Chemistry

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1964

SovietRxiv

Abstract

Full Text

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DECOMPOSITION OF BIS(CYCLOPENTADIENYL) DERIVATIVES OF TITANIUM IN SOLVENTS

In our previous papers (^{1,2}), homolytic reactions of the thermal decomposition of bis(cyclopentadienyl)diphenyltitanium in various organic solvents were investigated. It was shown that in all these cases $(C_5H_5)_2Ti(C_6H_5)_2$ loses two phenyl radicals and the tetravalent titanium compound is reduced to divalent—bis(cyclopentadienyl)titanium.

It was of interest to follow whether the character of the decomposition of $(C_5H_5)_2TiR_2$ changes when an aryl group is replaced by an alkyl group. For this purpose we studied the reactions of thermal decomposition of bis(cyclopentadienyl)diphenyltitanium and bis(cyclopentadienyl)dimethyltitanium in *n*-hexane and tetrahydrofuran. On heating solutions of these compounds in evacuated sealed ampoules, a change in color was observed, from yellow to dark green in *n*-hexane and to brown in tetrahydrofuran, occurring very rapidly after a certain induction period.

Fig. 1. Curve of the change in the relative magnitude of the EPR signal during the reaction of $(C_5H_5)_2Ti(C_6H_5)_2$ in THF

It was found that, on heating the reaction mixture in *n*-hexane, a line appeared in the electron paramagnetic resonance (EPR) spectrum characteristic of Ti^{3+} with $g = 1.98$. After prolonged heating of the ampoule, the EPR signal disappeared completely. In *n*-hexane the decomposition was accompanied by precipitation. At the same time, the system gave a strongly broadened and poorly reproducible EPR spectrum. The use of tetrahydrofuran as solvent proved more convenient, since a homogeneous reaction mixture is formed in it. After heating for one hour, an EPR line belonging to Ti^{3+} appears in the EPR spectrum. On further heating the intensity of this line increases sharply, reaches a maximum, and then decreases practically to zero (Fig. 1). All this indicates that the decomposition proceeds by successive detachment of radicals with the formation of intermediate compounds of trivalent titanium, which subsequently decompose to compounds of divalent titanium that give no EPR signal. Both bis(cyclopentadienyl)dimethyltitanium and bis(cyclopentadienyl)diphenyltitanium behave completely identically in these reactions. Thus, it may be assumed that the process proceeds according to the scheme:

$$(C_5H_5)_2TiR_2 \to (C_5H_5)_2TiR + R\cdot, \tag{1}$$

$$(C_5H_5)_2TiR \to (C_5H_5)_2Ti + R\cdot. \tag{2}$$

The only products of the transformation of phenyl and methyl radicals in tetrahydrofuran and *n*-hexane were benzene and methane, which were obtained in quantitative yield calculated for two groups.

From literature data it is known that bis(cyclopentadienyl)dimethyltitanium in a solution of *n*-hexane, under the action of hydrogen, is readily reduced to bis(cyclopentadienyl)titanium, which precipitates as an insoluble black solid ([3]). In this case the methyl groups give methane quantitatively. The formation of methane and an insoluble black precipitate was observed by us during the thermal decomposition of bis(cyclopentadienyl)dimethyltitanium in *n*-hexane.

A similar black precipitate was also obtained as a result of the decomposition of biscyclopentadienyldiphenyltitanium in *n*-hexane. The precipitate dissolves in tetrahydrofuran, giving a green solution which apparently contains one of the forms of the tetrahydrofuranate.

It was previously reported (4) that biscyclopentadienyltitanium, obtained by the interaction of titanium dichloride with sodium cyclopentadienide in tetrahydrofuran, forms more stable tetrahydrofuranates, which can exist in two forms. Under the conditions of our thermal reactions of biscyclopentadienyldiphenyltitanium and biscyclopentadienyldimethyltitanium in tetrahydrofuran solution, the brown form of the tetrahydrofuranate was obtained. Thus, biscyclopentadienyltitanium can be obtained not only by reduction with hydrogen, but also upon thermal decomposition of the indicated compounds.

When hydrogen chloride acts on the tetrahydrofuranate of biscyclopentadienyltitanium, hydrogen is evolved and 99% biscyclopentadienyltitanium dichloride is formed, calculated on the initial titanium:

$$(C_5H_5)_2Ti \cdot THF + 2HCl \to (C_5H_5)_2TiCl_2 + H_2 + THF. \tag{3}$$

The reaction with corrosive sublimate, proceeding with the formation of calomel and biscyclopentadienyltitanium dichloride, does not give a quantitative yield of the latter.

The formation of titanocene dichloride was observed in studying the interaction of biscyclopentadienyldimethyltitanium with chloroform and carbon tetrachloride. In these reactions it was also of interest to trace the effect of replacing the phenyl group by methyl. Upon thermal decomposition in chloroform, methane and biscyclopentadienyltitanium dichloride are formed in almost quantitative yield. As a result of the reaction in carbon tetrachloride, methyl chloride, hexachloroethane, and titanocene dichloride were isolated. Thus, it is evident that the products obtained correspond to a free-radical scheme, as in the case of biscyclopentadienyldiphenyltitanium. The initial act of the reaction is the decomposition of biscyclopentadienyldimethyltitanium with cleavage of methyl radicals, which interact with CCl_4, forming methyl chloride and hexachloroethane:

$$(C_5H_5)_2Ti(CH_3)_2 \to (C_5H_5)_2Ti + CH_3\cdot, \tag{4}$$

$$CH_3 \cdot + CCl_4 \to CH_3Cl + [\cdot CCl_3], \tag{5}$$

$$[\cdot CCl_3] \to \tfrac{1}{2}C_2Cl_6. \tag{6}$$

Biscyclopentadienyltitanium reacts with carbon tetrachloride, passing into biscyclopentadienyltitanium dichloride, as we proved by experiments carried out earlier (1):

$$(C_5H_5)_2Ti \xrightarrow{CCl_4} (C_5H_5)_2TiCl_2. \tag{7}$$

Exchange of methyl groups for halide can also proceed by a heterolytic route. The reaction was studied using as an example the interaction of biscyclopentadienyldimethyltitanium with corrosive sublimate, carried out on heating in CCl_4 solution with stirring in a nitrogen atmosphere. The formation, as the only products, of titanocene dichloride and methylmercury chloride made it possible to conclude that the exchange reaction proceeds according to the equation:

$$(C_5H_5)_2Ti(CH_3)_2 + 2HgCl_2 \to (C_5H_5)_2TiCl_2 + 2CH_3HgCl. \tag{8}$$

Thus, on the basis of the experimental data obtained, it may be concluded that the nature of the R radical does not affect the general character of the exchange and decomposition reactions of $(C_5H_5)_2TiR_2$.

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Received
2 VII 1964

CITED LITERATURE

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