROUP EXCHANGE BETWEEN TETRAMETHYLTITANIUM AND TRIMETHYLALUMINIUM

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(Received May 11th, 1973)

### Summary

The exchange of methyl groups between tetramethyltitanium and trimethylaluminium has been studied by the direct observation of a new resonance line in the  $^2\text{D}$  NMR spectrum of the reaction mixture containing perdeuterated and undeuterated organometallic compounds.

The kinetics and mechanism of the exchange reaction are influenced by the ethyl ether concentration in a hexane solution of the tetramethyltitanium compound. At a molar ratio  $\text{TiMe}_4/\text{Et}_2\text{O} > 1$  rapid exchange occurs between unsolvated metal alkyls. Tetramethyltitanium etherate reacts with trimethylaluminium in two steps, an initial fast complexation to  $\text{Me}_3\text{Ti} [\text{AlMe}_4]$  which accounts for the transfer of a single methyl group from the titanium to the aluminium atom and a subsequent slow reverse process which leads to the transfer of methyl groups from the aluminium to the titanium atom and which results ultimately in a random equilibrium distribution of the labelled methyl groups amongst both metal atoms.

Mixing the etherates of both titanium and aluminium methyl compounds led to the appearance of an extra signal downfield ( $\tau$  5.6 ppm) which is apparently due to the methyl resonance of the species  $[\text{TiMe}_3]^+ [\text{AlMe}_4]^-$  in the solvent-separated ion-pair form of the complex  $[\text{TiMe}_3]^+ [\text{AlMe}_4]^-$ .

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### Introduction

Investigations using NMR have revealed that organometallic exchange reactions sometimes involve the formation of mixed organometallic complexes as has been observed for methyl lithium with trimethylaluminium [1], dimethylmagnesium and dimethylzinc [2]. The case of titanium and aluminium alkyls is of especial interest since these compounds play an important part in Ziegler-Natta stereoregular polymerization reactions.

Following an earlier report [3], a longer account is given here of a study of

the exchange of perdeuteromethyl groups between tetramethyltitanium and trimethylaluminium as studied by deutron magnetic resonance (DMR) spectroscopy.

## Results

The transfer of the methyl group was followed directly by watching the appearance of a new deutron resonance line during exchange between perdeuterated and undeuterated metal alkyls dissolved in conventional protonated solvents [3]. In the range of temperatures examined ( $-70^{\circ}$  to  $-20^{\circ}$ ), the rate of exchange was sufficiently slow to enable discrete signals corresponding to the methyl groups bonded to aluminium and titanium to be observed. The reaction rate was sufficient however to allow a considerable portion of the methyl groups to be transferred from  $\text{Ti}(\text{CD}_3)_4$  to aluminium within 2 - 5 min (cf. Figs. 2, 3, 5 and 6). The amount of the ethyl ether initially present in the hexane solution of tetramethyltitanium significantly influences the kinetics and presumably also the mechanism of the exchange process. When the tetramethyltitanium concentration exceeded the ether concentration, it was found that the exchange was fast and that the perdeuteromethyl distribution attained after 3.5 min did not change appreciably after 32 min and even after 25 h (Fig. 1).

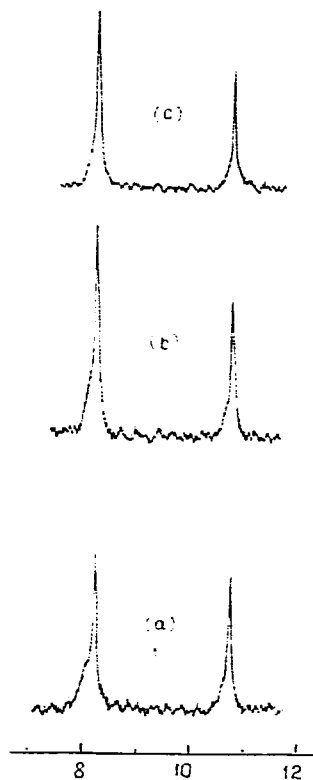


Fig. 1.  $^2\text{D}$  NMR spectra of  $\text{Ti}(\text{CH}_3)_4\text{-Al}_2(\text{CD}_3)_6$  in hexane at  $-30^{\circ}$ .  $(\text{C}_2\text{H}_5)_2\text{O}$  concn. 0.085 M; Ti concn. 0.15 M; Al concn. 0.15 M (a) After exchange for 3.5 min; (b) after 32 min; (c) after 25 h.

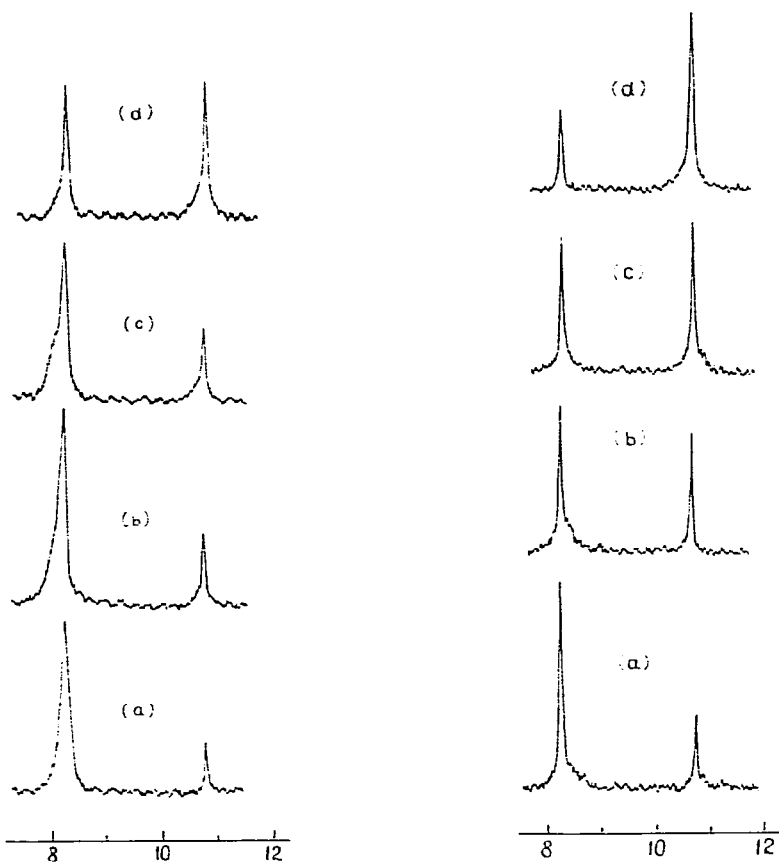


Fig. 2.  $^2\text{D}$  NMR spectra of  $\text{Ti}(\text{CD}_3)_4\text{-Al}_2(\text{CH}_3)_6$  in hexane at  $-60^\circ$ .  $(\text{C}_2\text{H}_5)_2\text{O}$  concn.  $0.6\text{ M}$ ; Ti concn.  $0.12\text{ M}$ ; Al concn.  $0.15\text{ M}$ . (a) After exchange for 2 min; (b) after 15 min; (c) after 45 min; (d) after 20 h.

Fig. 3.  $^2\text{D}$  NMR spectra of  $\text{Ti}(\text{CD}_3)_4\text{-Al}_2(\text{CH}_3)_6$  in hexane at  $-60^\circ$ .  $(\text{C}_2\text{H}_5)_2\text{O}$  concn.  $0.72\text{ M}$ ; Ti concn.  $0.08\text{ M}$ ; Al concn.  $0.15\text{ M}$ . (a) After exchange for 20 min; (b) after 60 min; (c) after 120 min; (d) after 20 h.

In the presence of a higher concentration of ether ( $> 0.5\text{ M}$ ), the  $\text{Ti}(\text{CD}_3)_4/\text{Al}_2(\text{CH}_3)_6$  exchange proceeded in a step-wise manner. A rapid reaction at  $-60^\circ$  resulted, after a few minutes, in the transfer of approximately 25% of the methyl groups from the titanium to the aluminium provided that the molar ratio  $\text{Al}/\text{Ti} > 1$  (Figs. 2 and 3). A slower reaction occurred in the system when  $\text{Al}/\text{Ti} > 2$  and after 1 h the intensity of the  $\text{CD}_3\text{-Ti}$  and  $\text{CD}_3\text{-Al}$  signals became equal (Fig. 3). Irrespective of the initial  $\text{Al}/\text{Ti}$  ratio, the subsequent reaction always proceeded at a slower rate. After 20 h, the perdeuteromethyl groups were randomly distributed between both metal atoms. In contrast, at similar concentrations of ether the reverse migration of methyl groups from  $\text{Al}_2(\text{CD}_3)_6$  to  $\text{Ti}(\text{CH}_3)_4$  always proceeded at a low rate (Fig. 4), a detectable intensity for the  $\text{Ti-CD}_3$  resonance being reached only after 20 min even though the reaction temperature was raised up to  $-20^\circ$ .

Replacing the hexane solution of trimethylaluminium by a specially prepared trimethylaluminium etherate brought about a significant change in the

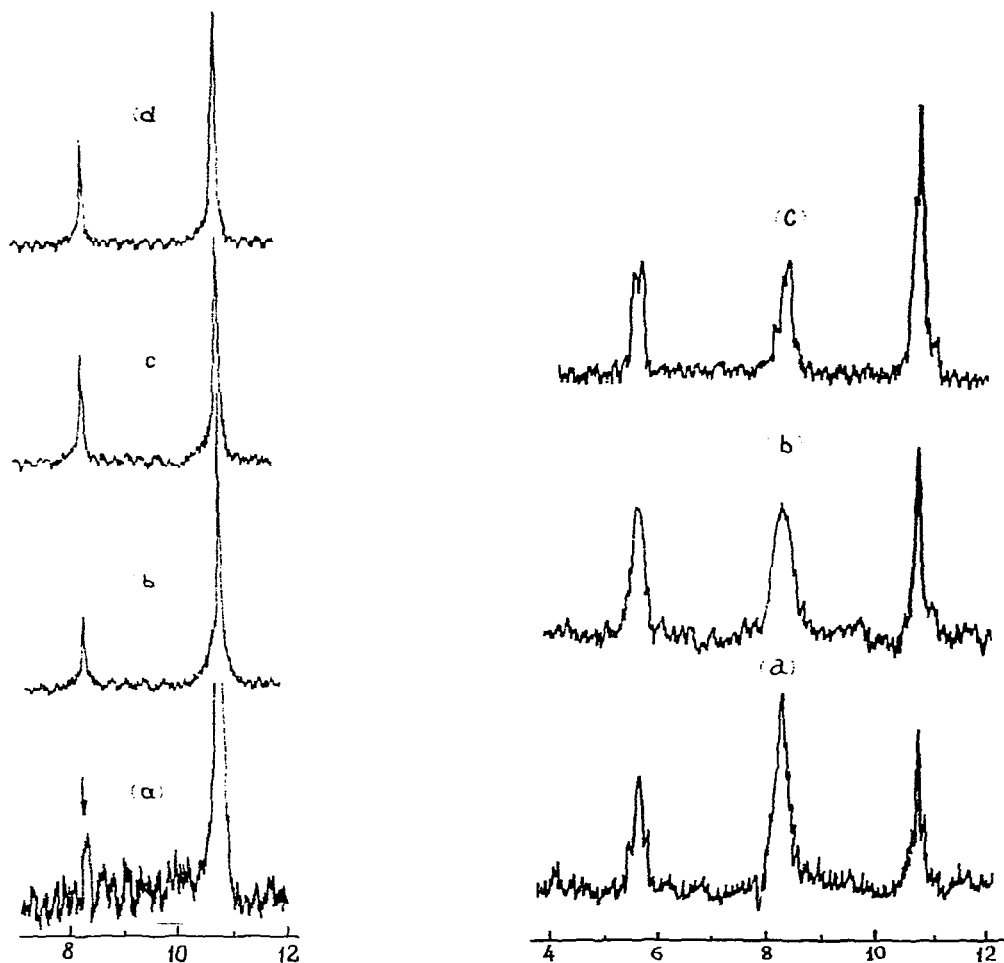


Fig. 4.  $^2\text{D}$  NMR spectra of  $\text{Ti}(\text{CH}_3)_4\text{-Al}_2(\text{CD}_3)_6$  in hexane at  $-20^\circ$ .  $(\text{C}_2\text{H}_5)_2\text{O}$  concn.  $2.75\text{ M}$ ; Ti concn.  $0.1\text{ M}$ ; Al concn.  $0.2\text{ M}$ . (a) After exchange for 12 min; (b) after 20 min; (c) after 45 min; (d) after 20 h.  
 Fig. 5.  $^2\text{D}$  NMR spectra of  $\text{Ti}(\text{CD}_3)_4\text{-Al}(\text{CH}_3)_3\text{-(C}_2\text{H}_5)_2\text{O}$  in hexane at  $-30^\circ$ .  $(\text{C}_2\text{H}_5)_2\text{O}$  concn.  $0.93\text{ M}$ ; Ti concn.  $0.12\text{ M}$ ; Al concn.  $0.14\text{ M}$ . (a) After exchange for 4 min; (b) after 15 min; (c) after 50 min.

spectra obtained from the system. At  $\text{Al/Ti} > 1$ , in addition to the resonances assigned to  $\text{CD}_3\text{-Ti}$  ( $\tau$  8.3 ppm) and  $\text{CD}_3\text{-Al}$  ( $\tau$  10.8 ppm), an additional signal appeared in the low-field region ( $\tau$  5.6 ppm). The intensity of the downfield signal increased at the expense of the  $\text{Ti-CD}_3$  absorption as the ratio  $\text{Al/Ti}$  was increased (cf. Figs. 5 and 6), the total concentration with respect to ether reaching  $0.9\text{ M}$  in these runs. It should be noted that the addition of excess ether to the final exchange products of the  $\text{Al}_2\text{Me}_6\text{-TiMe}_4\text{-Et}_2\text{O}$  system produced no change in the spectrum and no additional signal appeared at  $\tau$  5.6 ppm.

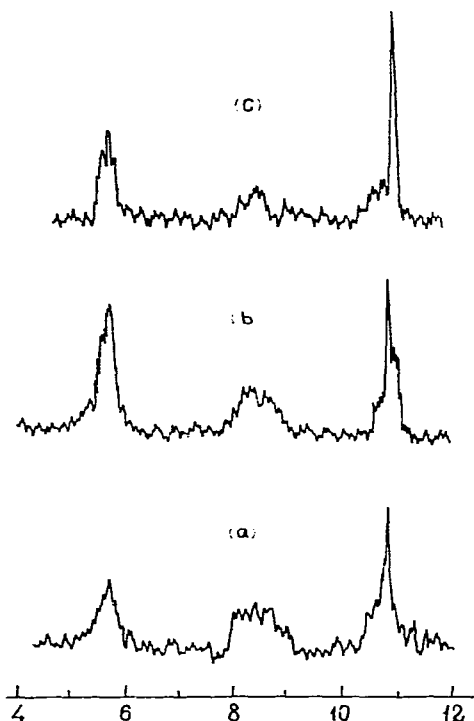


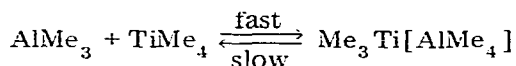
Fig. 6.  $^2\text{D}$  NMR spectra of  $\text{Ti}(\text{CD}_3)_4\text{-Al}(\text{CH}_3)_3\text{-(C}_2\text{H}_5)_2\text{O}$  in hexane at  $-30^\circ$ .  $(\text{C}_2\text{H}_5)_2\text{O}$  concn. 0.93 M; Ti concn. 0.11 M; Al concn. 0.2 M. (a) After exchange for 5 min; (b) after 10 min; (c) after 20 h.

## Discussion

The exchange of methyl groups at low ether contents in the tetramethyltitanium solution was too fast to enable the process to be followed in detail. It is, however, reasonable to suppose that the interchange involved two unsolvated metal alkyl species since the ratio  $\text{Ti}/\text{Et}_2\text{O} > 1$  and it is well known that uncomplexed aluminium alkyls undergo alkyl redistribution more readily than their respective etherates [4,5].

In more concentrated ether solutions, where the ratio  $\text{Ti}/\text{Et}_2\text{O} < 1$ , tetramethyltitanium is apparently completely complexed as an etherate. Our data indicate that under these conditions the trimethylaluminium exchanges directly with the tetramethyltitanium etherate. Preliminary formation of the complex  $\text{AlMe}_3\text{-Et}_2\text{O}$  is unlikely since the characteristic signal at  $\tau$  5.6 ppm obtained from mixtures of etherates was absent in this particular case (cf. Figs. 2, 3 and 4). These results may be explained in terms of the following mechanism. On adding trimethylaluminium to tetramethyltitanium etherate solution, a mixed 1/1 complex is rapidly formed whose structure is similar to that of  $\text{Li}[\text{AlMe}_4]$ . The formation of such a complex leads to the complete transfer of one methyl group from the titanium to the aluminium atom. The reverse process (the dissociation of the complex to the initial metal alkyls) leads to transfer of methyl groups from the aluminium to the titanium atom. If the dissociation is

slow and no intramolecular exchange occurs, random distribution of perdeuteromethyl groups should be attained only slowly due to the low mobility of the equilibrium process



Such a mechanism requires that labelled methyl groups migrate from  $\text{Al}_2(\text{CD}_3)_6$  to  $\text{Ti}(\text{CH}_3)_4 \cdot \text{Et}_2\text{O}$  at a slow steady rate which is indeed found (cf. Fig. 4).

It is possible that a 2/1 complex is also formed at ratios of  $\text{Al/Ti} > 2$  as occurs in the system  $\text{LiCH}_3\text{—Mg}(\text{CH}_3)_2$  [2]. Equal intensity of  $\text{CD}_3\text{—Ti}$  and  $\text{CD}_3\text{—Al}$  signals after an hour of exchange implies that two methyl groups attached to the titanium are transferred to the aluminium atom in this case by a comparatively rapid process. The low rate of any subsequent exchange is due to the slow dissociation of the complex.

An interesting feature of the spectra obtained for the  $\text{AlMe}_3 \cdot \text{Et}_2\text{O—TiMe}_4 \cdot \text{Et}_2\text{O}$  system is the additional resonance observed at  $\tau$  5.6 ppm. It is obvious that this signal should be ascribed to the methyl groups in a titanium-containing species since the strong absorption at  $\tau$  5.6 ppm is accompanied by the complete disappearance of the  $\text{CD}_3\text{—Ti}$  resonance (cf. Fig. 6). We assign the additional resonance line to the methyl groups attached to titanium cation in the solvent-separated ion-pair form of the mixed titanium—aluminium organometallic complex, i.e.  $[\text{TiMe}_3]^+ [\text{AlMe}_4]^-$ . The absorption corresponding to methyl groups attached to such a cation should appear considerably downfield with respect to the methyl resonance in the corresponding neutral organometallic species. The methyl signal of  $(\text{CH}_3)_2\text{Tl}^+$  in trifluoroacetate is actually observed at  $\tau$  8.45 ppm [6] whereas that of  $(\text{CH}_3)_3\text{Tl}$  appears at  $\tau$  9.48 ppm [7]. The  $\text{CD}_3\text{—Al}$  signal of the complex appeared at  $\tau$  10.8 ppm in good agreement with  $^1\text{H}$  data for the complex  $\text{Li}^+[\text{Al}(\text{CH}_3)_4]^-$  ( $\tau$  11.1 ppm [1]). It is interesting to note that the downfield shift induced by the formation of a cation is much greater than the upfield shift for the formation of an anion ( $\tau$  10.8 ppm for  $[\text{Al}(\text{CD}_3)_4]^-$  as against  $\tau$  10.3 ppm for  $\text{Al}_2(\text{CD}_3)_6$ ). This difference may be attributed to the positive inductive effect characteristic of the methyl group. The concentration of cations present as estimated from the spectra (about 0.06 *M* in Fig. 5 and  $\sim$  0.12 *M* in Fig. 6) far exceeds any conceivable concentration for the free ions in a hexane solution containing 0.9 *M* ether. The downfield signal must therefore be ascribed to the methyl groups present in the cations of the solvent-separated ion pairs. The results obtained on addition of ether to the  $\text{Al}_2\text{Me}_6\text{—TiMe}_4 \cdot \text{Et}_2\text{O}$  system indicate that the solvent-separated ion-pair form of the titanium—aluminium complex is only obtained with the trimethylaluminium etherate.

The most striking features of this study are that aluminium alkyls react more readily with tetramethyltitanium etherate than with excess ethyl ether. It is precisely this reactivity of aluminium alkyls during complexation with titanium derivatives, which results in the formation of a titanium-bearing cation, that presumably gives organoaluminium compounds their unique role in the preparation of highly active Ziegler catalysts. A titanium-bearing complex cation has already been suggested as the active site of Ziegler—Natta polymerization, this

conclusion being drawn from electro dialysis data obtained for the systems  $\text{Cp}_2\text{TiCl}_2\text{—AlR}_2\text{Cl}$  [8] and  $\text{Ti}(\text{OBu})_4\text{—AlEt}_3$  [9].

The slow dissociation of the active complex into the initial organometallic species as revealed by our data is consistent with the observed low relative probability of chain transfer to excess aluminium alkyl which results in the formation of long-chain macromolecules.

The mechanism outlined for methyl exchange between titanium and aluminium atoms may also be employed to explain certain features of the kinetics of Ziegler polymerization, viz. the decrease in the rate of polymerization at constant monomer concentration irrespective of the lack of termination [10]. A reaction mechanism involving fast initiation and living chain propagation accompanied by reversible deactivation has been suggested in this case. It seems reasonable to suggest that initiation occurs through the rapid formation of a titanium—aluminium organometallic complex and the subsequent slow reverse reaction accounts for the decrease in rate until equilibrium is attained; this then corresponds to the stationary rate of polymerization.

## Experimental

All operations involving organometallic compounds were performed under an argon atmosphere or in vacuum. Measured amounts of the reagents were introduced into an NMR tube and sealed. The trimethylaluminium solution was placed in a capillary inside of the NMR tube and mixing of the reactants was performed after the sample had reached thermal equilibrium in the probe of the spectrometer.

The preparation of tetramethyltitanium and trimethylaluminium has been described elsewhere [3]. The hexane used as the solvent was dried over calcium hydride. The concentrations of the various organometallic compounds were determined by decomposing sample aliquots with water. The aluminium content was subsequently determined by EDTA titration, while that of titanium was measured in terms of the percentage absorption at 385 nm of the titanium complex formed with hydrogen peroxide. The ethyl ether/hexane ratio of the solvent was estimated from  $^1\text{H}$  NMR spectra.

NMR spectra were recorded on a Bruker Spectrospin HX-90 spectrometer equipped with a low temperature probe using 90 MHz for protons and 13.81 MHz for deuterons. The trifluoromethyl signal of  $\text{CF}_3\text{CF}_2\text{COOCH}_3$  was used for  $^{19}\text{F}$  external lock and the  $^2\text{D}$  chemical shifts are referred to the perdeuteromethyl group of toluene- $d_8$  which was assigned a  $\tau$  value of 7.68 ppm [3,11]. The half-intensity width of this line was 0.2 Hz at room temperature while that of the  $\text{CD}_3\text{—Al}$  line in the mixture with tetramethyltitanium was 0.55 Hz at  $-20^\circ$ .

## Acknowledgment

The authors are grateful to V.P. Ivanova for valuable experimental assistance.

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