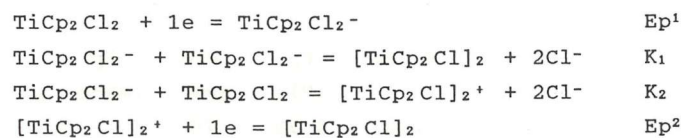


According to Savéant et al.⁶ the following mechanism for dimerization can be considered:



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 ($\text{K}_2 > \text{K}_1$).

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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

simple electron transfer processes can also be modified by adatoms.

We have now measured the influence of Bi, Cd and Pb adatoms on the kinetics of six redox couples, which were taken as models of "inner" and "outer sphere" mechanisms. Results are shown in table 1.

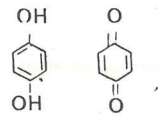
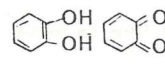
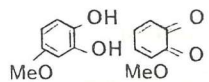
Couple	Medium	E /V vs HNE	10 ² k _s /cm s ⁻¹			
			None	Bi	Cd	Pb
	HClO ₄	0.70	0.001	0.13	0.001	0.03
	HClO ₄	0.76	0.004	1.8	0.004	0.3
	HClO ₄	0.77	0.07	1.2	0.07	0.6
Fe(CN) ₆ ⁴⁻ /Fe(CN) ₆ ³⁻	KNO ₃	0.69	1.8	2.3	2.0	2.3
Fe ²⁺ /Fe ³⁺	H ₂ SO ₄	0.68	0.2	2.6	0.24	2.4
IrCl ₆ ³⁻ /IrCl ₆ ²⁻	HClO ₄	1.02	3.0	3.5	3.7	5.0

Table 1 Standard rate constants as a function of adatom.

Remarkable catalytic effects were obtained, for example for the o-hydroquinone/o-benzoquinone redox couple at Pt/Bi_{ads}.

Such studies are now being extended to aprotic solvents. Results will be presented and discussed.

Acknowledgements

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