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THE OXIDATION–REDUCTION REACTION OF DICYCLOPENTADIENYLTITANIUM COMPLEXES IN APROTIC MEDIA

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Summary

Dicyclopentadienyltitanium(III) tetrahydridoborate, $(\pi\text{-Cp})_2TiBH_4$, is formed in aprotic solvents by the reaction of dicyclopentadienyltitanium(IV) dichloride, $(\pi\text{-Cp})_2TiCl_2$, with the tetrahydridoborate anion. The presence of traces of water in the reaction medium causes formation of an intensely blue compound, probably an aquotitanium(III) complex. It is suggested that the oxidation of $(\pi\text{-Cp})_2TiBH_4$ with oxygen and reduction of the resulting titanium(IV) compound with $LiBH_4$ are reversible processes. The one-electron oxidation of $(\pi\text{-Cp})_2TiBH_4$ produces oxygen radicals, which can initiate homogeneous hydrogeneation of olefins.

Introduction

The catalytic activity of titanium compounds is associated with a change of oxidation state of the titanium atom and in particular with the reversible character of that change. For example, it has been found [1] that reduction of $(\pi\text{-Cp})_2TiCl_2$ (II) with an excess of $AlEt_3$ in a H_2 atmosphere gives a complex in which the titanium atom is formally trivalent (according to its EPR spectrum). This complex is, in the presence of oxygen, catalytically active in the hydrogenation of olefins. The role of oxygen in this type of reaction has not yet been clearly explained.

As a possible contribution to understanding the nature of this oxidation–reduction reaction, we have studied the system $(\pi\text{-Cp})_2TiCl_2 + LiBH_4$ in acetonitrile and tetrahydrofuran. By use of polarography and EPR spectra, it was shown that the oxidation state of the titanium atom in the system is 3+. The Ti^{III} complex is readily converted by oxygen into a Ti^{IV} compound. The reversibility of this oxidation–reduction reaction $Ti^{III} \underset{LiBH_4}{\overset{O_2}{\rightleftharpoons}} Ti^{IV}$ under strictly anhydrous conditions was established.

Experimental

Polarographic measurements were made with Radelkis OH 102 and OH 99 polarographs in the three-electrode arrangement. A dropping mercury electrode (DME) with the following characteristics was used: flow rate measured in mercury m_b 2.12 mg/s, drop time t 3.12 s at a mercury reservoir height h of 60 cm at the potential of a saturated calomel electrode (SCE) in 0.1 M aqueous solutio of potassium chloride. SCE was used as a reference electrode [2], and was separ ted from the measurement chamber by a carbon junction on the SCE side and by a liquid junction (with a G4 sinter) on the solution side [3]. A platinum wire wound in a spiral around the capillary electrode was used as an auxiliary electrode. Measurements were carried out in an electrochemical vessel [3] maintained at 20 ± 0.02°C by use of a U 10 thermostat. Nitrogen was used as the inert gas; it was purified by passing through a column filled with BTS catalyst [4] (Fluka AG) and dried by passage through potassium hydroxide and then phosphorus pentoxide. The moisture content in the inert gas was measured during the reaction by the CH-1 hygrometer (Metra Blansko); the highest water content noted was 20 ppm.

The solvents THF and acetonitrile were purified by standard methods described elsewhere [5].

Bu_4NClO_4 and Et_4NClO_4 were prepared by reaction of appropriate quaternary ammonium hydroxides (Merck) with $HClO_4$ (Lachema, p.a.). $(\pi\text{-Cp})_2TiBH$ was prepared by a known reaction from $(\pi\text{-Cp})_2TiCl_2$ (Fluka AG) and $LiBH_4$ [6]

EPR spectra were measured on the Varian 4E instrument with an external magnetic field of intensity H = 3400 G. Spectra in the visible region were recorded with the Beckmann DK-1 instrument. All the spectroscopic results were obtained in acetonitrile in an argon atmosphere. Chromatograms of both acetonitrile samples and hydrogenated products were obtained by use of the Chrom 4 instrument at 80°C on columns filled with polyethyleneglycol 1500.

Results and discussion

Polarography of $(\pi\text{-Cp})_2TiCl_2$

(a) In acetonitrile. $(\pi\text{-Cp})_2TiCl_2$ exhibits in acetonitrile (0.1 M Et_4NClO_4) two diffusion-controlled irreversible cathodic waves at half-wave potentials $E_{1/2}$ −0.63 and −2.06 V (Table 1). These values are in good agreement with previous investigations [7, 8], but contrary to published reports, we did not observe an

TABLE 1

POLAROGRAPHIC CHARACTERISATION OF $(\pi\text{-Cp})_2TiCl_2$ IN ACETONITRILE

	This work	Gubin et al.
$E^1_{1/2}$ (V)	0.63	0.67 (0.10)[a]
$E^2_{1/2}$ (V)	2.06	1.90
i_{d_1} (μA)	1.2	1.2 (0.8)[a]
i_{d_2} (μA)	1.7	2.4

[a] Anodic wave

anodic wave at $E_{1/2}$ −0.10 V. In an attempt to explain this difference, the influence of water on the polarographic behaviour of II was studied, since water is the most frequent impurity. No substantial difference was found in the behaviour of II before and after addition of water (0.1 - 20 vol. %), except an apparent shift of $E_{1/2}$, attributable to $Ti^{IV} \rightarrow Ti^{III}$ reduction ($E_{1/2}$ −0.63 V), in a positive direction (up to 100 mV) and decrease in the limiting current (20%). Subsequently the influence of other impurities than water was investigated*. A strongly irreversible anodic wave was found at about 0.0 V in acetonitrile of only p.a. purity. This wave was seen after addition of II and showed a half-wave potential of −0.04 V. Gubin found [7,8] an anodic wave at −0.19 V and ascribed it to a reaction of II with mercury. Since throughout our work the DME was used exclusively as the working electrode, and an anodic wave of II has never been observed in either pure acetonitrile or THF, it is probable that the anodic wave is due to another type of reaction than that proposed by Gubin et al. This conclusion was confirmed by determination of the number of electrons transferred at the electrode reaction. In these experiments no mercury interference was found, although electrolysis of II was carried out using a mercury pool electrode as the working one. Electrolysis of $2.10^{-4} M$ acetonitrile solution of II ($9.3.10^{-6}$ mol) at controlled potential (−0.85 V) gave the value of n 0.98 ± 0.1 (Gubin et al. [7] found n 0.52 ± 0.1).

(b). In tetrahydrofuran. II showed two cathodic waves with $E_{1/2}$ −0.76 and −1.97 V (Table 2) in THF. The irreversible character of both these waves was evident after comparison of their $E_{1/2}$ values with summit potentials (E_p) under alternating current (AC) polarographic conditions (E_p −0.71 and −1.91 V, respectively). The half-widths were 210 and 180 mV for the waves under consideration. This fact demonstrates the strongly irreversible character of the waves [9], both of which were diffusive in nature. The wave with $E_{1/2}$ −0.76 V was ascribed to reaction 1 [7].

$$(\pi\text{-Cp})_2TiCl_2 + e^- \rightarrow (\pi\text{-Cp})_2TiCl + Cl^- \qquad (1)$$

TABLE 2

POLAROGRAPHIC CHARACTERISATION OF $(\pi\text{-Cp})_2TiCl_2$ AND $(\pi\text{-Cp})_2TiBH_4$ IN THF (0.1 M Bu_4NClO_4)

	$(\pi\text{-Cp})_2TiCl_2$	$(\pi\text{-Cp})_2TiBH_4$
$E^1_{1/2}$ (V)	0.76	0.04^a, $+0.15^a$
$E^2_{1/2}$ (V)	1.97	1.94
E^1_p (V)	0.71	0.17
E^2_p (V)	1.91	1.93
i_{d_1} (μA)	3.1	6.2^a, 2.9^a
i_{d_2} (μA)	2.6	6.4

[a] Anodic wave. E_p Peak potential in AC polarography.

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* Using chromatographic analysis it was shown that acetonitrile for spectroscopic purposes (Merck, Uvasol) contains only one impurity (about 30 ppm) while acetonitrile p.a. (Reanal) contains at least three impurities in higher amounts.

The wave with $E_{1/2}$ −1.97 V would correspond to the reduction:

$$(\pi\text{-Cp})_2\text{TiCl} + e^- \rightarrow (\pi\text{-Cp})_2\text{Ti} + \text{Cl}^- \qquad (2)$$

Addition of water to the THF solution of II caused a shift of the first cathodic wave in a positive direction (up to 200 mV at 10 vol. % of water), with a slight decrease in the limiting current of this wave, and gave rise to a maximum of the first kind on the second cathodic wave ($E_{1/2}$ −1.97 V).

Reaction of (π-Cp)$_2$TiCl$_2$ with LiBH$_4$

(a). In acetonitrile. Reaction of II with LiBH$_4$ in acetonitrile at 20°C takes place at an observable rate (the half-time of this reaction was approximately 1-2 min when the starting concentrations of both reactants were 1.10^{-3} *M*). The reduction of Ti$^{\text{IV}}$ to Ti$^{\text{III}}$ proceeds quantitatively; an anodic wave with $E_{1/2}$ 0.22 V and two cathodic waves with $E_{1/2}$ −0.97 and −1.65 V were found (i_d 1.4, 1.9 and 1.3 μA, respectively). Neither the character nor the nature of these waves were investigated in detail.

(b) In tetrahydrofuran. (π-Cp)$_2$TiBH$_4$ (I) is formed under similar conditions THF. Half-wave potentials of the sample prepared in this way were identical with those of isolated I [6]. Total reduction of Ti$^{\text{IV}}$ to Ti$^{\text{III}}$ was achieved when the starting ratio of reaction components was 1/1. The reaction mechanism can therefore be expressed by eqns. 3-5 [6], rather than by involving the unstable

$$(\pi\text{-Cp})_2\text{TiCl}_2 + \text{LiBH}_4 \rightarrow (\pi\text{-Cp})_2\text{TiCl(BH}_4) + \text{LiCl} \qquad (3)$$

$$(\pi\text{-Cp})_2\text{TiCl(BH}_4) \rightarrow (\pi\text{-Cp})_2\text{TiCl} + \tfrac{1}{2}\,\text{H}_2 + \tfrac{1}{2}\,(\text{BH}_3)_2 \qquad (4)$$

$$(\pi\text{-Cp})_2\text{TiCl} + \text{LiBH}_4 \rightarrow (\pi\text{-Cp})_2\text{TiBH}_4 + \text{LiCl} \qquad (5)$$

(π-Cp)$_2$Ti(BH)$_2$, in which two equivalents of BH$_4^-$ are necessary for quantitative reduction of Ti$^{\text{IV}}$ ion [6]. The reaction of II with LiBH$_4$ under pseudomonomolecular conditions was too fast to be studied polarographically. When stoichio metric amounts were used the decrease of Ti$^{\text{IV}}$ concentration complied with a second order rate equation of the type: $r = k[\text{BH}_4^-][\text{Ti}^{4+}]$. The values of the rate constant at 20°C were reproducible within the range 5-30 mol^{-1} l sec^{-1} ($c = 2 \times 10^{-3}$ mol l^{-1}). Compound I, prepared according to the literature [6], showed in THF one cathodic ($E_{1/2}$ −1.94 V) and two anodic waves ($E_{1/2}$ −0.04 and +0.15V) (Table 2). The strongly irreversible character of the cathodic wave was clear from the half-width value (230 mV) on AC polarographic recording [9]. Anodic waves were ill-defined, even with DC polarographic recording. The peak corresponding to the anodic wave with $E_{1/2}$ −0.04 V was completely absent on AC polarograph The cathodic wave probably corresponds to reduction of Ti$^{\text{III}}$ ions. One of the tw anodic waves corresponds to oxidation of I ($E_{1/2}$ −0.04 V) and the second to oxidation of the Cl$^-$ ion which is formed in the reaction (3). The limiting current of the cathodic and both anodic waves was a linear function of $\sqrt{h}$.

Reaction of (π-Cp)$_2$TiBH$_4$ with water

Addition of small amounts of water to acetonitrile or THF solutions of I resulted in formation of a deep blue complex, as seen in the visible spectrum (Fig. 1). The appearance of a similarly coloured complex has been described for

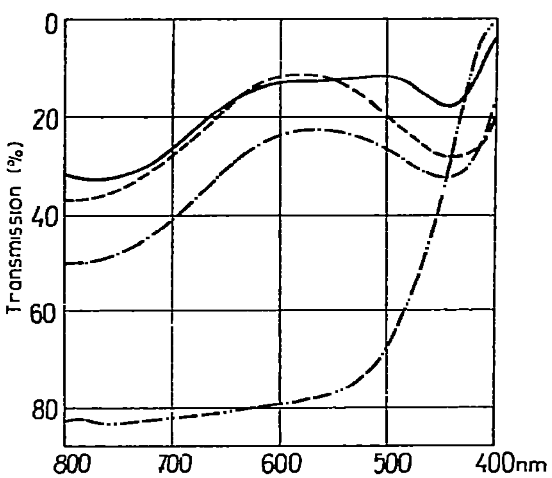


Fig. 1. Visible spectra of titanium complexes in acetonitrile solution. ——— $(\pi\text{-Cp})_2TiBH_4$; —·—·—·— $(\pi\text{-Cp})_2TiBH_4 + H_2O$ immediately after water addition; - - - - - - $(\pi\text{-Cp})_2TiBH_4 + H_2O$ 5 min after water addition; —··—··— after oxidation of the blue complex with oxygen.

substances of the type $(\pi\text{-Cp})_2TiR$ ($R = CH_3, C_6F_5$) and explained by the formation of a dinitrogen complex [10] or, more recently, by isomerization induced by indifferent electrolyte or by action of solvent [11]. The central atom in the blue complex in question is in its formally trivalent state ($E_{1/2}$ −1.94 V). The potential corresponding to the reduction $Ti^{III} \rightarrow Ti^{II}$ is, in THF, close to the reduction potential for $Li^{I} \rightarrow Li^{0}$ (s). The presence of the Ti^{III} ion in the blue complex was therefore confirmed using EPR spectroscopy (Fig. 2.). Compound II is not active in this spectrum (the central atom is in the $3d^0\,4s^0$ state). Compound I, in which the central atom is in the $3d^1\,4s^0$ state, shows resonance lines (splitting constant

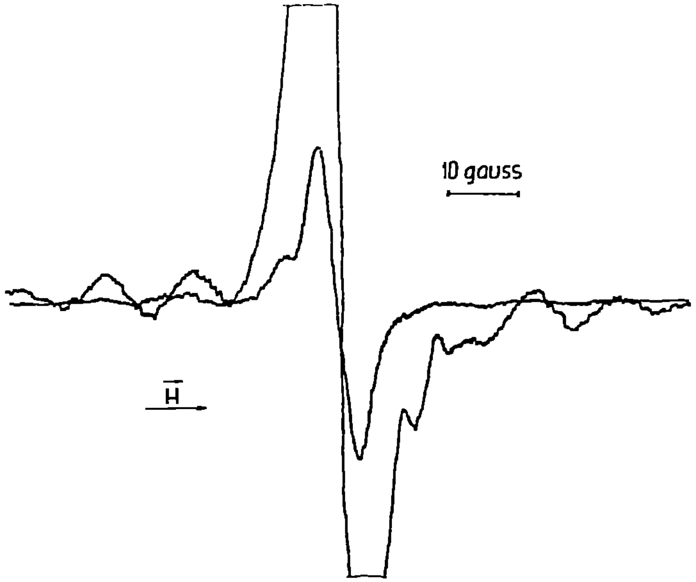


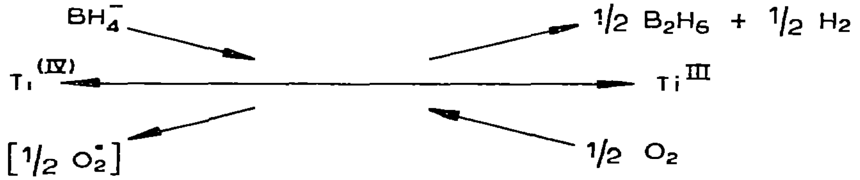
Fig. 2. EPR spectrum of the blue complex at two different sensitivities.

a_{Ti} 12.1 G). Overlap of resonance lines and hyperfine splitting corresponding to ^{47}Ti and ^{49}Ti are apparent in the spectrum. The blue complex of Ti^{III} is not formed when moisture is excluded, so it can reasonably be concluded that the b colour is an aquo-complex of I. The visible spectrum of I in acetonitrile shows two maxima (λ_{max} 600 and 710 nm); water gives rise to a marked maximum wi λ_{max} 580 nm. This value is in agreement with λ_{max} for the blue derivative of $(\pi\text{-}Cp)_2TiCH_3$ (λ_{max} 580 nm) [11] and with λ_{max} of the $^2E_g \rightarrow {}^2T_g$ transition in in the $[Ti(H_2O)_6]^{3+}$ complex (λ_{max} 575 and 500 nm) [12]. It was found that th blue complex of Ti^{III} is oxidized by gaseous oxygen and, in moist solvent, simultaneously hydrolyzes. The yellow products of the hydrolysis cannot be reduced with $LiBH_4$.

Reaction of $(\pi\text{-}Cp)_2TiBH_4$ with oxygen

With exclusion of moisture, I is oxidized by oxygen to a Ti^{IV} complex, wh can be reduced with $LiBH_4$ to I, as shown by the absence of the wave with $E_{1/2}$ −0.67 V. The signal in the EPR spectrum disappears after oxidation of II with gaseous oxygen and the wave with $E_{1/2}$ −0.67 V appears again after repeated oxidation by the same procedure. In our hands the cycle (see Scheme 1) was repeated four times with decreasing limiting diffusion current in each step. Yields of oxidations were successively 33, 18, 11 and 4.5%, as related to the limiting current of Ti^{IV} in compound II. The decrease can be explained by hydrolysis of the Ti^{IV} ion with residual moisture to non-reducible products (see above). This proposal is supported by the impossibility of carrying out the cycle in the presence of more water.

SCHEME 1



Since oxidation of Ti^{III} to Ti^{IV} is a single electron process, it is probable that oxygen radicals are generated in this reaction. These should be active in hydrogenations and the system II—$LiBH_4$—THF was actually found to be active in the hydrogenation of 1-hexene. When 2,6-di-t-butyl-4-methylphenol as a radical scavenger was added, the hydrogenation slows down remarkably. With the suggested mechanism it is possible to explain the hydrogenation of olefins with hydrogen-containing oxygen in the presence of $AlEt_3$—II [1, 13].

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