Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ELECTROCHEMICAL INVESTIGATION OF σ-BONDS IN π-COMPLEXES OF SOME TRANSITION METALS

V*. THE OXIDATION-REDUCTION REACTIONS OF CYCLOPENTADIENYLTITANIUM(IV) HALIDES

S. P. GUBIN AND S. A. SMIRNOVA
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

(Received June 29th, 1969)

SUMMARY

The polarographic reduction of Cp_2TiX_2 (I) ($X=F$, Cl, Br, I) in both protic and aprotic solvents and $CpTiCl_3$ (II) and its pentamethyl derivative, $(CH_3)_5C_5TiCl_3$, in DMF have been studied. Reduction has been shown to proceed with successive additions of one electron on the Ti–X bond.

The influence of substituents, supporting electrolytes and solvents on the reduction have been investigated.

The polarographic reduction of I, II and $TiCl_4$ have been shown to be similar, the only difference being the two-electronic character of the third stage of the reduction of $TiCl_4$.

In the previous papers of this series[1-3] certain empirical dependencies concerning the polarographic reduction of π-cyclopentadienyl and π-allylcarbonyl complexes of iron have been formulated. In these complexes the iron atom is combined by σ-bonds with halogens, carbons differing in their orbital hybridizations or with some other metals. In the activated complex, the homolytic activation of the σ-bonds has been shown to take place on the mercury surface, and the reaction rate is determined not by the electronegativity of the group splitting but by the thermodynamic stability of an anion resulting from the electron addition. For the carbon-containing compounds this stability is determined by the pK_a-values of the corresponding conjugative acids. In the later study[4] on the reduction of π-cyclopentadienyl complexes of tungsten containing σ-bonds of all the types mentioned above similar dependencies have again been reported.

In the present paper, the polarographic behaviour of the π-cyclopentadienyl complexes of titanium—the first element in the transition period—have been studied using the same methods. Although the polarographic reduction of the π-cyclopentadienyl compounds of titanium has been the subject of many papers[5-13], practically only one compound—dicyclopentadienyltitanium dichloride—has been considered. It has been shown that the first reduction stage is a reversible, one-electron process leading to titanium(III) compounds. A detailed mechanism of the first reduction stage of dicyclopentadienyltitanium dichloride has been studied recently by Dessy *et al.*[14] and by Valcher and Mastragostino[15]. Derivatives of cyclopentadienyltitanium are

---

* For Part IV, see ref. 28.

employed as catalysts in homogeneous catalysis where the oxidation–reduction reactions probably constitute the most important stages. This explains the increasing interest in the investigation of such reactions but this means that a more detailed study of all the stages in the reduction of cyclopentadienyltitanium compounds is needed.

EXPERIMENTAL

Polarographic measurements were carried out on PA-2 and PE-312 polarographs using the dropping mercury electrode, provided with a forced dropping system: $m=1.34$ mg·sec^{-1}, $t=0.37$ sec; ($H=50$ cm; 0.1 M KCl), capillary constant 1.14 mg$^{\frac{2}{3}}$·sec$^{-\frac{1}{2}}$. A saturated aqueous calomel electrode (SCE) served as a reference electrode. The measurements were conducted in a cell thermostatted at 25±0.1° according to the procedure described previously[3].

Solvents, DMF, CH_3CN and alcohol, were purified by standard methods used in electrochemical studies. Chemically pure KCl, LiCl and $(C_2H_5)_4NClO_4$ prepared and purified by known procedures were used as supporting electrolytes. Coulometric and oscillopolarographic measurements and ESR-control were carried out as already described[3].

All the derivatives of cyclopentadienyltitanium investigated in the present work were obtained and purified by standard procedures and their characteristics are in agreement with the literature data.

The polarographic reduction of dicyclopentadienyltitanium dihalides, $(C_5H_5)_2TiX_2$ (X=F, Cl, Br and I), monocyclopentadienyltitanium trichloride $(C_5H_5TiCl_3)$ and its pentamethyl derivative, $(CH_3)_5C_5TiCl_3$, was investigated and $TiCl_4$ was also studied for comparison.

Reduction of dicyclopentadienyltitanium dihalides

I. Reduction in dimethylformamide

Supporting electrolyte—0.1 N $(C_2H_5)_4NClO_4$. Polarographic characteristics of the reduction of halides (I)–(IV) in DMF (0.1 N $(C_2H_5)_4NClO_4$) are shown in Table 1.

Under the conditions described, dichloride (I) shows one anodic and two cathodic waves in the polarograms (Fig. 1). The anodic wave is a diffusion wave: its limiting current is proportional to the concentration and $\sqrt{H}$. Measurements

TABLE I

POLAROGRAPHIC CHARACTERISTICS OF Cp_2TiX_2 IN DMF
(0.1 N $(C_2H_5)_4NClO_4$; DMF; $c=2\cdot10^{-3}$ M; SCE)

Compound	$-E^1_{\frac{1}{2}}$ (V)	i_{d_1} (μA)	$-E^2_{\frac{1}{2}}$(V)	i_{d_2} (μA)
Cp_2TiF_2 (IV)	1.21	0.8	2.17	0.4
Cp_2TiCl_2 (I)	0.18[a]	0.4	1.94	1.6
	0.63	1.0		
Cp_2TiBr_2 (II)	0.22[b]	2.0	1.95	1.9
Cp_2TiI_2 (III)	0.26[b]	2.1	1.99	2.0

[a] Anodic wave; [b] anodic–cathodic wave

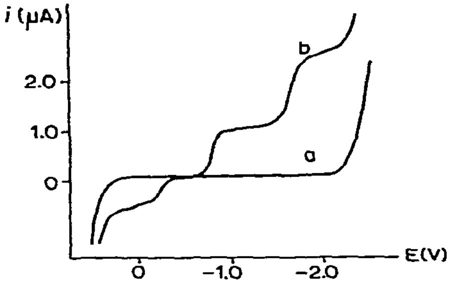

Fig. 1. Polarogram of Cp_2TiCl_2 in DMF (0.1 N $(C_2H_5)_4NClO_4$);$c=2\cdot10^{-3}$ M. (a) Curve of supporting electrolyte; (b) polarogram of Cp_2TiCl_2.

conducted using a Kalousek commutator method with the fast-dropping capillary usually employed indicate the irreversible character of this wave. The first cathodic wave is clearly defined and diffusive in character. Its limiting current and $E_{\frac{1}{2}}$ depend on the concentration, and with ten-fold increase of the latter the $E_{\frac{1}{2}}$-value shifts by 55 mV to the negative side. The slope of the curve $\log[i/(i_d-i)]/E$ (130 mV, $t=0.37$ sec) is not consistent with a one-electron reversible process. The irreversibility of this stage of reduction is also supported by the measurements with the Kalousek commutator method.

The second cathodic wave is also of diffusive character. Its $E_{\frac{1}{2}}$-value is strongly concentration-dependent: a ten-fold increase in concentration shifts $E_{\frac{1}{2}}$ by 180 mV to the negative side. The irreversibility of the second reduction stage was proved by the measurements with the Kalousek commutator method. The slope of the curve log $[i/(i_d-i)]/E$ (180 mV, $t=0.37$ sec) again indicates an irreversible reduction.

A microcoulometric determination of the number of electrons for the first cathodic wave of dichloride (I) at the potential of the limiting current (−1.2 V) gave the value 0.52±0.1*. The same measurements show that the total number of electrons is 1.8 for the first and second stages. Electrolysis of dichloride(I) ($c=5\cdot10^{-3}$ M, 0.1 N $(C_2H_5)_4NClO_4$, DMF) in a cell mounted in a resonator of an ESR spectrometer, carried out at the limiting current of the first cathodic wave, produced a signal reminiscent of that of $(C_5H_5)_2TiCl$ (V). After storage in air, the solution exhibited no signal. At the potential of the limiting current of the second wave (−2.4 V) the product of the electrolysis again displays no signal**.

Cathodic waves observed for compound (1) indicate a double-stage one-electron irreversible reduction process:

$$Cp_2TiCl_2+e \rightarrow Cp_2TiCl+Cl^- \quad \text{first cathodic wave}$$

followed by (I)

$$Cp_2TiCl+e \rightarrow (Cp_2Ti)+Cl^- \quad \text{second cathodic wave.}$$

As seen from Table 1, the limiting current of the first cathodic wave is essentially

---

* As is shown below, dichloride (I) reacts with mercury without imposition of potential. We assume that this process effects (diminishes) the results of the microcoulometric measurements where a solution of the substance is in a contact with mercury.

** Dicyclopentadienyltitanium was prepared by reduction of $(C_5H_5)_2Ti(CH_3)_2$ with hydrogen[10], but the compound was insoluble in both DMF and acetonitrile thus preventing its polarographic investigation. The dicyclopentadienyltitanium obtained gave no signal in its ESR spectrum.

lower than that of the second wave. However, the sum of the heights of the anodic and first cathodic waves is approximately equal to that of the second cathodic wave.

The plot of limiting current *vs.* concentration is of an analogous pattern (Fig. 2), both anodic and the first cathodic wave are less steep, than the second cathodic wave, but the overall limiting current of the anodic and first cathodic waves is approximately equal to that of the second cathodic wave. The heights of the first and second waves are essentially different, not because of the higher second cathodic wave but because of the decreasing limiting current of the first cathodic wave (caused by processes to be discussed later).

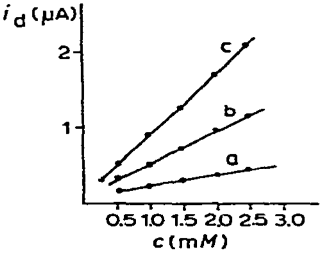

Fig. 2. Current *vs.* concn. for the waves of Cp_2TiCl_2 in DMF (0.1 *N* $(C_2H_5)_4NClO_4$). $E_{\frac{1}{2}}$: (a) −0.18; (b) −0.63; (c) −1.94 V.

Under the same conditions, up to a depolarisor concentration of $c = 1 \cdot 10^{-3}$ *M*, polarograms of dibromide (II) and diiodide (III) contain an anode–cathodic wave but only a second cathodic wave. Only at the higher concentrations is a poorly defined first cathodic wave observed, but it is appreciably lower than the second wave, *i.e.*, the first cathodic wave decreases to a greater extent for dibromide (II) and diiodide (III) than for dichloride (I).

The second cathodic wave of the reduction of bromide (II) and iodide (III) is also of a diffusive character, and it is of interest that in the plot of limiting current *vs.* depolarise concentration (Fig. 3) two linear parts intersect at $c = 1 \cdot 10^{-3}$ *M* with corresponding slopes in log $[i/(i_d - i)]/E$) of 200 and 220 mV ($t = 0.37$ sec).

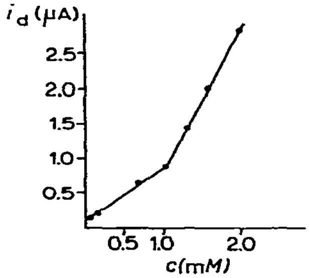

Fig. 3. Current *vs.* concn. of Cp_2TiBr_2 in DMF (0.1 *N* $(C_2H_5)_4NClO_4$).

This specific behaviour of dicyclopentadienyltitanium dihalides (I)–(III) is, in our opinion, a result of interaction with metallic mercury.

We have found that cyclopentadienyltitanium halides (I) and (II) react very slowly with metallic mercury before imposition of potentials. The colour intensity of a solution of (I) gradually decreases during 2 h. Polarograms of individual tests taken from the solution above the mercury surface show that the limiting current of the anodic wave increases with time, the wave slowly converting into the anode–cathodic wave and the limiting current of the first cathodic wave decreasing*, while that of the second wave remains unchanged. The reaction rate with mercury depends essentially on the ionic composition of the solution: in pure DMF the rate is very slow, in 0.1 *N* LiCl in DMF significant changes take place only after a 12 h-standing over mercury; on the other hand, in $(C_2H_5)_4NClO_4$ as supporting electrolyte, more profound changes occur during 2 h and the reaction rate is much faster at a concentration of 0.3 *N* than 0.1 *N* $(C_2H_5)_4NClO_4$. Dibromide (II) always reacts much faster than dichloride (I).

For example, a solution of dibromide (II) ($c = 5 \cdot 10^{-3}$ *M*, 0.1 *N* $(C_2H_5)_4NClO_4$, DMF) changes colour from brown-orange to swamp-green (trivalent titanium) upon shaking with metallic mercury in an argon atmosphere for 1 h. Furthermore, even before imposition of potential, the freshly-prepared solution of dibromide (II) in DMF (0.1 *N* $(C_2H_5)_4NClO_4$) above the mercury surface in a cell of a resonator of the ESR spectrometer shows a signal reminiscent of that from trivalent titanium. Its intensity sharply increases with gradually increasing potential until its value approaches that corresponding to the limiting current observed for the first wave in the reduction of (I). The signal slowly loses intensity with further increase in potential and, as in the case of (I), disappears at the potential corresponding to the limiting current for the second wave.

Calomel may be a possible reaction product of dichloride (I) with mercury: the reduction potential of this salt coincides well with the $E_{\frac{1}{2}}$-value for the anode–cathodic wave under the same conditions. Thus, before imposition of potential, the following reaction takes place between dichloride (I) and mercury:

$$2\,Cp_2TiCl_2 + 2\,Hg \rightarrow 2\,Cp_2TiCl + Hg_2Cl_2 \qquad \text{(II)}$$

It is probable that the anodic dissolution of mercury is taking place during the polarographic study of the solution of Cp_2TiCl_2 in DMF (0.1 *N* $(C_2H_5)_4NClO_4$):

$$Cp_2TiCl_2 + 2\,Hg \rightarrow Cp_2Ti^{+} + Hg_2Cl_2 + e \qquad \text{(III)}$$

The reaction first entails oxidation of two mercury atoms to Hg^{1+}, then reduction of Ti^{4+} to Ti^{3+}. In general, this process is a one-electron oxidation of mercury

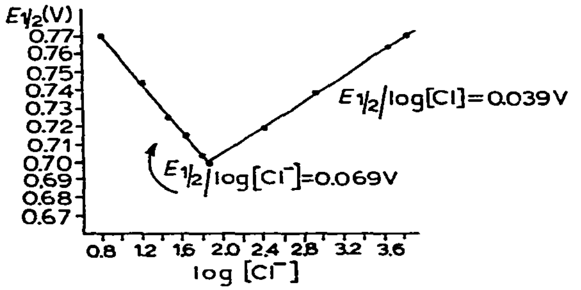

Fig. 4. $E_{\frac{1}{2}}$ of the first cathodic wave of Cp_2TiCl_2 (0.1 *N* $(C_2H_5)_4NClO_4$ in DMF) *vs.* concn. of Cl^- ions.

---

* Under the same conditions, compound (I) does not give an anodic wave on the rotating Pt electrode.

restricted by the surface of the mercury drop and is therefore weakly dependent on the concentration of depolariser (within the interval investigated) and independent of the dropping period of an electrode. Thus, at the same concentrations, reaction (III) may be assumed to proceed more readily for bromide (II) and iodide (III).

Polarograms of difluoride (IV) in DMF (0.1 N $(C_2H_5)_4NClO_4$) (Table 1) display only two cathodic waves, the first wave is clearly defined and is probably reversible ($\log[i/(i_d-i)]/E=82$). Both stages of reduction of the difluoride proceed at more negative potentials than in case of other halides and are not complicated by dissociation and interaction with mercury.

The reduction of derivatives of dichloride (I) where the hydrogens in the C_5H_5-ligand are substituted by methyl groups—$(CH_3C_5H_4)(C_5H_5)TiCl_2$ (VI) and $(CH_3C_5H_4)_2TiCl_2$ (VII)—has also been studied (Table 2).

TABLE 2

POLAROGRAPHIC CHARACTERISTICS OF $\begin{smallmatrix}R{-}C_5H_4\\R^1{-}C_5H_4\end{smallmatrix}\!>\!TiCl_2$ $(R=H, CH_3)$

Compound	0.1 N KCl, C_2H_5OH–water (1:1)		0.1 N $(C_2H_5)_4NClO_4$, DMF		0.1 N LiCl, DMF
	$-E_{\frac{1}{2}}^1$ (V)	$-E_{\frac{1}{2}}^2$ (V)	$-E_{\frac{1}{2}}^1$ (V)	$-E_{\frac{1}{2}}^2$ (V)	$-E_{\frac{1}{2}}$ (V)
Cp_2TiCl_2 (I)	0.50	1.52	0.63	1.94	0.63
$CH_3{-}CpTi\begin{smallmatrix}Cp\\Cl_2\end{smallmatrix}$ (VI)	0.55	1.58			
$(CH_3{-}Cp)_2TiCl_2$ (VII)	0.58	1.60	0.73	2.04	0.72

The mechanism observed for the reduction of the CH_3-substituted derivatives (VI) and (VII) carried out under the same conditions, either in aqueous or in aprotic solvents, does not differ from that for the unsubstituted chloride. Introduction of one or two methyl groups into the cyclopentadienyl ring shifts additively the potentials of the first and second waves to more negative values by an average of 50 mV per one methyl group.

Thus, the effect of the methyl groups on the reduction of dichloride (I) under different conditions and various supporting electrolytes supports the reduction mechanism proposed.

It should be pointed out that an analogous effect of the CH_3-groups on potential was observed during oxidation–reduction reactions of other transition metal π-complexes: ferrocene[17] and dibenzenechromium[18].

Supporting electrolyte—*0.1 N LiCl.* The three halides (I)–(III) in 0.1 N LiCl as supporting electrolyte show one well-defined diffusion wave (Table 3) corresponding to the first reduction stage. With dichloride (I) as an example, $E_{\frac{1}{2}}$ has been shown to depend on the concentration and $\sqrt{H}$. Either with slowly ($t=1.1$ sec)—or rapidly ($t=0.37$ sec)—dropping capillaries, the slopes observed in $\log[i(i_d-i)]/E$ (126 and 200 mV) essentially differ from those of the reversible process.

However, under the same conditions the reduction product suggested to result at this stage—dicyclopentadienyltitanium monochloride prepared by the reduction of a solution of (I) in a Jones reductor—exhibited an anodic oxidation wave

TABLE 3

POLAROGRAPHIC CHARACTERISTICS OF Cp_2TiX_2 IN DMF (0.1 N LiCl; $c=2\cdot 10^{-3}$ M; SCE)

Compound	0.1 N LiCl, DMF	
	$-E_{\frac{1}{2}}$ (V)	i_d (μA)
Cp_2TiF_2 (IV)	0.84	0.4
Cp_2TiCl_2 (I)	0.63	1.2
Cp_2TiBr_2 (II)	0.65	0.9
Cp_2TiI_2 (III)	0.68	1.1

at about the same potential as in the case of the cathodic wave in the reduction of (I) (0.57 and 0.59, respectively)*.

When the work was carried out with a capillary provided with a forced dropping system commonly used ($t=0.37$ sec) using a Kalousek commutator method, the reduction wave of (I) indicated the irreversibility of the process. However, it becomes reversible with the slowly-dropping capillary ($t=2$ sec). It is known from the literature[20] that varying characteristics of the dropping electrode one may effect the extent of reversibility of the electrode reaction.

The reduction of cyclopentadienyltitanium compounds under the conditions described may serve as an example of the process in which a reversibility or irreversibility is depending to a large extent on the conditions of the experiment.

The potential of the first wave of chloride (I) depends on the concentration of the Cl^- anions, the corresponding plot consisting of two intersecting lines (Fig. 3). At higher concentrations ($3\cdot 10^{-1}$ M–$1\cdot 10^{-2}$ M) the slope is 69 mV (an analogous dependency has been observed[15] for the same concentration range); at lower concentrations this dependency is also linear with a slope of 39 mV. The potential again increased with decrease in concentration of Cl^- ions.

Taking into account the results of the present work as well as those of ref. 15 it is safe to suggest that the first reduction stage of dichloride (I) dependent on significant concentrations of chlorine ions may be depicted by the scheme:

$$CpTiCl_2 + e \rightleftarrows Cp_2TiCl + Cl^- \qquad (IV)$$

Two other halides, (II) and (III), reduce in the same manner according to scheme (IV). The potentials of their clearly defined diffusion waves are somewhat negatively shifted in passing from chloride (I) to iodide (III). The reduction of dibromide (II) in a supporting electrolyte of the same anion -0.1 M LiBr, shows no substantial change in the character of the first reduction stage. Under the same conditions, difluoride (IV) reduces at more negative potentials than other halides.

II. Reduction in aqueous alcohol (50%) *medium.* Under these conditions we have investigated the polarographic reduction of dicyclopentadienyltitanium halides

---

* In the reduction in a Jones reductor, together with the compounds of trivalent titanium, $ZnCl_2$ able to complexate (V)[19] is also generated. This is known to influence the $E_{\frac{1}{2}}$ value. We have found that $E_{\frac{1}{2}}$ of the cathodic wave of chloride (I) markedly changes with increasing concentration of $ZnCl_2$. At a certain concentration, the potentials of both cathodic and anodic waves are completely equivalent.

TABLE 4

POLAROGRAPHIC CHARACTERISTICS OF Cp_2TiX_2 IN AQUEOUS ALCOHOL (1:1)
$c=2\cdot10^{-3}$ *M* (SCE)

Compound	0.1 *N* KCl; $C_2H_5OH:H_2O(1:1)$				0.1 *N* KX(X=F, Cl, Br, I) $C_2H_5OH:H_2O(1:1)$ (supporting electrolyte of the same ion)			
	$-E_{\frac{1}{2}}$ (V)		i_d (μA)		$-E_{\frac{1}{2}}$ (V)		i_d (μA)	
	$-E^1_{\frac{1}{2}}$	$-E^2_{\frac{1}{2}}$	i_{d_1}	i_{d_2}	$-E^1_{\frac{1}{2}}$	$-E^2_{\frac{1}{2}}$	i_{d_1}	i_{d_2}
Cp_2TiF_2 (IV)	0.78	—	0.4	—	0.90	—	0.8	—
Cp_2TiCl_2 (I)	0.50	1.48	0.6	1.8	0.50	1.48	0.6	1.8
Cp_2TiBr_2 (II)	0.50	1.48	0.6	1.9	0.50	1.48	0.6	1.7
Cp_2TiI_2 (III)	0.52	1.52	0.8	1.8	0.52	1.50	0.8	1.7

(I)–(IV) (Table 4) in 0.1 *M* KCl as supporting electrolyte. Our experiments differ from those of the previous studies in the use of the aqueous alcohol medium and a capillary with a forced dropping system which influences the final results. Polarograms of the three halides (I)–(III) display two clearly defined cathodic waves (Fig. 5) which were not complicated by the maxima reported by previous investigators[11].

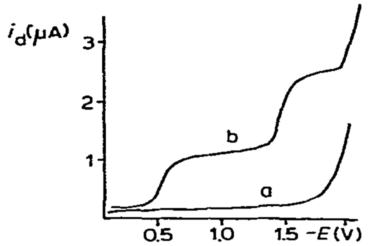

Fig. 5. Polarogram of Cp_2TiCl_2 (0.1 *N* KCl in 50% aqueous alcohol, $c=2\cdot10^{-3}$ *M*). (a) Curve of supporting electrolyte; (b) polarogram of Cp_2TiCl_2.

For all three derivatives both waves are of diffusion character: the limiting current is linearly dependent on the concentration and $\sqrt{H}$. The first reduction stage is reversible: (a) for (I) with the slowly-dropping capillary ($t=1.1$ sec) the slope of the plot $\log[i/(i_d-i)]/E$ was 69 mV, approaching the theoretical value for the one-electron reversible process.

(b) Furthermore, in a plot of $(dE/dt)/E$ the peaks of the cathodic and anodic waves are superimposed in oscillopolarograms of (I) (0.1 *M* KCl, 50% CH_3OH, $c=2\cdot10^{-3}$ *M*).

(c) Measurements with a Kalousek commutator method also verify the reversibility of this stage. The slope, $\Delta E_{\frac{1}{2}}/p\text{-H}=0.054$ mV, observed in the graph of $E_{\frac{1}{2}}$ *vs.* pH indicates a participation of one proton in the first stage of the reduction as has already been shown[15]. For (I)–(III) the potential of this stage is practically independent of halogen combined with titanium. For bromide (II), polarographic characteristics of the first reduction stage do not change upon replacement of the anion of the supporting electrolyte. For bromide (II) with 0.1 N KCl and 0.1 N KBr the slopes of curves $\log[i/(i_d-i)]/E$ corresponding to the first stage are equivalent. These results show that in the reduction of all three halides (I)–(III) the particle reacting on the surface of electrode is always the same. Taking into account published data on the hydrolysis of dichloride (I) and dibromide (II)[5,21–22], we arrive at the conclusion that in all these cases the cation ,$(C_5H_5)_2TiOH^+$, should be such a particle. This is in accordance with our results that when halides (I)–(III) are reduced in aqueous alcohol the first stage of the reduction obeys a mechanism which does not differ from that proposed by Valcher and Mastragostino[15] for reactions in aqueous solutions.

$$Cp_2Ti(OH)^+ + e + H^+ \rightleftarrows Cp_2Ti^+ + H_2O \qquad \text{(V)}$$

The second stage of reduction takes place at more negative potentials (about -1.5 V), and the wave observed is of diffusion character. The plot $\log[i/(i_d-i)]/E$ has a slope of 160 mV ($t = 1.1$ sec) indicating an irreversible reduction. All three halides have identical polarographic characteristics for the second reduction stage. In our opinion, the reduction of the $(C_5H_5)_2Ti^+$ ion always involves the addition of one electron (the second stage of reduction of halides was studied in detail in dimethylformamide). Attention should be drawn to the fact that in aqueous alcohol the first wave has a limiting current which is even lower with respect to the second wave than in dimethylformamide.

The behaviour of difluoride (IV)* differs from that of the other halides investigated: in aqueous alcohol only one clearly defined diffusion wave is reminiscent of the first stage of reduction of other halides but it is shifted somewhat to more negative potentials. The $E_{\frac{1}{2}}$ is determined by the anion of the supporting electrolyte: in 0.1 N KF the reduction occurs at more negative potentials than in KCl. We assume that, owing to the lower degree of ionization and much slower (in respect to other halides) hydrolysis, the non-dissociated molecule of difluoride (IV) reduces on the electrode surface, the second wave being displaced beyond the discharge region of the background electrolyte (-1.8 V).

Thus, in aqueous and aprotic solvents, the reductions of dicyclopentadienyltitanium halides (I)–(III) are substantially different; these differences do not change on replacement of aqueous alcohol by aqueous dioxane, or by the substitution of DMF by acetonitrile (see Table 5).

Reduction of monocyclopentadienyltitanium trichloride ($CpTiCl_3$)

$CpTiCl_3$ (Table 6) in DMF (0.1 N $(C_2H_5)_4NClO_4$) shows three diffusion cathodic waves of about equal height.

Their limiting currents correspond to one-electron transitions. Under the same conditions, $CpTiCl_3$ displays an anodic wave similar to that of Cp_2TiCl_2. In special experiments it was shown that, as in the case of Cp_2TiCl_2, $CpTiCl_3$ reacts with metallic mercury before imposition of potentials. Thus, it may be suggested that the shape of the anodic wave of $CpTiCl_3$ is similar to that of Cp_2TiCl_2. For $CpTiCl_3$

---

* Polarograms of difluoride (IV) are notably time-dependent; under polarographic conditions the compound probably completely decomposes during 0.5 h. Experiments were therefore conducted only with freshly prepared solutions of (IV).

TABLE 5

POLAROGRAPHIC CHARACTERISTICS OF Cp_2TiCl_2 IN BOTH PROTIC AND APROTIC SOLVENTS

	0.1 *N* KCl, alcohol–water (1:1)	0.1 *N* $(C_2H_5)_4NClO_4$, dioxane–water (90%)	0.1 *N* $(C_2H_5)_4NClO_4$, DMF	Acetonitrile
$-E_{\frac{1}{2}}$ (V)	0.52 1.52	0.52 1.70	0.18^a 0.63 1.94	0.10^a 0.67 1.90
i_d (μA)	0.6 1.8	1.2 3.2	0.4 1.1 1.6	0.8 1.2 2.4

^{a} Anodic wave

TABLE 6

POLAROGRAPHIC CHARACTERISTICS OF MONOCYCLOPENTADIENYLTITANIUM HALIDES
0.1 *N* $(C_2H_5)_4NClO_4$, DMF; $c=2\cdot10^{-3}$ *M*

Compound	$-E_{\frac{1}{2}}^{a}$ (V)	i_{d_a} (μA)	$-E_{\frac{1}{2}}^{1}$ (V)	i_{d_1} (μA)	$-E_{\frac{1}{2}}^{2}$ (V)	i_{d_2} (μA)	$-E_{\frac{1}{2}}^{3}$ (V)	i_{d_3} (μA)
$TiCl_4$	anod. curr.		0.73	1.0	1.58	1.2	2.34	2.6
$CpTiCl_3$ (VIII)	0.16	3.2	0.87	1.2	1.60	1.4	2.04	1.0
$(CH_3)_5C_5TiCl_3$ (IX)	0.14	2.5	1.06	1.2	1.56	1.7	2.34	1.6
Cp_2TiCl_2 (I)	0.18	0.4	0.63	1.1			1.94	1.5

in a supporting electrolyte of the same anion as in the complex (0.1 *N* LiCl) the two cathodic waves observed have the same potentials as they had in 0.1 *N* $(C_2H_5)_4NClO_4$.

In view of the data obtained the polarographic reduction of $CpTiCl_3$ may be illustrated by the following scheme involving successive reduction of three Ti–Cl bonds:

$$CpTiCl_3+e \longrightarrow CpTiCl_2+e \longrightarrow CpTiCl+e \longrightarrow [CpTi] \qquad \text{(VI)}$$

Reduction of pentamethylcyclopentadienyltitanium trichloride indicates that bonds between titanium and the five-membered cycle are preserved at all stages: the electron donation from the methyl groups shifts the reduction potentials to more negative values and, what is the most important, the potential of the third cathodic wave also becomes more negative.

As can be seen from the results of Table 6, the polarographic reduction of monocyclopentadienyltitanium trichloride is similar to that of titanium tetrachloride*. The only difference is the two-electron character of the third stage of the reduction of $TiCl_4$.

DISCUSSION OF RESULTS

The structures of cyclopentadienyltitanium halides investigated in the present work are very similar to the structure of titanium tetrachloride: X-ray studies of

---

* We have failed to observe an anodic wave but $TiCl_4$ is known to react readily with metallic mercury, reducing to Ti^{3+} before imposition of potentials.

dicyclopentadienyltitanium dichloride[24] show that the configuration of titanium is a distorted tetrahedron with the angles and the Ti–Cl bond lengths close to those in $TiCl_4$; electronographic investigation indicated that $CpTiCl_4$ has a "piano chair"-like structure (also a distorted tetrahedron), with almost the same angles and the Ti–Cl bond lengths as in $TiCl_4$.

The present data are in a good agreement with the concepts of the geometric analogy between the bonds formed by titanium in the compounds investigated. Varying the conditions of the polarographic measurements we have shown that such derivatives as Cp_2TiCl_2, $CpTiCl_3$ and $TiCl_4$ differ essentially only at the last reduction stages where the halogen-free particles are produced. Successive replacement of the chlorines in $TiCl_4$ by cyclopentadienyls does not significantly change the polarographic properties of the Ti–Cl bond either in respect of its readiness towards reduction or in the stability of the resulting intermediates. According to the quantum-mechanical calculation of Ballhausen and Dahl[26], the titanium atom in Cp_2TiCl_2 has a sufficiently low vacant orbital. By interacting with an essentially strong electron-releasing agent, the titanium atom is suggested to increase its coordination number accepting electrons on its orbital. Similar arguments were employed by Jensen[27] in his explanation of the nucleophilic exchange of halogens in Cp_2TiX_2. Taking into account these assumptions, we find substantial differences in the polarographic behaviour of the present cyclopentadienyl derivatives of titanium and the cyclopentadienylmetaldicarbonyl halides having occupied electron shells previously investigated.

Unlike our previous investigations, in the present work we in fact have never reduced the real covalent Ti–Hal bonds, the reduction was always complicated by such processes as hydrolysis, complexation and specific solvation. In this regard, reductions of dicyclopentadienyltitanium halides are rather reminiscent of organomercuric halides reduction.

ACKNOWLEDGEMENTS

The authors are indebted to Dr. O. V. Nogina and Mr. V. A. Dubovitskii for supplying the compounds investigated in the present work and for useful advice during discussion of the results.

REFERENCES

1 S. P. Gubin and L. I. Denisovich, *Elektrokhimiya*, in press.
2 L. I. Denisovich, S. P. Gubin and Yu. A. Chapovski, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1967) 2373.
3 S. P. Gubin and L. I. Denisovich, *J. Organometal. Chem.*, 15 (1968) 471.
4 L. I. Denisovich, S. P. Gubin, Yu. A. Chapovski and N. A. Ustynyuk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1968) 924.
5 G. Wilkinson and I. M. Birmingham, *J. Am. Chem. Soc.*, 76 (1954) 4281.
6 V. Gutmann and E. Nedbalek, *Monatsh. Chem.*, 88 (1957) 3, 320.
7 V. Gutmann and G. Schöber, *Monatsh. Chem.*, 88 (1957) 2, 206.
8 V. Gutmann and G. Schöber, *Z. Anal. Chem.*, 171 (1959) 339.
9 V. Gutmann and G. Schöber, *Monatsh. Chem.*, 93 (1962) 6, 1353.
10 H. S. Hsiung and G. H. Brown, *J. Electrochem. Soc.*, 110 (1963) 1085.
11 I. A. Korshunov and N. I. Malyugina, *Zh. Obshch. Khim.*, 34 (1964) 734.
12 V. Gutmann and M. Michmayr, *Monatsh. Chem.*, 99 (1968) 316.
13 K. Andrä, *J. Organometal. Chem.*, 11 (1968) 567.

14 R. E. DESSY, R. B. KING AND M. WALDROP, *J. Am. Chem. Soc.*, 88 (1966) 5112.
15 S. VALCHER AND M. MASTRAGOSTINO, *J. Electroanal. Chem.*, 14 (1967) 219.
16 K. CLAUSS AND H. BESTIAN, *Ann.*, 654 (1962) 8.
17 S. P. GUBIN AND E. G. PEREVALOVA, *Dokl. Akad. Nauk SSSR*, 143 (1962) 1351.
18 G. FURLANI, *Ric. Sci.*, 36 (1966) 989.
19 C. G. VONK, private communication.
20 C. G. MAIRANOVSKII, *Catalytic and Kinetic Waves in Polarography*, Izd. "Nauka", 1966, p. 9.
21 G. WILKINSON, P. L. PAUSON AND J. M. BIRMINGHAM, *J. Am. Chem. Soc.*, 75 (1953) 1011.
22 Y. I. ISRAELI, *Bull. Soc. Chim. France*, 3 (1966) 837.
23 I. M. KOLTHOFF AND F. G. THOMAS, *J. Electrochem. Soc.*, 111 (1964) 1065.
24 N. V. ALEKSEEV AND I. A. RONOVA, *Zh. Strukt. Khim.*, 7 (1966) 103.
25 G. PAOLO AND A. GIUSEPPE, *Atti Accad. Naz. Lincei Rend. Classe Sci. Fis. Mat. Nat.*, 33 (1962/1963) 303.
26 C. J. BALLHAUSEN AND J. P. DAHL, *Acta Chem. Scand.*, 15 (1961) 1333.
27 A. JENSEN, *Proc. 7th Intern. Conf. Coordin. Chem.*, 1962, p. 254.
28 L. I. DENISOVICH, A. A. JOHANNSSON, S. P. GUBIN, N. E. KOLOBOVA AND K. N. ANISIMOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1969) 258.