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FIXATION OF MOLECULAR CARBON DIOXIDE IN THE SYSTEM $TiCl_4$—Mg IN TETRAHYDROFURAN UNDER MILD CONDITIONS

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Summary

We have found that in the system $TiCl_4$—Mg—THF two CO_2 moles per titanium mole can be fixed. $[THFTi(OOCH)_2MgCl_{1.5}]$ is formed. This reacts with acid to give HCOOH, and with C_2H_5I to give the ester $HCOOC_2H_5$. The system $TiCl_4$—Mg—THF under argon yielded $[THFMg_2Cl_2Ti]_2$ which was isolated and which kept its activity towards carbon dioxide.

Introduction

The system $TiCl_3 \cdot 3THF + Mg + THF$ has been examined by several authors for its ability to fix and reduce molecular nitrogen [1], carbon monoxide [2] and ketones [3], under mild conditions.

$$TiCl_3 \cdot 3THF + 2.5Mg + 0.5N_2 \rightarrow TiNMg_2Cl_2 \cdot THF + 1/2MgCl_2(THF)_2 \quad (1)$$

$$TiCl_3 \cdot 3THF + 2.5Mg + 2CO \rightarrow \text{product} \xrightarrow{H_2O} C_2H_2 \quad (2)$$

$$TiCl_3 \cdot 3THF + Mg + THF \xrightarrow[40^\circ C]{Ar} [M] \quad (3)$$

$$[M] + RR'C=O \xrightarrow[40^\circ C]{} RR'C=CRR' \quad (4)$$

Molecular nitrogen (1) forms the compound $TiNMg_2Cl_2 \cdot THF$ which after hydrolysis yields the stoichiometric amount of ammonia. Carbon monoxide (2) gives rise to a product which after hydrolysis yields acetylene. The introduction of ketone to that system (reaction 4) under argon atmosphere at 40°, results in the formation of the appropriate unsaturated hydrocarbon. Also the fixation of two CO_2 molecules per titanium atom has been observed in this system [1c]. We have examined the mechanism and the rate of the carbon dioxide fixation by the system $TiCl_4 \cdot 2THF + Mg + THF$ under mild conditions as well as the new compounds formed and their method of preparation.

Results

CO_2 fixation by the system $TiCl_4$—Mg—THF was studied by treating various molar concentrations of $TiCl_4 \cdot 2THF$ in tetrahydrofuran with metallic magnesium at various stoichiometric ratios (Table 1), under argon. During the reaction the solution changes its colour from yellow via green and blue to black. 20 h after the reaction started, argon was replaced by the pure carbon dioxide. With excess magnesium a complex was formed, which was assigned the formula $[THF \cdot Ti(OOCH)_2MgCl_{1.5}]$, on the basis of quantitative analysis, EPR and magnetic susceptibility measurements and the IR spectra (reaction 5). The compound is diamagnetic and in the IR, besides the frequencies of the coordinated tetrahydrofuran molecule, the frequencies 1640, 1530, 1420 and 830 cm^{-1} of a coordinated carbon dioxide molecule were observed.

$$2TiCl_4 \cdot 2THF + 6Mg + 2THF \xrightarrow[20\ h,\ 20^\circ]{Ar} [THF \cdot Cl_2Mg_2Ti]_2 + 2MgCl_2(THF)_2 \longrightarrow$$

$$\xrightarrow{CO_2} [THF \cdot Ti(OOCH)_2MgCl_{1.5}] \qquad (5)$$

We did not succeed in isolating the pure compound $[THF \cdot Cl_2Mg_2Ti]_2$ formed in reaction 5 under argon. The composition of the complex isolated by addition of cyclohexane to the system varies between $THF \cdot Cl_{2.3}Mg_{2.1}Ti$ and $THF \cdot Cl_{2.7}Mg_{2.4}Ti$. This probably indicates the presence of $MgCl_2$ impurities in the real compound. The complex isolated $[THFCl_2MgTi]_2$ is diamagnetic and keeps its activity after isolation. Its benzene solution can also fix the carbon dioxide. The reaction of $[THFTi(OOCH)_2MgCl_{1.5}]$ with the dilute sulphuric acid yields formic acid, in about 30% yield based on the carbon dioxide fixed (Table 1). The reaction with C_2H_5I yields ethyl formate.

The typical example of the rate of carbon dioxide fixation in the system $TiCl_4$—Mg—THF is given in Fig. 1. CO_2 fixation is practically complete in 20 min. Carbon dioxide is soluble in tetrahydrofuran to the extent of 158 ml/50 ml at 20°, under normal pressure. The total amount of the magnesium that reacts in the system $TiCl_4$—Mg—THF under argon is 3 moles per mole of titanium. At a Mg/Ti ratio $\geqslant 3$, 2 moles of CO_2 are fixed per titanium (curve A, Fig. 1), whereas at Mg/Ti ratios of 1 or 2 only 1 mole of CO_2 is fixed per titanium mole (curve B, Fig. 1). The amount of CO_2 fixed depends only on the magnesium/titanium ratio, not on its concentration (Table 1). EPR studies of the solutions at various

TABLE 1

DEPENDENCE OF THE CARBON DIOXIDE UPTAKE ON THE MAGNESIUM/TITANIUM MOLAR RATIO AND ITS CONCENTRATION IN THE SYSTEM $TiCl_4$—Mg—THF

$TiCl_4 \cdot 2THF$/Mg molar ratio	Concentration of the $TiCl_4 \cdot 2THF$ (mol l^{-1})	CO_2/Ti molar ratio	Percentage of CO_2 converted to HCOOH
1/0.5	0.070	0.5	
1/1	0.070	0.91	
1/2	0.070	0.97	
1/3	0.070	2.01	31.8
1/20	0.057	2.01	30.9
1/20	0.095	2.02	31.2
1/20	0.178	1.98	31.7
1/20	0.270	2.03	31.2

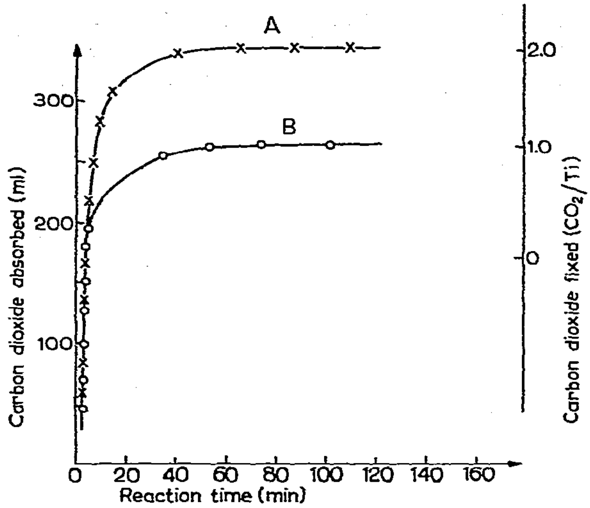


Fig. 1. CO_2 fixation by $TiCl_4$—Mg system at 20°C. Curve A: $TiCl_4$/Mg molar ratio = $1/x$ (x = 3, 4, ..., 20). Curve B: $TiCl_4$/Mg molar ratio = 1/1 or 1/2.

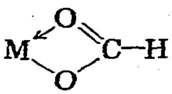
titanium/magnesium ratios indicated weak paramagnetism of the compounds even at a hundredfold excess of magnesium and a field strength of 2.00 G (the signal only appears after 100 fold reinforcement). CO_2 fixation did not occur when the reaction using the system $TiCl_4$ —Mg—THF was carried out under a carbon dioxide atmosphere (the solution was diamagnetic). This is most probably due to the deactivation of the metallic magnesium surface by carbon dioxide and as a result the reduction of the titanium(IV) is impossible. During the reaction under argon atmosphere and during CO_2 fixation, hydrocarbons, principally methane, and hydrogen were liberated. Chromatographic studies indicated that the hydrolysis products obtained under argon atmosphere without CO_2, and the products containing fixed carbon dioxide were identical.

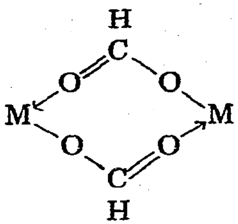
Discussion

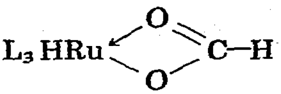
On the basis of the results obtained in the system $TiCl_4$—Mg—THF the reaction may be written as in eqn. 6, in which Ti^{IV} is reduced to Ti^{II} by metallic

$$2TiCl_4 \cdot 2THF + 6Mg + 4THF \rightarrow [THF \cdot Cl_2Mg_2Ti]_2 + 2MgCl_2(THF)_2 \qquad (6)$$

magnesium. This is suggested by the similarity of the potentials of Mg/Mg^{2+} and Ti^{4+}/Ti^{+2}, which were determined polarographically in tetrahydrofuran [4]. Magnesium in the complex $[THF \cdot Cl_2Mg_2Ti]_2$ is in the zero oxidation state, as indicated by the studies of Yamamoto et al. [1a, b] who proved that one of the magnesium atoms in $TiNMg_2Cl_2 \cdot THF$ is in the zero oxidation state. In the system $TiCl_4$—Mg—THF the reduction of Ti^{IV} by metallic magnesium gives rise to $MgCl_2(THF)_2$. Magnetic susceptibility measurements indicated the complex $[THF \cdot Cl_2Mg_2Ti]_2$ to be diamagnetic, which since titanium is in the +2 oxidation state (d^2) indicates a strong exchange interaction of the type $-JS_1S_2$. The carbon dioxide fixation probably occurs as follows: carbon dioxide molecules in the complex [THF·Ti(OOCH)$_2$MgCl$_{1.5}$] are coordinated by oxygen, (A) or (B), as suggested by the IR vibration frequencies at 1640, 1530, 1420 and 830 cm^{-1}, which are similar to those in (C) [5]. Reaction of [THF·Ti(OOCH)-MgCl$_{1.5}$] with C$_2$H$_5$I yields ethyl formate and its hydrolysis yields the formic acid (eqn. 7). This indicates that hydrogen is bound to the carbon atom of the coordinated CO$_2$ molecule. Thus, in the system discussed, titanium hydride or magnesium hydride are most probably formed as intermediate products, since only metal hydride complexs are known to react with carbon dioxide with the formation of carbon—hydrogen bonding [5, 6]. Additional evidence is provided in the IR for the [THF·Cl$_2$Mg$_2$Ti]$_2$ complex, in which no Ti—H vibrations are observed possibly indicating the presence of magnesium hydride. Weak paramagnetic properties of solutions in the system discussed, together with the hydrocarbons and hydrogen liberated, indicate that Ti$^{\mathrm{II}}$ reacts with tetrahydrofuran. As a result the hydrocarbons are formed and titanium is oxidised to Ti$^{\mathrm{III}}$ under the influence of a small amount of water that is also formed in that process [7]. Ti$^{\mathrm{III}}$ is reduced again by the magnesium excess, and the hydrogen liberated can react with magnesium to form its hydride.


(A) (M = Ti, Mg)


(B)


(C)

$$[\mathrm{THF}\cdot\mathrm{Cl_2Mg_2Ti}]_2 + 2\mathrm{CO_2} \rightarrow [\mathrm{THF}\cdot\mathrm{Ti(OOCH)_2MgCl_{1.5}}] \left\{ \begin{array}{l} \xrightarrow{\mathrm{H^+}} \mathrm{HCOOH} \\ \xrightarrow{\mathrm{C_2H_5I}} \mathrm{HCOOC_2H_5} \end{array} \right. \qquad (7)$$

Experimental

Examination of the CO$_2$ fixation rate

The rate of CO$_2$ fixation in the system TiCl$_4$·2THF + Mg + THF was determined in a glass vessel with a reflux condenser connected to a burette filled with mercury. The vessel was thermostatted to ± 0.1°. The pressure was kept constant and the amount of carbon dioxide fixed was read off the burette. The solution of the appropriate TiCl$_4$·2THF concentration in tetrahydrofuran was treated with metallic magnesium (chips) in various stoichiometric concentrations (Table 1). 20 h after the reaction started, argon was replaced by carbon dioxide at 20° and the reaction time was measured from that moment. The amount of the carbon dioxide fixed was established by the diminishing CO$_2$ solubility in tetrahydrofuran.

Analytical methods

The amount of the formic acid was determined as follows: The [THF·Ti(OOCH)$_2$MgCl$_{1.5}$] complex containing the fixed carbon dioxide was filtered off from magnesium under argon and the excess tetrahydrofuran was distilled off. The remains were treated with dilute sulphuric acid (1/10) and distilled. The distillate was treated with 50 ml 0.1 *N* $KMnO_4$, neutralized with Na_2CO_3 and heated on the water bath for 30 min. After cooling, the solution was diluted to 100 ml, acidified with dilute sulphuric acid and 2 g KI were added. The liberated iodine was titrated against 0.1 *N* $Na_2S_2O_3$.

IR measurements were made in nujol mulls and KBr discs on a Perkin—Elmer 621, and the EPR measurements on a JEOL 3BX. Chromatographic measurements were performed on an N-503 of Polish production.

Substrates

$TiCl_4 \cdot 2THF$ was obtained by the slow addition of $TiCl_4$ to tetrahydrofuran under argon with constant stirring. The product was recrystallized from tetrahydrofuran and dried under vacuum.

Carbon dioxide, obtained by treatment of Na_2CO_3 with H_2SO_4, was passed through a molecular sieve column. Tetrahydrofuran was distilled from $LiAlH_4$ immediately before each reaction.

Syntheses

[THF·Ti(OOCH)₂MgCl₁.₅]. $TiCl_4 \cdot 2THF$ (2 g) was dissolved in tetrahydrofuran (50 ml) under argon and metallic magnesium (2 g, chips) was added. The solution turned from yellow via green and blue to black. During the exothermic reaction the liberation of hydrogen and hydrocarbons, mainly methane, was observed. After two hours the black filtrate was removed and washed with tetrahydrofuran. We failed to recrystallize the product because it was insoluble in benzene, tetrahydrofuran, diethyl ether, petroleum ether and acetone. (Found: C, 25.64; H, 3.27; Cl, 18.53; Ti, 16.89; Mg, 8.47; $C_6H_{10}Cl_{1.5}MgO_5Ti$ calcd.: C, 25.14; H, 3.49; Cl, 18.40; Ti, 16.69; Mg, 8.47%).

$[THF \cdot Cl_2Mg_2Ti]_2$. $TiCl_4 \cdot 2THF$ (2 g) was dissolved in tetrahydrofuran (50 ml) under argon and metallic magnesium (2 g) was added. After 20 h the solution was separated from the excess magnesium and treated with cyclohexane under an argon atmosphere. The isolated black filtrate was washed with a mixture of cyclohexane and tetrahydrofuran. The quantitative composition of the filtrate varied within the limits from $THF \cdot Cl_{2.3}Mg_{2.1}Ti$ to $THF \cdot Cl_{2.7}Mg_{2.4}Ti$.

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