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THE FORMATION OF ORGANOTITANIUM-(II) AND -(IV) COMPOUNDS FROM TITANIUM TRICHLORIDE

S.I. BEILIN, S.B. GOLSTEIN and B.A. DOLGOPLOSK *

Institute of Petrochemical Synthesis of the U.S.S.R. Academy of Sciences, Moscow V-71 (U.S.S.R.)

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Summary

Interaction between titanium trichloride and trimethylsilyllithium (RLi) in hydrocarbon media provides TiR_2 and TiR_4 .

Recently, it has been shown [1,2], that interaction of $TiCl_4$ with trimethylsilyllithium (RLi) or $RMgCl$ provides TiR_4 or compounds of general formula R_nTiCl_{4-n} depending on the reagents ratio.

In this paper we describe the results obtained in the study of the reaction between $TiCl_3$ and $LiCH_2Si(CH_3)_3$ in hydrocarbon media. The experimental data are given in Table 1. The interaction of these reagents at a molar ratio of $Li/Ti = 1.5$ (see Table 1, exp. 1—3) results in a partial dissolving of titanium, LiR being completely used. The NMR spectra of the soluble reaction products are identical to that of TiR_4 [1]. The decomposition of these products, the solvent being preliminary removed in vacuum, by 5% aqueous H_2SO_4 produced about 4 mol of tetramethylsilane (RH) per mol of titanium.

We also investigated the composition of the precipitate (Table 1, exp. 1—3). For this purpose the precipitate was completely dissolved in deaerated H_2SO_4 solution. Mass-spectral measurements showed that the gas evolved during the decomposition consists only of hydrogen and tetramethylsilane. The quantitative composition of this gas was studied by GLC and volumetric methods. The content of titanium(II) was calculated using the data of hydrogen formation. The comparison of H_2 and RH amounts leads us to the conclusion that this precipitate consists of TiR_2 . Data of the total content of Ti and Cl in H_2SO_4 solution enable us to calculate the amounts of unreacted $TiCl_3$ and LiCl. Nearly all the titanium was transferred into solution when the reaction proceeds at a molar ratio $Li/Ti = 10$ (Table 1, exp. 4,5). In this case the equimolar amounts of TiR_4 and TiR_2 were found in the solution. The solubility of TiR_2 appeared to be due to complexation of this compound with the excess of LiR.

TiR_4 which can also be synthesised by another method proved to be a stable

TABLE I
COMPOSITION OF PRODUCTS OBTAINED IN THE INTERACTION OF TiCl_3 WITH $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$ (MMOL)
Temperature 20°C ; solvent, toluene/hexane (1 : 1 v/v)

Experiment number	Initial amount of TiCl_3	Initial mole ratio Li/Ti	Compounds identified after the action of dilute H_2SO_4 on the reaction products		Composition of reaction products (based on the analysis of gas and solution)						
			Ti	RH	TiR ₄	TiR ₂	LiR	TiCl ₃			
			From precipitate		From solution						
			Ti	H ₂	Ti	H ₂	RH				
			Total		Ti	H ₂	RH				
1	1.0	1.5	0.74	0.14	0.60	0	1.0	0.26	0.28	0	0.45
2	0.8	1.5	0.62	0.10	0.45	0	0.73	0.18	0.20	0	0.42
3	0.8	1.5	0.60	0.09	0.37	0	—	0.20	0.18	0	0.42
4	0.5	10	0.03	—	—	0.47	0.1	0.25	0.22	3.3	0.03
5	0.6	10	0.02	—	—	0.58	—	0.58 ^a	3.9	3.9	0.02

^a TiR₄ + TiR₂.

compound, which was soluble in hydrocarbons. This fact as well as the aforementioned experimental data show that the disproportionation reactions of titanium(III) compounds proceed at the stage of alkyltitanium chlorides formation.

References

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