APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2001; **15**: 161–168

Synthesis of magnesium dicyclopentadienide catalyzed by titanium and vanadium derivatives†

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Synthesis of magnesium dicyclopentadienide from metal and cyclopentadiene in THF is effectively catalyzed by the derivatives of vanadium and titanium. The kinetics of the synthesis, as well as thermodynamic parameters of reagents adsorption on the magnesium surface, have been determined. The process catalyzed by titanium derivatives is accompanied by the quantitative hydrogenation of cyclopentadiene to cyclopentene whereas the catalysis by vanadium derivatives leads to hydrogen gas evolution. A number of reaction intermediates including Cp_2TiCl, Cp_2TiH_2MgCl, $Cp_2Ti(cyclo\text{-}C_5H_7)$ and Cp_2V, were identified by the electron spin resonance method. The equilibrium constants, enthalpies and entropies of adsorption of metal halides on the magnesium surface were calculated.

Keywords: magnesium; dicyclopentadienide; cyclopentadiene; kinetics; catalytic; titanocene; vanadocene; hydrogenation

INTRODUCTION

The synthesis of magnesium dicyclopentadienide from metal and cyclopentadiene in THF catalyzed by $CpTiCl_3$ has been known for quite a long time.[1]

$$3CpH + Mg \xrightarrow{CpTiCl_3,THF} Cp_2Mg + C_5H_8 \qquad (1)$$

Hydrogen of a cyclopentadiene molecule is not evolved as a gas during the reaction but is quantitatively consumed on the hydrogenation of cyclopentadiene to cyclopentene. Later it was found that different derivatives of titanium(IV) including $TiCl_4$, Cp_2TiCl_2 and $Ti(OBu)_4$, effectively catalyze reaction [1].[2] The reaction can be accomplished at moderate conditions (even at 0 °C) and with high yield (up to 95%). It was proven that the role of titanium compounds is not limited to the activation of the metal surface. Magnesium activated by iodine or dibromoethane did not react with cyclopentadiene.[1]

However, very little information was obtained about the kinetics and mechanism of the reaction. It was suggested[2] that the low-valent titanium complex $[THF{\cdot}TiMg_2Cl_2]^3$ (*I*) participates in the catalytic cycle, but no evidence was provided for it.

Therefore, studying the kinetics and intermediates of the reaction is important for optimizing reaction conditions and understanding its mechanism. Moreover, the catalytic properties of this system are relevant to other important processes, such as nitrogen and hydrogen fixation, polymerization, oligomerization and isomerization and other important reactions.

In this work we studied the following:

- the effect of catalyst nature (titanium and vanadium derivatives) on the kinetics, mechanism and product yields of the reaction;
- the kinetics of separate steps of the catalytic process and the thermodynamic characteristics

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† Presented at the XIIIth FECHEM Conference on Organometallic Chemistry, 27 August–3 September 1999, Lisbon, Portugal.

of the reagent's adsorption on the surface of magnesium.

EXPERIMENTAL

All reactions were carried out under vacuum or under anhydrous and oxygen-free argon. Tetrahydrofuran and diglyme were dried over sodium hydroxide and distilled over sodium–benzophenone composition. Diethyl ether and benzene were dried over calcium chloride and distilled over sodium wire.[4] Cyclopentadiene was distilled shortly before the reaction. Magnesium turnings and magnesium wire ($d = 0.5$ mm, magnesium content >99.9%) were used without additional treatment of the surface. Titanium chloride (**IV**) was purified by distillation over copper wire.[5] The solution of $TiCl_3$ in THF was obtained by reducing $TiCl_4$ by 3% excess of metallic magnesium in THF and then used *in situ*.

Vanadium chloride (**III**) was dissolved in THF, recrystallized and then used as $VCl_3 \cdot 3THF$.[6] The concentrations of VCl_3 and $TiCl_4$ in the solutions were determined by the analysis on chlorine and metals.[7] The complex **I**,[3] Cp_2V[8] and Cp_2TiCl[9] were synthesized by known methods.

The kinetics of Cp_2Mg and cyclopentene formation from CpH and magnesium in the presence of titanium and vanadium derivatives was studied as follows. To magnesium turnings, a known quantity of the titanium or vanadium compound solution in THF was added. The reaction started almost immediately with the color of the reaction mixture changing from yellow via violet to black (in the case of $TiCl_4$) or from red via green to black (in the case of VCl_3 and Cp_2TiCl_2). Then a certain volume of cyclopentadiene was added. During the reaction, probes of the reaction mixture were taken and analyzed for Cp_2Mg and cyclopentene concentration.

Magnesium dicyclopentadienide concentration was determined by the acido-basic titration. Cyclopentene was analyzed by gas chromatography; conditions of analysis: glass column 3000 × 5 mm with 10% Reoplex on Cellit 545 at 25 °C, helium flow rate 60 ml min^{-1}. The quantity of dihydrogen evolved from reaction mixtures was determined volumetrically and by gas chromatography; conditions of analysis: glass column 1000 × 5 mm with activated charcoal at 30 °C, helium flow rate 40 ml min^{-1}.

The rates of the magnesium reactions with titanium and vanadium chlorides were measured by controlling the electric resistance of the magnesium wire put in the reaction mixture.[10] This method was modified for experiments performed in inert atmosphere.

Electron spin resonance (ESR) spectra were recorded on a Bruker ESR-2000-SRC spectrometer with a standard double resonator ER-4105-DR with a frequency of 9.5 GHz. Diphenylpicrylhydrazyl was used as a reference for determining the *g*-factor. The concentration of paramagnetic species was estimated by using the THF solution of Cp_2TiCl (0.012 mol l^{-1}) as a reference. ESR measurements were performed in the analytical center of the G. A. Razuvaev Organometallic Chemistry Institute (Nizhny Novgorod, Russia) by Professor Vladimir K. Cherkasov.

RESULTS AND DISCUSSION

It transpired that both titanium and vanadium complexes in any state of oxidation effectively catalyze the formation of magnesium dicyclopentadienide from metal and cyclopentadiene in THF at room temperature. Diethyl ether, diglyme and benzene have been tried as a solvent, but only the polymerization of CpH occurred instead of Cp_2Mg synthesis.

The following catalysts were compared in terms of the Cp_2Mg yield (related to cyclopentadiene) and reaction time: $TiCl_4$, $TiCl_3$, Cp_2TiCl_2, VCl_3. The results of the comparison are given in the Table 1. The yields and reaction times in the case of $TiCl_4$, $TiCl_3$ and Cp_2TiCl_2 are of the same order as each other and coincide with previous results.[2] The small advantage in the rate of the reaction in the case of $TiCl_4$ may be explained by a stronger activation of the magnesium surface by $TiCl_4$. The catalysis by

Table 1 Reaction times and yields of Cp_2Mg related to cyclopentadiene in the Cp_2Mg synthesis catalyzed by $TiCl_4$, $TiCl_3$, Cp_2TiCl_2 and VCl_3. The catalyst concentrations are 0.08 mol l^{-1}, the starting concentrations of CpH are 2 mol l^{-1}; $T = 303$ K

Catalyst	Yield, (%)	Reaction time, (min)
$TiCl_4$	64	240
$TiCl_3$	63	300
Cp_2TiCl_2	65	300
VCl_3	81	1600

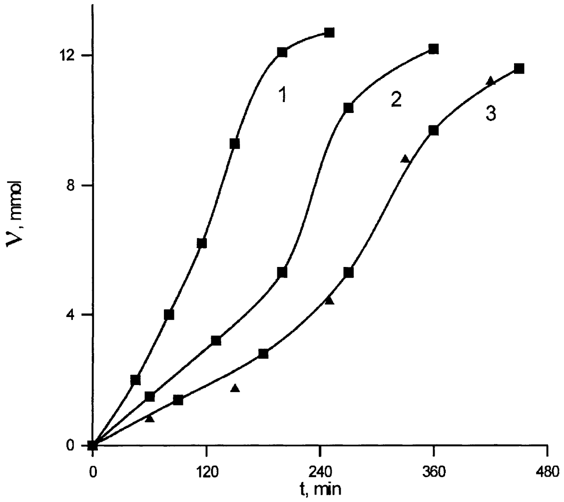


Figure 1 The formation of Cp_2Mg and cyclopentene during the interaction of magnesium with the solution of cyclopentadiene ($2\ mol\ l^{-1}$) in THF, in the presence of $TiCl_4$, V = 20 ml; T = 293 K; $C_{TiCl_4} = 0.08\ mol\ l^{-1}$ (1); $C_{TiCl_4} = 0.06\ mol\ l^{-1}$ (2); $C_{TiCl_4} = 0.04\ mol\ l^{-1}$ (3); ■ Cp_2Mg; ▲, cyclopentene.

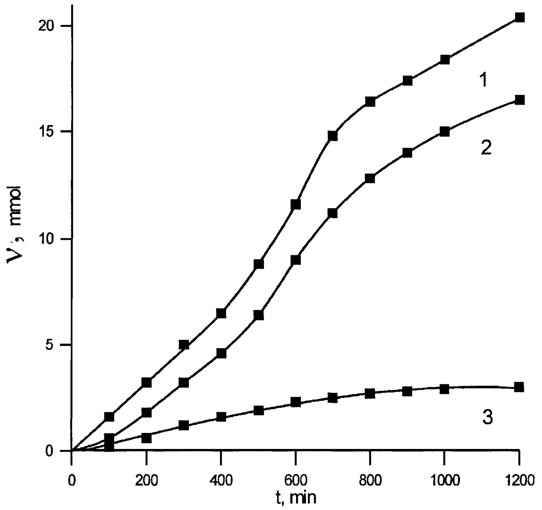


Figure 2 The formation of Cp_2Mg, hydrogen and cyclopentene during the interaction of magnesium with the solution of cyclopentadiene ($3\ mol\ l^{-1}$) in THF in the presence of VCl_3 ($0.11\ mol\ l^{-1}$); V = 20 ml; T = 293 K; (1) Cp_2Mg; (2) hydrogen gas; (3) cyclopentene.

vanadium derivatives occurs significantly more slowly (approximately five times). However, using vanadium compounds as catalyst has one advantage. Since less cyclopentadiene is hydrogenated, the yield of Cp_2Mg relative to CpH is approximately 20% higher.

The kinetics of the reaction have been studied for the following systems: $TiCl_4$–Mg–CpH–THF, $TiCl_3$–Mg–CpH–THF, $(TiMg_2Cl_2{\cdot}THF)_2$–Mg–CpH–THF, VCl_3–Mg–CpH–THF.

Typical kinetic curves of products formation in the presence of titanium and vanadium derivatives are shown in Figs 1 and 2. All these curves have an S-shape which is evidence for accumulation of catalytically active intermediates during the reaction. The catalysis by titanium derivatives is accompanied by the simultaneous quantitative hydrogenation of cyclopentadiene to cyclopentene, whereas a similar reaction catalyzed by vanadium derivatives gives rise to hydrogen gas, the yield of which depends on the conditions of the process and is 85% or more relative to starting cyclopentadiene. In this case the formation of cyclopentene does not correlate with dicyclopentadienide magnesium formation (Fig. 2).

The reaction of complex **I** with cyclopentadiene in the absence of magnesium did not lead to the formation of the magnesium dicyclopentadienide. However, cyclopentene is formed in the solution with 70% yield relative to the metal complex. Signals of titanium(III) compound appear in the EPR spectrum. Thus, the synthesis of Cp_2Mg is a heterogeneous process and cannot be accomplished in the absence of metallic magnesium. On the other hand, the formation of cyclopentene can also occur in the solution.

The ESR method was used to identify paramagnetic derivatives of titanium(III). During the reaction catalyzed by titanium derivatives the following signals are consequently observed in the isotropic spectra of the reaction mixture: (1) $g_1 = 1.951$, $a_{Ti} = 17.2$ G; (2) $g_2 = 1.978$; (3) $g_3 = 1.970$; (4) $g_4 = 1.984$, (5) $g_5 = 1.992$. When the reaction is completed, the triplet of multiplets with $g_6 = 1.993$, $a_{H_1} = 7.4$ G and $a_{H_2} = 0.43$ G prevails in the reaction mixture (Fig. 3).

The first signal probably belongs to $TiCl_3$ coordinated with $MgCl_2$.[11] The second one corresponds to Cp_2TiCl.[11] Signals three and four ($g_3 = 1.970$ and $g_4 = 1.984$) are hard to ascribe to a certain compound, though the former may belong to $CpTiCl_2$.[11] The signal with $g_5 = 1.992$ probably corresponds to allylic derivatives of titanocene.[12,13] A number of allylic compounds of titanocene were obtained by reacting the hydride derivative of titanocene (Cp_2TiAlH_4) with the corresponding

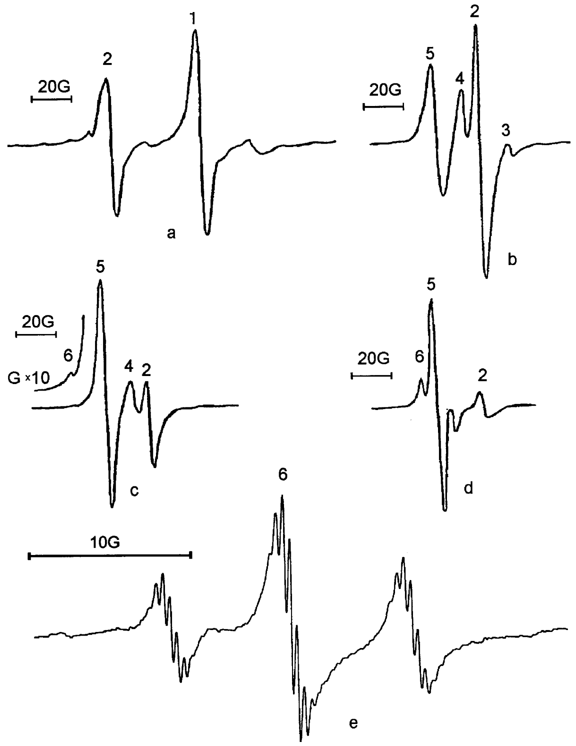
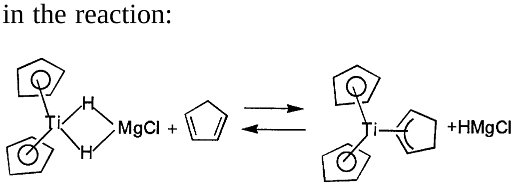


Figure 3 ESR spectra of the reaction mixture during the synthesis of magnesium dicyclopentadienide by the magnesium oxidation with cyclopentadiene ($2\,\mathrm{mol\,l^{-1}}$) in THF in the presence of $TiCl_4$ ($0.08\,\mathrm{mol\,l^{-1}}$); T = 295 K (a) 25 min; (b) 45 min; (c) 110 min; (d) 250 min; (e) 24 h after the beginning of the reaction.

dienes. ESR spectra of these compounds were characterized in detail. Their *g*-factors range from 1.9925 to 1.9937. The multiplicity of the signal depends on the allyl structure and dialkyl-substituted compounds give a multiplet with the order of hyperfine splitting constant 0.2–0.3 G.[13] In the reaction mixture there was only one diene that potentially could form allylic derivatives—cyclopentadiene. Thus, the signal probably belongs to dicyclopentadienylcyclopentenyltitanium formed in the reaction:



[2]

Unfortunately, it was not possible to achieve sufficiently high resolution of the ESR spectra in order to observe a hyperfine splitting on Cp-protons clearly. Finally, the parameters of the last signal correspond to the dihydride complex Cp_2TiH_2MgCl.[14,15]

The fact that dicyclopentadienylcyclopentenyltitanium was not preparatively obtained similar to the derivatives of other dienes[12] may be explained by equilibrium [2]. The signal of the allylic compound is observed only with excess of CpH. As CpH is consumed in the reaction, equilibrium [2] is shifted backwards. Similar results were obtained for different types of dienes.[13] In the case of cyclopentadiene the allylic derivative exists only as a transient species when excessive CpH is present. It is worthwhile noting that when the reaction was performed with excess of cyclopentadiene in comparison with magnesium metal, the signal of the allylic compound was observed even a week after the completion of the reaction and no dihydride signal appeared in the spectra.

ESR-monitored experiments with Cp_2TiCl_2 as a catalyst gave the same signals except for the first one ($g_1 = 1.951$, $a_{\mathrm{Ti}} = 17.2$ G) which is typical for inorganic derivatives of titanium(III). This is the evidence for the similarity of the catalysis mechanism, which does not depend on the form of the starting titanium compound.

The quantitative measurement of the titanium(III) compounds concentration during the reaction revealed that their average total concentration during the synthesis of Cp_2Mg is about 55% of the total titanium content. For example, 60 min after the beginning of the reaction ($C_{\mathrm{CpH}} = 2\,\mathrm{mol\,l^{-1}}$, $C_{\mathrm{TiCl_4}} = 0.08\,\mathrm{mol\,l^{-1}}$) the concentration of Cp_2TiCl was found to be around $0.03\,\mathrm{mol\,l^{-1}}$ whereas the concentration of $Cp_2Ti(cyclo\text{-}C_5H_7)$ was approximately $0.015\,\mathrm{mol\,l^{-1}}$. The dynamics of Cp_2TiCl and $Cp_2Ti(cyclo\text{-}C_5H_7)$ concentration during the reaction is shown in the Fig. 4. It turned out that the highest concentration of Cp_2TiCl is observed long before the rate of Cp_2Mg formation reaches its maximum, whereas the concentration of Cp_2Ti $(cyclo\text{-}C_5H_7)$ follows the rate of the products formation. This fact leads to the conclusion that $Cp_2Ti(cyclo\text{-}C_5H_7)$ may be an active intermediate of the process. The concentration of the Cp_2TiH_2MgCl at the end of the reaction reaches $0.035\,\mathrm{mol\,l^{-1}}$.

Kinetic data, as well as the results of ESR measurements, were the ground for some conclusions about the mechanism of the reaction. A number of the dicyclopentadienyltitanium derivatives found in the reaction mixture could be evidence for titanocene participation in the cata-

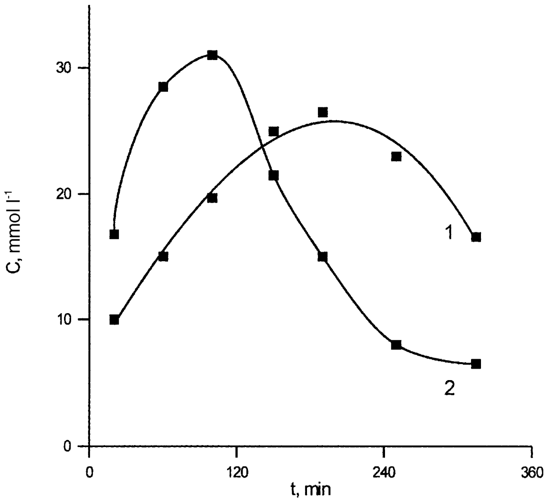
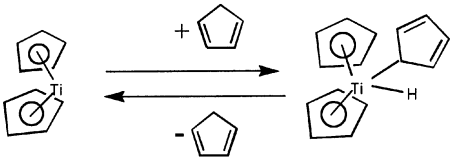


Figure 4 Changes of the concentration of $Cp_2TiC_5H_7$ (1) and Cp_2TiCl (2) during the synthesis of Cp_2Mg and cyclopentene by the oxidation of magnesium with CpH ($2\,mol\,l^{-1}$) in the THF solution in the presence of $TiCl_4$ ($0.08\,mol\,l^{-1}$); T = 295 K.

lysis. The formation of titanocene occurs via the reduction of Cp_2TiCl_2 by the metallic magnesium. In the case when $TiCl_4$ is used as a catalyst, Cp_2TiCl is formed in the reaction mixture and then also reduced to titanocene. The origination of Cp_2TiCl in the reaction mixture was not investigated in the present work, but there are two possible ways in which it could be formed. One is the reaction of $TiCl_3$ with Cp_2Mg.[16] However, it is not clear how Cp_2Mg could originate in the reaction mixture before the formation of the catalytically active particles. It was proven that Cp_2Mg cannot be formed by the direct reaction of CpH with magnesium in the absence of a catalyst or by a homogeneous reaction of CpH with **I**. Thus, it is possible that Cp_2Mg forms as a result of the interaction of low-valent titanium complexes with cyclopentadiene on the magnesium surface.

Titanocene possesses so-called ‘carbenoid’ properties, the most important being the ability to insert into labile C—H bonds.[17] When no active bonds are present in the system, the titanium atom of titanocene inserts into the C—H bond of its own Cp-ring, e.g. forming fulvalen compounds.[17–19] Permethyltitanocene was obtained by the decomposition of a corresponding dinitrogen complex. However, even in this relatively stable compound, titanium atom inserts into the C—H bond of a methyl group with a consequent decomposition.[20] Even the C—H bond of the phenyl group attached to the Cp ring is active towards low-valent titanium compounds.[21] However, when the system contains other active compounds, they can also interact with the titanium center. Cyclopentadiene contains the most active C—H bond among hydrocarbons. Thus, the insertion of the ‘carbenoid’ titanium atom in the acid C—H bond and consequent transmetallation gives rise to Cp_2Mg and hydride derivative of titanocene (Eqns [3] and [4]).



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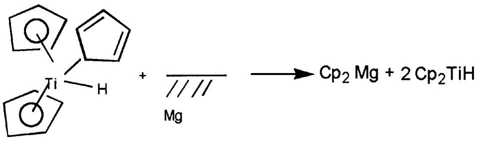
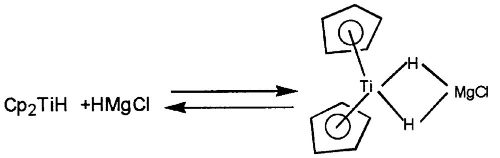
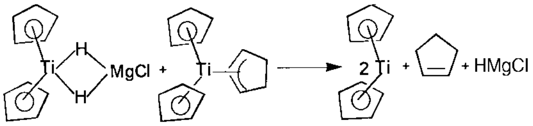


[4]

The latter forms the allylic derivative as a result of the reaction with cyclopentadiene (Eqn [2]). Finally, cyclopentene is formed and titanocene is released back in the reaction mixture (Eqn [6]).



[5]



[6]

Since titanocene is a highly unstable compound and cannot be detected directly, more evidence was needed in order to confirm the participation of metallocenes in the catalytic cycle.

Unlike titanocene, vanadocene is a relatively stable compound. Thus, it can be detected in the reaction mixture by using, e.g., the ESR method. Indeed, in the case of catalysis by vanadium derivatives the EPR signal corresponding to Cp_2V ($g_7 = 2.003$, $a_V = 23\,G$) was identified in the anisotropic spectrum of the reaction mixture. Cp_2V arises in the reaction mixture approximately 90 min after the beginning of the reaction and its quantity remains approximately stable throughout the reaction. The reason for a high yield of dihydrogen in this system is that hydride derivatives of vanadocene are less stable than those of titanocene,[22] which leads to their fast decomposition and hydrogen evolution. The hydrogenation of small amounts of cyclopentadiene to cyclopentene occurs probably as a result of a side process — reaction of the low-valent vanadium complex analogous to **I** with cyclopentadiene. In order to prove this proposal vanadocene was introduced in the mixture of cyclopentadiene, THF and magnesium excess. Indeed, in 72 h 1 mol of Cp_2Mg and 1 mol of dihydrogen per 2 mol of cyclopentadiene were formed, while cyclopentene was not found in the reaction mixture. Thus, the important feature of the catalysis by vanadium compounds is a higher yield of Cp_2Mg with respect to cyclopentadiene and the absence of the hydrogenation process.

Separate process stages were studied: the oxidation of magnesium by titanium(IV), titanium(III) and vanadium(III) chlorides in THF as well as the interaction of magnesium, with the system $(TiMg_2Cl_2 \cdot THF)_2$–cyclopentadiene–THF. The dependencies of the metal oxidation rate by $TiCl_3$ as well as by VCl_3 on their concentrations correspond to the Langmuir isotherm (Figs 5 and 6) and the reaction can be described by the Langmuir–Hinshelwood scheme.[22]

$$\mathrm{Ox} + S_1 \underset{}{\overset{K_{\mathrm{OX}}}{\rightleftharpoons}} \mathrm{Ox}(S_1) \tag{7}$$

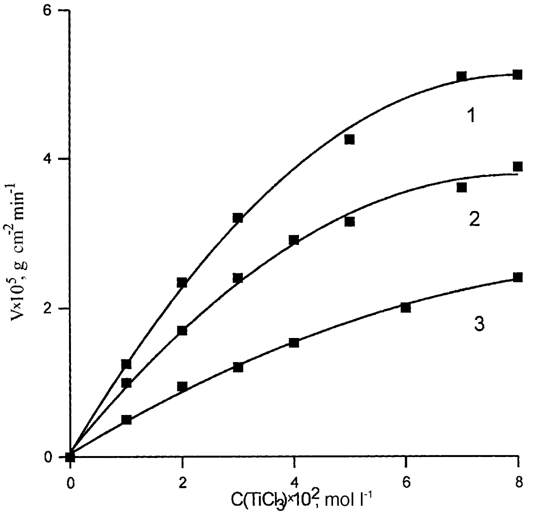


Figure 5 The dependence of the magnesium oxidation rate on the $TiCl_3$ concentration in the THF solution T = 303 K (1); T = 293 K (2); T = 283 K (3).

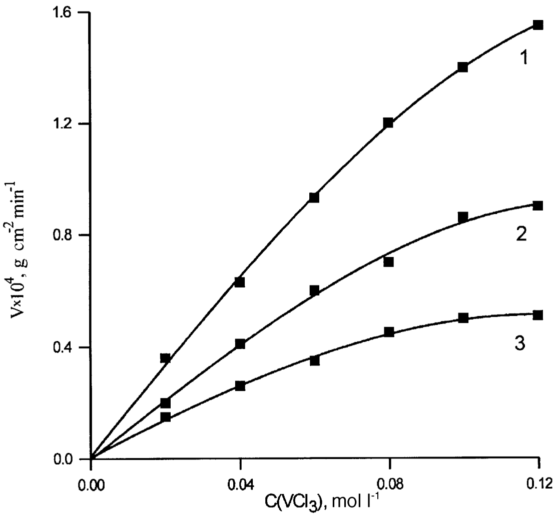


Figure 6 The dependence of the magnesium oxidation rate on the VCl_3 concentration in THF. T = 303 K (1); T = 293 K (2); T = 283 K (3).

$$\mathrm{L} + S_2 \overset{K_{\mathrm{L}}}{\rightleftharpoons} \mathrm{L}(S_2) \tag{8}$$

$$\mathrm{Ox}(S_1) + \mathrm{L}(S_2) \xrightarrow{k'} \mathrm{Products} \tag{9}$$

where K_{OX} and K_L are adsorption equilibrium constants of the oxidizer and substrate correspondingly; k' is the rate constant of the surface reaction; S_1 and S_2 are adsorption centers.

The realization of this mechanism is also confirmed by the fact that the shape of the reaction rate plotted *vs* the concentration of the oxidizer remains unchanged when the solvent concentration is varied.

As the surface concentration of both reagents is expressed by the Langmuir isotherm, the rate of the process corresponds to Eqn [10]

$$W = k' \frac{S_1 S_2 K_{\mathrm{OX}} K_{\mathrm{L}} C_{\mathrm{OX}} C_L}{(1 + K_{\mathrm{OX}} C_{\mathrm{OX}}) * (1 + K_{\mathrm{L}} C_{\mathrm{L}})} \tag{10}$$

Equation [10] can be linearized in the coordinates $1/W - 1/C$:

$$\frac{1}{W} = \frac{1}{k}\left(\frac{1}{K_{\mathrm{OX}} C_{\mathrm{OX}} K_{\mathrm{L}} C_{\mathrm{L}}} + \frac{1}{K_{\mathrm{OX}} C_{\mathrm{OX}}} + \frac{1}{K_{\mathrm{L}} C_{\mathrm{L}}} + 1\right) \tag{11}$$

where $k = k' S_1 S_2$.

Table 2 Equilibrium constants, enthalpies and entropies of adsorption of reagents during the oxidation of magnesium by metal halides in THF solution

Reagent	T (K)	K_{ads}	$-H_{\mathrm{ads}}$ (kJ mol^{-1})	S_{ads} (J mol^{-1} K^{-1})
VCl_3	283	4.7	26 ± 4.0	−8 ± 8.0
	293	3.5		
	303	2.2		
$TiCl_3$	283	16.9	5.0 ± 1.0	6.0 ± 1.0
	293	16.1		
	303	14.7		

(11) can be expressed as

$$\frac{1}{W}=\frac{1}{K_{\mathrm{OX}}}\,\frac{1}{k}\left(\frac{1}{K_{\mathrm{L}}C_{\mathrm{L}}}+1\right)\frac{1}{C_{\mathrm{OX}}}+\frac{1}{k}\left(\frac{1}{K_{\mathrm{L}}C_{\mathrm{L}}}+1\right) \tag{12}$$

If one denotes $(1/K_{\mathrm{OX}})(1/k)[(1/K_{\mathrm{L}}C_{\mathrm{L}})+1]$ as A and $(1/k)[(1/K_{\mathrm{L}}C_{\mathrm{L}})+1]$ as B, then $K_{\mathrm{OX}}=B/A$.

Given the experimental dependencies $V=f(C_{\mathrm{MCl_3}})$ at different temperatures, by using the linear regression, it was possible to calculate the values of equilibrium constants, enthalpies and entropies of adsorption of metal halides (Table 2). As the dependency of the reaction rate on the THF concentration was nearly linear (no saturation was observed), the equilibrium constant was very low and could not be calculated with acceptable error.

High equilibrium constants of adsorption together with low absolute values of adsorption enthalpies are probably the evidence of chemisorption of oxidizers on the metallic surface. Chemisorption may lead to a significant deformation or complete dissociation of the original molecule which increases the observed enthalpy of adsorption. In the case of vanadium the deformation of the V—Cl bond is significantly less than that of the Ti—Cl bond which is indicated by lower values of adsorption enthalpies.

CONCLUSIONS

1. Metallocene derivatives of titanium and vanadium actively participate in the catalytic synthesis of Cp_2Mg from magnesium and cyclopentadiene in THF solution. The hydrogenation of cyclopentadiene occurs via the formation of hydridic and allylic metallocene derivatives.

2. The reaction catalyzed by vanadium derivatives is generally slower than that catalyzed by titanium compounds. Owing to a lower stability of vanadocene hydride derivatives, the synthesis in the presence of vanadium derivatives is not accompanied by the hydrogenation of cyclopentadiene to cyclopentene and gives a higher yield of Cp_2Mg.

3. The reaction of magnesium with titanium and vanadium chlorides was treated according to the Langmuir–Hinshelwood scheme. Thermodynamic parameters of adsorption were calculated.

REFERENCES

1. Saito T. *Chem. Commun.* 1971; **22**: 1422.
2. Chernyshov EA, Reshetova MD, Rodnikov IA. *Russ. J. Gen. Chem.* 1980; **50**: 1037–1039.
3. Jezowska-Trzebiatovska B, Sobota B. *J. Organomet. Chem.* 1974; **76**: 43–47.
4. Gordon N, Ford R. *Chemist's Companion*. Mir: Moscow, 1976; 437 (Russian edn).
5. Brauer G. *Handbook of Preparative Inorganic Chemistry*. Vol. 4. Mir: Moscow, 1985; 1438 (Russian edn).
6. Yamamoto A, Go S, Ookawa M, Takahashi M, Ikeda S, Keii T. *Bull. Chem. Soc. Jpn.* 1972; **45**: 3110–3117.
7. Sharlo G. *Methods of Analytical Chemistry*. Khimiya: Moscow, 1968; 587–588 (Russian edn).
8. Nesmeyanov AN, Nikitina TV, Nogina OV et al.. *Methods of Elemento-Organic Chemistry. IB, IIIB, IVB, VB, VIB, VIIB groups, Lanthanides and Actinides VI.* Nauka: Moscow, 1974; 405 (in Russian).
9. Natta G, Dall'asta G, Mazzanti G, Giannini U, Cesca S. *Angew. Chem.* 1959; **71**: 205–210.
10. Zhukov SA, Lavrentyev IP, Nifontova TA. *React. Kinet. Catal. Lett.* 1974; **4**: 1105–1112.
11. Goodman BA, Raynor JB. *Adv. Inorg. Chem. Radiochem.* 1970; **13**: 228–235.
12. Martin HA, Jellinek F. *J. Organomet. Chem.* 1968; **12**: 149.
13. Mach K, Antropiusova H, Hanus V. *Transition Met. Chem.* 1985; **10**: 302–307.
14. Soloveichik GL, Bulychev BM. *Usp. Khim.* 1983; **52**: 72–103.
15. Troyanov SI, Varga V, Mach K. *J. Organomet. Chem.* 1993; **461**: 85–90.
16. Reid AF, Wailes PC. *Aust. J. Chem.* 1966; **19**: 307–309.
17. Pez GP, Armor GN. *Adv. Organomet. Chem.* 1981; **19**: 1–47.
18. Lemenovski DA, Fedin VI. *Usp. Khim.* 1986; **55**: 303–332.
19. Troyanov SI, Antropiusova H, Mach K. *J. Organomet. Chem.* 1992; **427**: 49–55.
20. Bercaw JB. *J. Am. Chem. Soc.* 1972; **96**: 5087–5095.
21. Kupfer V, Thewalt U, Horacek M, Petrusova L, Mach K. *Inorg. Chem. Commun.* 1999; **2**: 540–544.

22. Razuvaev GA, Latayeva VN, Gladyshev EN, Krasilnikova EN, Lineva AN, Kozina AP. *Inorg. Chim. Acta.* 1978; **31**: 357–360.
23. Bremer G, Wendlandt K-P. *Introduction into Heterogeneous Catalysis*. Mir: Moscow, 1981; 48–49 (Russian edn).