

CYCLIC VOLTAMMETRIC STUDIES OF ORGANOMETALLIC COMPOUNDS AT A PLATINUM ULTRAMICROELECTRODE.

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Ultramicroelectrodes are particularly suited for the determination of Kinetic parameters of fast chemical reactions (rate constants above 10^2 s^{-1}) coupled with electron transfer reactions. In fact, as IR drop effect is negligible and the ratio of faradaic to non-faradaic current increases as electrode area diminishes, non distorted cyclic voltammograms can be run at very high potential scan rates (up to 10^3 Vs^{-1}).¹

In the present work experiments were carried out at a platinum disc ultramicroelectrode (10 μm diameter) and the potential scan rates were in the range 10^2 – 10^4 Vs^{-1} . The experimental details are described elsewhere¹.

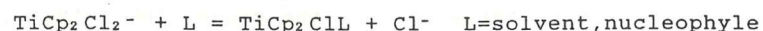
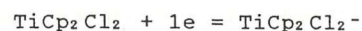
The complexes $[\text{MoCp}_2(\text{ArN}_3\text{Ar}')][\text{PF}_6](\text{Cp}=\text{C}_5\text{H}_5)$ ² undergo two monoelectronic oxidations. The reversibility of the first process depends on the substituents on the aromatic groups of the triazenido ligands. When $\text{Ar}=\text{Ar}'=\text{p-CH}_3\text{C}_6\text{H}_4$, $\text{p-CH}_3\text{OC}_6\text{H}_4$ the oxidation is diffusion controlled; when $\text{Ar}=\text{C}_6\text{H}_5$ and $\text{Ar}'=\text{p-CH}_3\text{C}_6\text{H}_4$ an EC process is observed, reversible C.V.s only being obtained at scan rates above 10 Vs^{-1} . When $\text{Ar}=\text{Ar}'=\text{C}_6\text{H}_5$, as the coupled chemical reaction is much faster ultramicroelectrodes and fast cyclic voltammetry had to be used, in order to get a reversible C.V.

The Kinetic data obtained is presented on table 1; the lifetimes were calculated from the dimensionless plots of Nicholson and Shain³.

TABLE 1 - Lifetimes of $[\text{MoCp}_2(\text{ArN}_3\text{Ar}')] [\text{PF}_6] 1.2 \times 10^{-3} \text{ M}$
in $\text{CH}_3\text{CN}/(\text{Bu}_4\text{N})(\text{PF}_6) 0.1 \text{ M}$

COMPLEX	v/Vs^{-1}	I_p^c/I_p^a	LIFETIME/s
Ar = C_6H_5	0.5	0.64	1.1
	1.0	0.72	0.8
Ar' = $p\text{-CH}_3\text{C}_6\text{H}_4$	2.0	0.82	0.7
	100	0.78	0.007
Ar = Ar' = C_6H_5	300	0.89	0.006
	500	0.94	0.006

Ultramicroelectrodes were also used to study the electrochemical reduction of TiCp_2Cl_2 . According to Laviron et.al.⁴ this complex undergoes a ligand displacement reaction after the uptake of one electron:

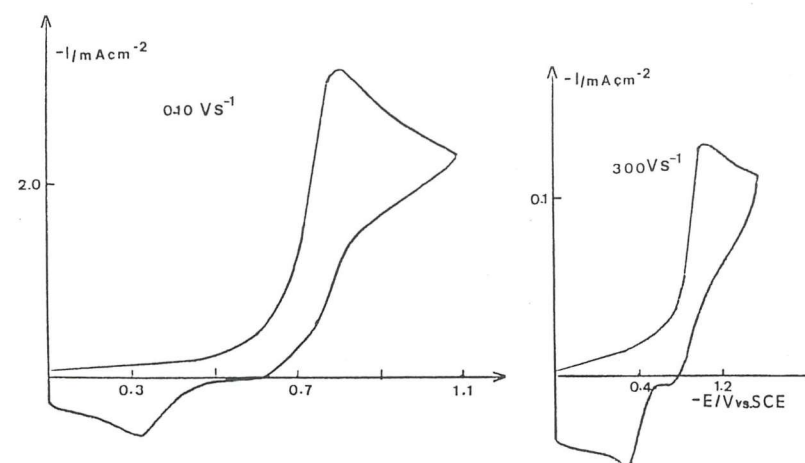


In this communication we discuss an alternative mechanism involving a follow-up dimerization reaction. Such dimerization is known to occur when TiCp_2Cl_2 is chemically reduced by Zn or Hg in THF⁵. Our results, obtained in THF, ACN and DMF, are summarised on table 2 and typical C.V.s are shown in figure 1.

In THF and at scan rates up to 0.1 Vs^{-1} the monoelectronic reduction is diffusion controlled. At higher scan rates the reduction is no more reversible and a new oxidation wave appears at higher potentials. In ACN the reduction is irreversible at the slower scan rates and the oxidation peak referred to above is also shown (figure 1). When ultramicroelectrodes are used at high scan rates the reduction process becomes more reversible. In DMF two monoelectronic reductions are observed, but the second one decreases drastically above 500 Vs^{-1} .

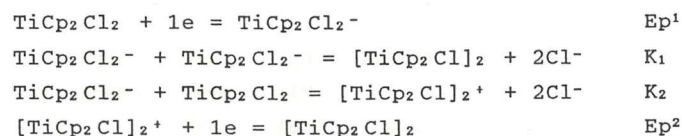
TABLE 2 - Electrochemical data for the reduction of TiCp_2Cl_2
a) at a Pt disc electrode
b) at a Pt disc ultramicroelectrode ($\phi=10\mu\text{m}$)

solvent	v (Vs^{-1})	$-I_p^c$ (mAcm^{-2})	I_p^c/I_p^a	$-E_p^1$ (V)	ΔE_p (mV)	$-I_p^c$ (mAcm^{-2})	$-E_p^2$ (V)
THF	0.100 a)	2.2	1.0	0.99	70	-	-
	0.500 a)	3.7	0.93	1.02	80	-	-
	200 b)	85.1	0.60	1.10	80	-	-
	1000 b)	160	0.62	1.12	80	-	-
	0.100 a)	2.1	-	0.74	80	-	-
	0.500 a)	4.5	-	0.77	80	-	-
ACN	200 b)	83.9	-	0.85	80	-	-
	1000 b)	169.5	-	0.90	80	-	-
	0.100 a)	1.5	-	0.75	80	1.5	1.11
	0.500 a)	2.6	-	0.78	80	2.4	1.12
	200 b)	54.7	-	0.80	80	55.8	1.20
	1000 b)	86.6	-	0.90	80	27.0	1.24



Cyclic voltammograms of $\text{TiCp}_2\text{Cl}_2 10^{-2} \text{ M}$ in $\text{ACN}/(\text{Bu}_4\text{N})(\text{PF}_6) 0.1 \text{ M}$:
a) at a Pt disc electrode;
b) at a Pt disc ultramicroelectrode ($\phi=10\mu\text{m}$)

According to Savéant et al.⁶ the following mechanism for dimerization can be considered:



The diffusion controlled reduction observed in THF is expected when equilibrium of the dimerization reaction is reached very quickly. However, at the higher scan rates, as equilibrium is not attained during the scan, the reduction becomes irreversible. Simultaneously oxidation of the reaction product is observed at higher potentials (Ep^2).

In ACN equilibrium is not reached during the scan and an EC mechanism can be considered.

The observed pattern in DMF ($\text{Ep}^1 > \text{Ep}^2$) means that K_1 is smaller than K_2 , as these two values are related as follows:

$$\text{Ep}^2 - \text{Ep}^1 = 0,059 (\text{pk}_2 - \text{pk}_1)$$

In conclusion, the electrochemical reduction of TiCp_2Cl_2 can be rationalised in terms of a follow-up dimerization reaction. In both THF and ACN the dimer is reduced at higher potentials ($\text{K}_1 > \text{K}_2$) and in DMF the dimer is reduced at lower potentials ($\text{K}_2 > \text{K}_1$).

References

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HOW TO INDUCE REVERSIBILITY; AD-ELECTRODES

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For a long time electrochemists have aimed to be able to change the kinetics of electron transfer reactions.

In real systems there are processes that one would like to make as irreversible as possible, for example, those related to the deterioration of metals. On the other hand, there are several others, e.g. those related to the production of energy, which one would prefer to occur at lower overpotentials and high current densities: reversibility is then desired. Nobel metals partially covered by sub-monolayers of heavy metals - ad-electrodes - I have been demonstrated to have the ability to catalyse many reactions^{1,2}.

In the last twenty years several authors have obtained either catalysis or inhibition of some electrochemical reactions at ad-electrodes, but the subject is not yet fully understood. One of the most successful achievements has been the electrocatalytic oxidation of inexpensive small-molecule organic fuels, such as CH_3OH and HCOOH at Pt electrodes partially covered by adatoms of Bi, Pb, Tl and Cd.

By using potential step techniques we have been able to study the catalysis of the oxidation of HCOOH as a function of the adatom chosen and coverage³. Quite recently, it has also been demonstrated by Kokkinidis⁴ and by other authors that the irreversibility of some