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Oxidation of Magnesium with Cyclopentadiene in Tetrahydrofuran Solution, Catalyzed by Chlorides of Group IV–VI Transition Metals

R. A. Ignat'ev, S. V. Maslennikov, I. V. Spirina, A. N. Artemov, V. P. Maslennikov, and A. N. Lineva

Research Institute of Chemistry, Lobachevskii Nizhni Novgorod State University, Nizhni Novgorod, Russia

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Abstract—Chlorides of Ti(IV), V(III), Nb(V), and Mo(VI), in contrast to Cr(III) and Zr(IV) chlorides, catalyze oxidation of magnesium with cyclopentadiene to magnesium cyclopentadienide. The kinetic features of the process were revealed, and the composition and yield of reaction products were determined. Certain details of the reaction mechanism were discussed.

The yields of products and kinetic features of magnesium oxidation with cyclopentadiene (CpH), catalyzed by Ti(IV) and V(III) salts, in tetrahydrofuran solution were determined in [1–4]. The goal of this work was to find the optimal reaction conditions and refine the mechanism of magnesium cyclopentadienide (Cp_2Mg) synthesis.

Published data [2–4] and experimental results of this work show that the possibility and direction of magnesium oxidation with cyclopentadiene, catalyzed by transition metal compounds, and the product yields largely depend on particular transition metal (Table 1).

Below are the experimentally observed rates of synthesis of magnesium dicyclopentadienide (V, mol l^{-1} min^{-1}) in oxidation of Mg with cyclopentadiene (3 M) in tetrahydrofuran at 303 K, and also the reaction rates recalculated to 1 M concentration of the catalyst (V', mol l^{-1} min^{-1}).

Catalyst,	$TiCl_4$,	VCl_3,	Cp_2ZrCl_2,	$NbCl_5$,	$MoCl_5$,
M	0.06	0.11	0.10	0.04	0.10
$V \times 10^4$	84.0	22.5	0.7	35.4	22.0
$V' \times 10^2$	14.0	2.1	0.07	8.9	2.2

Such calculations are based on the following facts. The shapes of the kinetic curves of product accumulation were similar for different catalysts (see figure). The apparent activation energy with Ti(IV) and Nb(V) chlorides as catalysts was 5.8 and 7.0 kcal mol^{-1}, respectively. The experimentally determined reaction order with respect to the oxidant is unity [3]. With Ti(IV) and V(III) chlorides as catalysts, the reaction order with respect to their initial concentrations was also close to unity.

Our results show that Cr(III) chloride does not catalyze synthesis of magnesium dicyclopentadienide. Dicyclopentadienylzirconium dichloride shows a very low catalytic activity. The highest rate of magnesium

Table 1. Oxidation of magnesium with cyclopentadiene in tetrahydrofuran solution, catalyzed by titanium, vanadium, chromium, zirconium, niobium, and molybdenum chlorides

Metal chloride (M)	CpH, M	T, K	Yield, mole per mole of converted CpH			t, h
			Cp_2Mg	*cyclo*-C_5H_8	H_2	
$TiCl_4$ [2] (0.045)	1.7	298	0.318	0.308	–	48
$TiCl_4$ [3] (0.6)	2.0	303	0.301	0.303	–	24
VCl_3 [4] (0.11)	3.0	293	0.433	0.051	0.383	35
$CrCl_3$ (0.15)	3.0	298	–	–	–	450
Cp_2ZrCl_2 (0.15)	3.0	298	0.151	[a]	[a]	450
$NbCl_5$ (0.04)	2.0	303	0.402	0.096	0.296	10
$NbCl_5$ (0.10)	3.0	298	0.401	[a]	[a]	15
$MoCl_5$ (0.10)	3.0	303	0.397	0.043	0.348	15
Cp_2MoCl_2 (0.15)	3.0	298	0.335	0.314	[a]	48

[a] Not determined.

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dicyclopentadienyl formation is observed in the presence of Ti(IV) chloride. However, about 30% of cyclopentadiene molecules are converted to cyclopentene. The most effective catalysts of magnesium dicyclopentadienide synthesis are VCl_3, $NbCl_5$, and $MoCl_5$. With these catalysts, the yield of the target product is 0.40 – 0.43 mol per mole of the initial cyclopentadiene. The yield of hydrogen is somewhat lower than the yield of the organometallic compound; part of hydrogen is spent for hydrogenation of cyclopentadiene to cyclopentene.

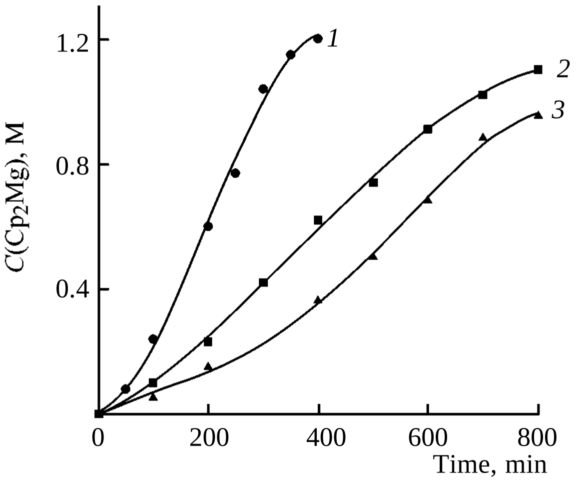
According to [5, 6], oxidation of magnesium with Ti(IV) and V(III) chlorides in THF solution yields the complexes $[TiMg_2Cl_2(THF)]_2$ and $[VHMg_2Cl_{1.5} \cdot (THF)]$, respectively. Data on the content of cluster magnesium and hydride hydrogen in the complexes formed by reaction of magnesium with Ti(IV), V(III), Cr(III), Nb(V), and Mo(V) chlorides in tetrahydrofuran solution at 298 K are listed below.

MCl_n,	$TiCl_4$,	VCl_3,	$CrCl_5$,	$NbCl_5$,	$MoCl_5$,
M	0.19	0.14	0.15	0.10	0.15
Mg/M, mol mol^{-1}	1.95	1.44	3.27	1.50	2.75
H/M, mol mol^{-1}	–	1.56	2.08	2.25	1.02

With chromium(III) chloride as catalyst of magnesium dicyclopentadienide synthesis, the reaction performed for 450 h at 298 K did not yield even traces of magnesium cyclopentadienide, cyclopentene, and hydrogen. At the same time, according to [3, 4] and to the results of this work, when the complexes formed by oxidation of magnesium with Ti(IV), V(III), Nb(V), and Mo(V) chlorides in tetrahydrofuran are mixed with cyclopentadiene at 293 K, cyclopentene is formed within 24 h.

CpH, M	2.0	3.0	3.0	1.9	1.8
MCl_n,	$TiCl_4$,	VCl_3,	$CrCl_3$,	$NbCl_5$,	$MoCl_5$,
M	0.042	0.110	0.150	0.086	0.102
cyclo-C_5H_8/MCl_n,	0.51	1.36	–	1.51	2.10

Magnesium cyclopentadienide was detected in none of the experiments. This fact shows that magnesium dicyclopentadienide is formed on the metal surface.



Accumulation of Cp_2Mg in oxidation of metal with cyclopentadiene (3 M) in tetrahydrofuran, catalyzed by (*1*) 0.10 M $NbCl_5$, (*2*) 0.10 M $MoCl_5$, and (*3*) 0.11 M VCl_3; 303 K.

Carbenoid properties of metallocenes are determined by the nature of the central atom; according to [7], they can appreciably affect the rate of formation of the target product in the catalytic synthesis of magnesium dicyclopentadienide. According to [8], chromocene is incapable of coordination with a third cyclopentadienyl ligand, i.e., it should not cleave the C–H bond in cyclopentadiene. On the contrary, “titanocene” [7] exhibits pronounced carbenoid properties:

$$Cp_2Ti + CpH \longrightarrow Cp_3TiH. \qquad (1)$$

The energy changes in reaction (1) and similar reactions with related V, Cr, Zr, Nb, and Mo derivatives were estimated by ZINDO/1 calculations [9]. The calculation results are listed in Table 2. It should be emphasized that the calculation results are suitable only for qualitative assessment of the probability of a particular intermediate stage of the catalytic cycle. For the second row of transition elements, the calculation results are considerably less reliable than for the first row. The calculated energy characteristics of

Table 2. Changes in the enegry of the system (kcal mol^{-1}) in the course of the reaction $Cp_2M + CpH \longrightarrow (\pi\text{-}Cp)_2 \cdot M(\sigma\text{-}Cp)H$[a]

Ti		V		Cr	
S^b	T	D^b	Q	S	T^b
–98	–12	–108	–22	143	–37
Zr		**Nb**		**Mo**	
S	T^b	D^b	Q	S^b	T
31	141	43	87	–4	–66

[a] Results of ZINDO/1 calculations with the following parameters: σ–σ = 0.65 and π–π = 0.35. S, T, D, and Q are the singlet, triplet, doublet, and quintuplet states, respectively.
[b] Ground electronic state.

bis(cyclopentadienyl) derivarives of d elements of the third period (Ti, V, Cr) are close to the values listed in [9].

The optimal condition for insertion by the carbenoid mechanism [reaction (1)] is the occurrence of the molecules in the singlet state [10]. This conclusion is consistent with data in Table 2 for the cene derivatives of titanium and molybdenum. The ground state of vanadocene and niobocene is the doublet state. According to [4], in synthesis of magnesium cyclopentadienide catalyzed by V(III) chloride, the vanadium derivative containing three Cp fragments can be an intermediate:

$$Cp_2V + CpH \longrightarrow Cp_3V + 1/2H_2. \qquad (2)$$

Then, η^1,η^5-tricyclopentadienylvanadium reacts with magnesium to form magnesium dicyclopentadienide and vanadocene. A similar reaction, as suggested by data in Tables 1 and 2, should occur with Nb(V) chloride used as catalyst.

According to the calculation results (Table 2), for chromocene the singlet and doublet states are not realized. This fact apparently accounts for the lack of the catalytic activity of this compound in oxidation of magnesium with cyclopentadiene.

The formation of Cp_2Mg in the reaction performed with Cp_2ZrCl_2 as catalyst is due to the fact that the singlet state of zirconocene lies only slightly higher than the ground triplet state.

EXPERIMENTAL

Magnesium of MCh-1 grade [GOST (State Standard) 804–86] was 99.9% pure. In kinetic experiments, we used magnesium turnings with the specific surface area of 170 $cm^2\ g^{-1}$. The magnesium consumption in the reaction did not exceed 5% of the initial metal amount. Organic solvents were purified and dried by standard procedures [11]. Liquid reagents were degassed by repeated freeze–pump–thaw cycles. All manipulations on preparing solutions, carrying out the reactions, and analyzing the products were performed under anaerobic conditions. Chlorides of Ti(IV), V(III), Cr(III), Zr(IV), Nb(V), and Mo(V) (analytically pure grade) were used without additional purification. Dicyclopentadienylmolybdenum dichloride was prepared as described in [12] and identified by analysis for metal and halogen [13] and by the melting point {244°C (dec.) [14]}.

Magnesium dicyclopentadienide was analyzed by its conversion to ferrocene, followed by spectrophotometric determination of the ferricenium ion [15], or by alkalimetric titration [16].

The content of hydride hydrogen in the products of magnesium oxidation with transition metal chlorides was determined by iodolysis, as suggested in [6]. Cyclopentene was determined chromatographically (Tsvet-530 chromatograph, thermal conductivity detector, 3000 × 5-mm glass column, stationary phase 10% Reoplex-400 on Cellit-545, injector temperature 110°C, carrier gas helium, flow rate 60 ml min^{-1}).

Hydrogen released in the course of synthesis of magnesium dicyclopentadienide (or in reaction of cluster magnesium with water in the course of hydrolysis of the products formed by oxidation of magnesium with transition metal chlorides in tetrahydrofuran) was determined volumetrically taking into account its solubility, or chromatographically (Tsvet-104 chromatograph, thermal conductivity detector, 1000 × 5-mm glass column, NaX sorbent, 30°C, carrier gas helium, flow rate 40 ml min^{-1}).

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REFERENCES

1. Saito, T., *Chem. Commun.*, 1971, no. 22, pp. 1422–1423.
2. Chernyshev, E.A., Reshetova, M.D., and Rodnikov, I.A., *Zh. Obshch. Khim.*, 1980, vol. 50, no. 5, pp. 1037–1038.
3. Maslennikov, S.V., Spirina, I.V., Cherkasov, V.K., Piskunov, A.V., and Artemov, A.N., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 4, pp. 542–544.
4. Ignat'ev, R.A., Maslennikov, S.V., Piskunov, A.V., Spirina, I.V., and Lineva, A.N., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 9, pp. 1567–1570.
5. Jezowska-Trzebiatowska, B. and Sobota, P., *J. Organomet. Chem.*, 1976, vol. 74, pp. 43–47.
6. Jamamoto, A., Go, S., Ookawa, M., Takahashi, M., Ikeda, S., and Keii, T., *Bull. Chem. Soc. Jpn.*, 1972, vol. 45, pp. 3110–3117.
7. Lemenovskii, D.A. and Fedin, V.P., *Usp. Khim.*, 1984, vol. 55, no. 2, pp. 303–333.
8. *Metody elementoorganicheskoi khimii. Ti, Zr, Hf, Cr, Mo, W* (Methods of Organometallic Chemistry. Ti, Zr, Hf, Cr, Mo, and W), Nesmeyanov, A.N., Ed., Moscow: Nauka, 1975.
9. Pez, G.P. and Armor, G.M., *Adv. Organomet. Chem.*, 1984, vol. 19, no. 7, pp. 1–47.

10. Nefedov, O.M., Ioffe, A.I., and Mechnikov, L.G., *Khimiya karbenov* (Carbene Chemistry), Moscow: Khimiya, 1990, p. 70.
11. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
12. Cooper, R.L. and Green, M.L.H., *Z. Naturforsch. B*, 1964, vol. 14, p. 652.
13. Charlot, G., *Les methods de la chimie analytique. Analyse quantitative minerale*, Paris: Masson, 1961, 4th ed.
14. Freidlina, R.Kh., Brainina, E.M., and Nesmeyanov, A.N., *Dokl. Akad. Nauk SSSR*, 1961, vol. 138, no. 6, pp. 1370–1371.
15. Reid, A.F. and Warles, P.S., *Aust. J. Chem.*, 1966, vol. 19, no. 2, pp. 307–309.
16. Ioffe, S.G. and Nesmeyanov, A.N., *Metody elementoorganicheskoi khimii. Magnii, berillii, kal'tsii, strontsii, barii* (Methods of Organometallic Chemistry. Magnesium, Beryllium, Calcium, Strontium, and Barium), Moscow: Akad. Nauk SSSR, 1963.