

AN ELECTROCHEMICAL STUDY OF $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{NCS})_2$

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Summary

The reduction of titanocene dithiocyanate in various solvents has been examined using the techniques of polarography, voltammetry, controlled potential electrolysis and cyclic voltammetry. In THF and CH_2Cl_2 , $\text{Cp}_2\text{Ti}(\text{NCS})_2$ undergoes successive one-electron transfer reactions, and by using a combination of electrochemical and EPR techniques it has been possible to confirm the stability of $[\text{Cp}_2\text{Ti}(\text{NCS})_2]^-$ in these solvents. In DMF, however, an irreversible dimerization follows the first electron transfer.

Introduction

The reduction of Cp_2TiX_2 ($\text{Cp} = \eta\text{-C}_5\text{H}_5$, $\text{X} = \text{halogen}$) has received considerable attention. Most workers [1–4] have assumed that separation of a chloride ion occurs during the reduction, but on the other hand, El Murr et al. [5] have concluded that the uptake of the electron leads to the stable radical anion $[\text{Cp}_2\text{TiX}_2]^-$. Related compounds have been examined by several authors who have obtained very different results [6,7].

In this paper we report on an electrochemical examination of $\text{Cp}_2\text{Ti}(\text{NCS})_2$ which has been made in order to establish the variations introduced by pseudohalides into the behaviour of titanocene derivatives.

Experimental

The electrochemical measurements were carried out under a nitrogen atmosphere. The polarography and cyclic voltammetry were carried out with an Amel Model 461, and with an Amel Model 4881 A in conjunction with a Hewlett-Packard 7040 A X-Y recorder, respectively. The coulometric experiments were carried out with a

Beckman Electroscan-30. Values potential were with referenced to the saturated potassium calomel electrode (SCE), which was separated from the cell by a KCl bridge. The polarographic measurements were made at a dropping mercury with a dropping time of 4.5 s. Cyclic voltammetry experiments were made at a platinum working electrode. In the coulometry, the working electrode was a 9 cm² platinum plate which was separated from auxiliary platinum disk by a glass frit. All the electrochemical measurements were carried out at 25 °C. The EPR spectra were recorded at room temperature with a Varian E-12, at a microwave (X Band) frequency of 9 GHz using DPPH for calibration.

The solvents, DMF, THF, CH₂Cl₂ and pyridine, were purified by the standard methods used in electrochemical studies. Tetra-n-butylammonium hexafluorophosphate (Fluka) was recrystallised from aqueous ethanol and dried in vacuo; it was deoxygenated and dehydrated by melting under vacuum before use.

Preparation of $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{NCS})_2$

In a 100 ml two-neck flask, fitted with N₂ inlet, magnetic stirrer and pressure-equalized dropping funnel, $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ [8] (2 g, 8.5 mmol) was dissolved in Et₂O (50 cm³) under a N₂ atmosphere. The solution was cooled to -20 °C and a solution of (SCN)₂ (1 g, 9 mmol) in Et₂O (20 cm³) was added through the funnel. A red solid separated immediately and evolution of CO was observed. The solid was filtered off on a cooled sintered glass disk (-20 °C), washed several times with cooled Et₂O and dried in vacuo at room temperature. Yield 90%. Found: C, 48.6; H, 3.2; N, 9.3; Ti, 15.9. C₁₂H₁₀N₂S₂Ti calcd.: C, 48.9; H, 3.4; N, 9.5; Ti, 16.2%.

Results and discussion

The polarogram (dropping mercury electrode) of Cp₂Ti(NCS)₂ in THF exhibits three reduction waves A, B and C, whose $E_{1/2}$ values are respectively -0.53, -1.74 and -2.27 V. The height of B depends on the mercury drop time, τ , and increases when τ increases. The first wave, A, is clearly defined and diffusion controlled in character. A plot of E vs. $\log i/(i_d - i)$ gives a straight line of slope 60 mV; this value is consistent with a one-electron reversible process. The other two reduction waves are associated with irreversible processes. On a platinum rotating disk electrode, Cp₂Ti(NCS)₂ also gives three reduction waves whose half-wave potentials are -0.52, -1.70 and -2.32 V, respectively.

The cyclic voltammogram of Cp₂Ti(NCS)₂ at a hanging mercury or Pt electrode shows three corresponding reduction peaks (Fig. 1). At a scan rate of 0.1 V s⁻¹ the first electron transfer is reversible* while the other two reductions are irreversible. The first reduction step remained reversible at a Pt electrode for sweep rates from 10 mV s⁻¹ to 1 V s⁻¹, as shown by the peak spread and the direct proportionality between the peak height and the square root of the scan rate. The ratio i_a/i_c has values slightly lower than unity at scan rates below 40 mV s⁻¹, which indicates that the reduction is followed by a very slow chemical reaction.

Complete electrolysis of Cp₂Ti(NCS)₂ at -0.9 V, on the plateau of wave A, requires 1 F, and gives a green-yellow solution. This solution gives a polarogram

* The peak spread for this first step is identical to that of the Cp₂Fe⁺/Cp₂Fe system, which is known to be completely reversible in THF [9].

similar to that of the precursor, except that the wave A is anodic. Electrolysis of $\text{Cp}_2\text{Ti}(\text{NCS})_2$ at potentials corresponding to wave B give pale-blue solutions after the transfer of two electrons.

In CH_2Cl_2 , the polarogram of $\text{Cp}_2\text{Ti}(\text{NCS})_2$ shows only two reduction waves, A and B, because of the cathodic limit of the solvent; the half-wave potentials are -0.59 and -1.79 V, respectively. Both are well-defined and diffusion controlled. A graph of potential against $\log(i/i_d - i)$ for the first wave has a slope of 64 mV, which is near to the theoretical value for a one-electron reversible process. The second wave corresponds to an irreversible process. On a platinum rotating disk electrode, $\text{Cp}_2\text{Ti}(\text{NCS})_2$ shows two reduction waves, with $E_{1/2}$ of -0.51 and -1.82 V, respectively. The results obtained from the cyclic voltammetry, and the coulometric measurements of $\text{Cp}_2\text{Ti}(\text{NCS})_2$ in CH_2Cl_2 , show a very similar behaviour to that in THF.

The EPR spectra of the product of electrolysis in THF and CH_2Cl_2 of the complex (at -0.9 V) on the plateau of the first wave show (Fig. 2) an intense central signal, which corresponds to the molecules with titanium isotopes having a zero value of the nuclear spin; it is split into five lines due to the superhyperfine interaction with the equivalent nitrogen atoms. This central signal is flanked by six satellites due to the hyperfine interaction of the unpaired electron with the ^{47}Ti ($I = 5/2, 7.75\%$) and ^{49}Ti ($I = 7/2, 5.51\%$) nuclei. The titanium hyperfine constant in this eight-line pattern is 13.5 G, which is in agreement with that reported for other mononuclear cyclopentadienyltitanium(III) complexes [10,11]. An examination of the low field titanium hyperfine signals shows that it is also split into five lines. The five-line nitrogen superhyperfine pattern results from the interaction of the unpaired electron with two equivalent nitrogen atoms from the thiocyanate ligands. The

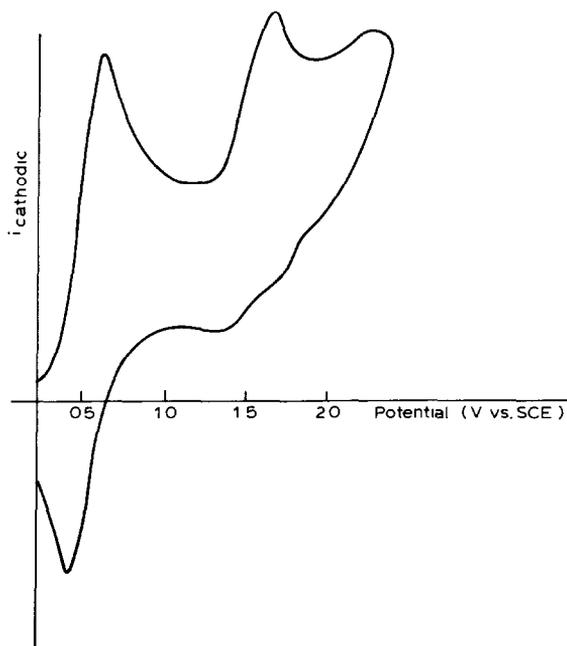


Fig. 1. Cyclic voltammogram of $\text{Cp}_2\text{Ti}(\text{NCS})_2$ in THF containing 0.1 M Bu_4NPF_6 , at a platinum electrode and a scan rate of 0.1 V s^{-1} .

nitrogen A value is 2.7 G (Table 1), which is in agreement with that of other titanium(III) complexes [11].

The polarographic runs in dimethylformamide (DMF) show four successive reduction waves, A, B_1 , B_2 and C, whose $E_{1/2}$ values are -0.49 , -1.53 , -1.78 and -2.08 V, respectively. The heights of B_1 and B_2 are depending on τ with B_1 decreasing and B_2 increasing when τ increases. However, the sum of their heights is always approximately equal to that of the first wave, A. This is clearly defined and its limiting current is proportional to η (indicating adsorption controlled process), and the slope of $\log(i/i_d - i)$ vs. E is 112 mV. The last wave, C, corresponds to an irreversible process. In the polarogram there is also a very small anodic wave which increases in intensity if the solution is stirred with mercury, indicating that it results from a reaction of the substrate with mercury; this behaviour has been also observed [3] with dicyclopentadienyltitanium dihalides.

On a platinum rotating disk electrode, $\text{Cp}_2\text{Ti}(\text{NCS})_2$ gives four reduction waves, at -0.56 , -1.18 , -1.94 and -2.08 V.

Cyclic voltammetry in DMF at a Pt electrode of $\text{Cp}_2\text{Ti}(\text{NCS})_2$ in concentrations higher than 0.005 M shows three successive electrochemical steps (Fig. 3). At a scan rate of 0.25 V s^{-1} the first electron transfer reaction, $E_{p_c} - 0.51$ V, is highly reversible, which the other two transfers ($E_{p_c} - 1.22$ and -2.05 , respectively) are irreversible. When concentrations lower than 0.002 M are used, another reduction peak occurs at -1.63 V, whose height peak depends on the scan rate; i_p decreasing when the sweep rate is increased. With a scanning rate of 0.015 V s^{-1} the first wave is only slightly reversible. Furthermore, this first reduction stage shows some properties which are characteristic of an adsorption process, since the first cathodic peak is closely accompanied by a small peak at a more negative potential, and two corresponding anodic peaks are observed on the return half-cycle. The second peak, which at large scan rates appears as a shoulder, is shifted in the positive direction by increasing depolarizer concentration; this being an effect characteristic of an adsorp-

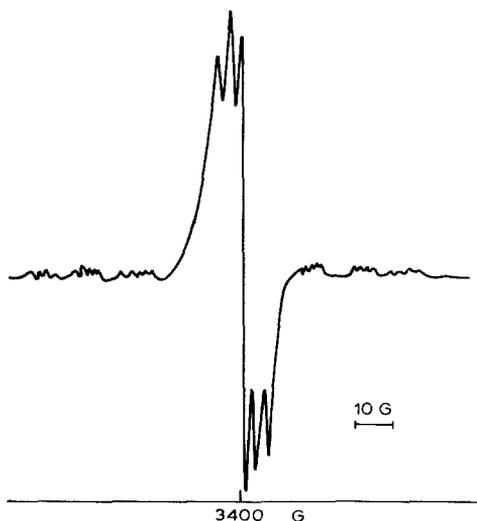


Fig. 2. EPR spectrum of $[\text{Cp}_2\text{Ti}(\text{NCS})_2]^-$ in THF at room temperature.

tion peak [12]. Likewise, the ratio of the adsorption to the diffusion current increases with increasing rate of polarization, and decreases with increasing depolarizer concentration [12]. These results, and the observations made above, suggest strong adsorption of the substrate.

Repeated CV scans did not affect the appearance of the voltammograms, provided that the potential was not swept beyond the value of the second cathodic transfer (which is usually 0.2 to 0.4 beyond E_p). If this did occur, the electrode response subsequently shows a marked inhibition of the first reduction peak which could only be corrected by recleaning the electrode.

Complete electrolysis of a 0.01 M DMF solution of $\text{Cp}_2\text{Ti}(\text{NCS})_2$ at a Pt electrode at -0.95 V on the plateau of wave A requires 1 F and gives a yellow-green solution. The polarogram of this solution shows an anodic wave, whose $E_{1/2}$ is -0.34 V, and two cathodic waves, B and C. Polarographic evidence is obtained for the existence of free SCN^- ions from the presence of an anodic wave whose $E_{1/2}$ is $+0.18$ V. Electrolysis of $\text{Cp}_2\text{Ti}(\text{NCS})_2$ at potentials corresponding to B gives, after the transfer of two electrons, blue solutions and highly insoluble white powder.

When $\text{Cp}_2\text{Ti}(\text{NCS})_2$ is reduced in DMF at -0.9 V the product does not give any EPR signal. However, if the electrolysis is carried out in presence of pyridine a broad and very intense signal can be observed at $g=1.975$ (Table 1), without hyperfine coupling of the titanium with the nitrogen atoms. This fact can be explained by assuming that in the reduction process a diamagnetic dimer, similar to that obtained with Cp_2TiCl_2 [13], is formed, which is not obtained in presence of pyridine, when a paramagnetic species is produced. This behaviour has been observed in the reaction of the dimer, $[\text{Cp}_2\text{TiCl}]_2$, with pyridine and other donors [14] and it has been postulated to occur in the electrochemical reduction of Cp_2ZrCl_2 [1].

The formation of this dimer should be by an irreversible dimerization process [15] in which the chemical reaction is slow in comparison with the rate of mass transfer. At high scan rates the process is purely diffusion controlled and the reversibility is complete within the CV, being practically constant at the peak potential. When the sweep rates are decreased the process shifts from a purely diffusion-controlled behaviour towards a purely kinetic-controlled behaviour and becomes partially reversible, the magnitude of the slope in the plot of E_p vs. $\log v$ being approximately 20 mV per decade [15,16]. Furthermore the irreversibility of the dimerization reaction is consistent with the irreversible character of the polarographic wave and with the existence of free pseudohalide ions after the electrolysis.

The change observed in the EPR spectra when pyridine is added to DMF is also reflected in the voltammetric study. The cyclic voltammogram of $\text{Cp}_2\text{Ti}(\text{NCS})_2$ in DMF shows a drastic change on the addition of 10% pyridine by volume (Fig. 3). The peak A disappears and a new cathodic peak D is observed at -0.85 V, which

TABLE 1
EPR PARAMETERS FOR THE REDUCED FORM OF $\text{Cp}_2\text{Ti}(\text{NCS})_2$

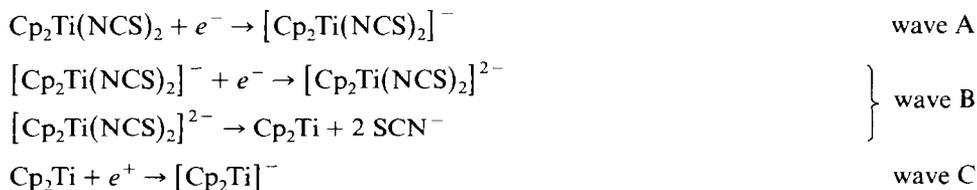
Solvent	$A_{150}\text{Ti}$ (G)	g_{150}	A_N (G)
CH_2Cl_2	13.5	1.980	2.77
THF	13.3	1.981	2.76
DMF + Py		1.975	

corresponds to an electron transfer which is only slightly reversible at a scan rate of 0.25 V s^{-1} . Also, the peak B is displaced to more negative potentials. Similar effects are observed when free SCN^- is added to the solution. These results indicate that pyridine and SCN^- prevent the dimerization reaction, and so a different reduction product is obtained.

It has been reported [18,19] that in the case of Cp_2TiCl_2 a Cl^- ion is rapidly lost after the uptake of the first electron, and that this process is followed by a recombination reaction whose rate is dependent on several factors [19].

For $\text{Cp}_2\text{Ti}(\text{NCS})_2$ a pseudo-reversible behaviour could be observed if the rate of recombination were high enough. However this possibility can be discarded because no modification of the backward peak is observed in the voltammogram of $\text{Cp}_2\text{Ti}(\text{NCS})_2$ on decreasing the temperature to -35°C or by using of sweep rate of 50 V s^{-1} .

Therefore our results on the electrochemical behaviour and EPR spectra show without doubt that $[\text{Cp}_2\text{Ti}(\text{NCS})_2]^-$ does exist in THF and CH_2Cl_2 . The electrochemical data can be rationalized in terms of the following scheme:



On the other hand, for $\text{Cp}_2\text{Ti}(\text{NCS})_2$ the first peak potential is more positive than for Cp_2TiCl_2 ; this fact and the stability of the anionic species points to a decreased electron density on the metal [19] resulting from the presence of empty π^* molecular

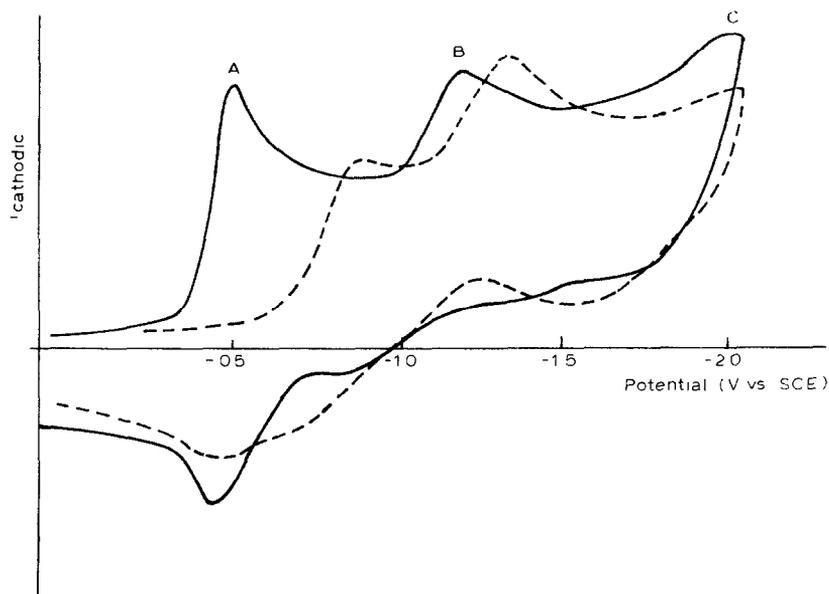


Fig. 3. Cyclic voltammograms of $\text{Cp}_2\text{Ti}(\text{NCS})_2$ at a platinum electrode and a scan rate of 0.25 V s^{-1} ; with $0.1 \text{ M Bu}_4\text{BPF}_6$ in DMF (—), or in DMF containing 10% pyridine by volume (---).

orbitals in the thiocyanate group such electron delocalization is in accordance with the nitrogen superhyperfine coupling observed in the EPR spectra.

All results obtained in DMF suggest the formation of a dimer following the first electron transfer. The different behaviour in our case cannot be attributed to the use of too low concentrations as was reported previously for Cp_2TiCl_2 [17], because a large range of concentrations has been studied. In the absence of additional spectral and electrochemical data it is impossible to determine the exact nature of the subsequent reduction process.

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