

Fig. 4 - Complex plane plots
 a) modulated normalized transmittance
 b) complex capacitance

References

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DIGITAL SIMULATION APPLIED TO THE IDENTIFICATION OF THE OXIDATION MECHANISM OF $[\text{FeH}(\text{CNMe})(\text{dppe})_2][\text{BF}_4]$

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ABSTRACT

The anodic behaviour of an hydride-isocyanide iron(II) complex, $[\text{FeH}(\text{CNMe})(\text{dppe})_2][\text{BF}_4]$, was investigated using a digital simulation computer program applied to cyclic voltammetry experiments. The proposed mechanism is of an ECECE type, and the homogeneous rate constants were evaluated.

RESULTS and DISCUSSION

The anodic oxidation of the iron(II) complex $[\text{FeH}(\text{CNMe})(\text{dppe})_2][\text{BF}_4]$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) was studied by cyclic voltammetry, at a platinum electrode, in a 0.2M $[\text{Bu}_4\text{N}][\text{BF}_4]/\text{THF}$ electrolyte solution, and by controlled potential electrolysis at a platinum gauze in the same electrolyte solution, as described previously [1].

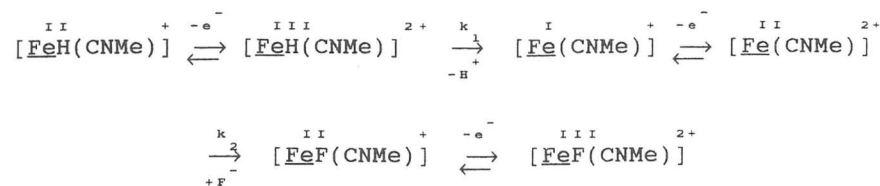
The cyclic voltammogram shows two anodic waves. The current function for the first wave increases for lower scan rates, whereas the second wave disappears at high scan rates.

The number of electrons involved, as determined by c.p.e., are two for the first wave and one for the second wave.

The product obtained by controlled potential electrolysis at the first wave was isolated from the electrolyte solution and identified as the fluoro-isocyanide complex of iron(II) $[\text{FeF}(\text{CNMe})(\text{dppe})_2][\text{BF}_4]$; its cyclic voltammogram shows a single-electron reversible oxidation wave at $E_{1/2}$ coincident with that of the above mentioned second wave.

Through the analysis of these results and comparison with published data [2], we have proposed the ECECE mechanism for the anodic behaviour of that complex indicated in the

scheme, where the fluoride ion was originated from BF_4^- .



Scheme - Postulated mechanism for the anodic oxidation of $[\text{FeH}(\text{CNMe})][\text{BF}_4^-]$; $[\text{Fe}]$ stands for trans- $\text{Fe}(\text{dppe})_2$

A] - SIMULATION PROGRAM:

In order to investigate this postulated mechanism we have developed a simulation program which was written in Turbo Pascal (from Borland International) and run on an IBM PS/2 50 equipped with a math coprocessor (from Intel 80287-10) to speed up the calculation time.

The "BOX METHOD" [3] was applied to solve the partial differential equations that describe the mechanism.

Twenty boxes have been considered in our calculations, a number that is considerably small; nevertheless, the results are in good agreement with experimental cyclic voltammetry, both at high and low scan rates.

We have used a box thickness of 10^{-3} cm, which gave a diffusion layer thickness of 0.2 mm.

The method used to integrate these differential equations was the 4th order RUNGE KUTTA method.

B] - THE INFLUENCE OF THE HOMOGENEOUS RATE CONSTANTS:

We have studied the influence of the homogeneous rate constants, at constant values of all the other involved parameters. By increasing the second homogeneous rate constant (k_2) (fig.1), an increase in the fluoride complex concentration results, as expected, and the 2nd wave becomes better defined. There is also a small increase in the peak current for the 1st wave which becomes more important for higher values of the first homogeneous rate constant.

Upon increasing the first homogeneous rate constant (k_1), for a constant value of k_2 , an enhancement of the first wave intensity is observed in agreement with the formation of a greater amount of iron(I) complex which is then oxidized at this potential. Moreover, the amount of fluoride complex formed increases with k_1 , therefore leading to a concomitant increase of the peak current for the second wave.

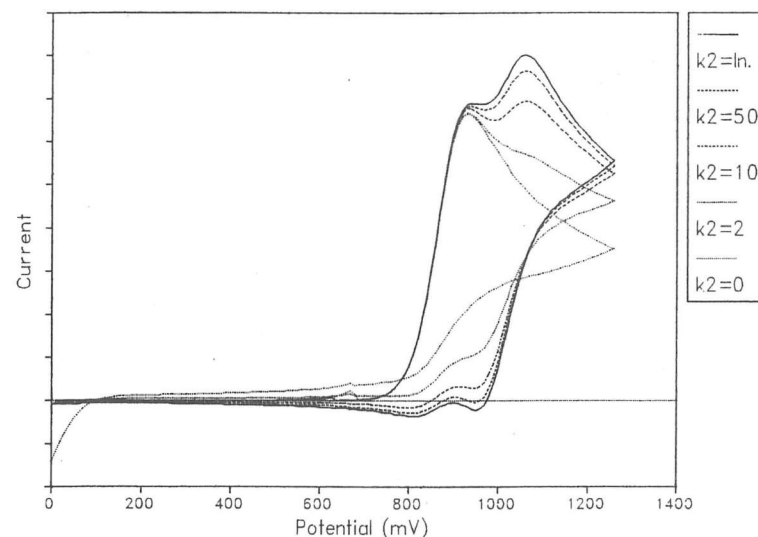


Figure 1 - Influence of the second homogeneous rate constant on the simulated voltammograms for an ECECE mechanism, evaluated at 200 mv/s. $k_1 = 5 \text{ s}^{-1}$, k_2 varied from 0 to infinity. The heterogeneous rate constants were all made equal to 0.01 cm.s^{-1} and the α parameters were considered to be 0.5 for all the electrode reactions. Current in an arbitrary unit.

Comparison between the simulated and experimental data indicated that the best fit was obtained for $k_1 = 1.5 \text{ s}^{-1}$ and k_2 as infinity (see fig. 2).

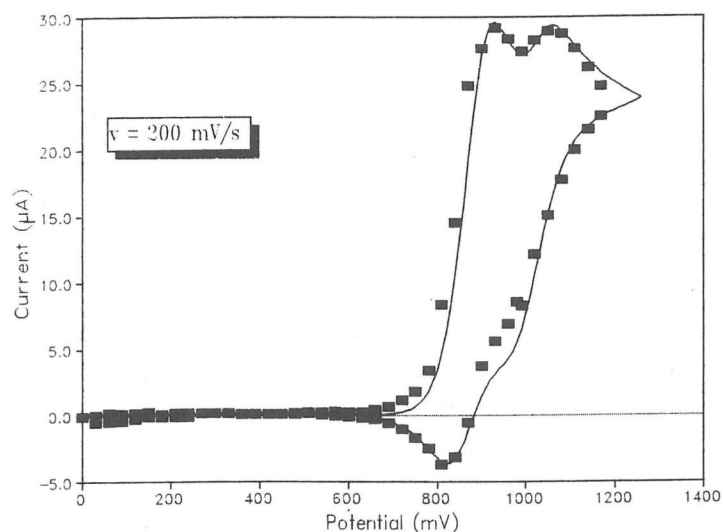


Figure 2 - Comparison between the experimental data (■) and a simulated voltammogram with $k_1 = 1.5 \text{ s}^{-1}$ and k_2 as infinity.

Although the general agreement between the experimental and the simulated cyclic voltammograms is evident, there are still some discrepancies, namely involving the cathodic peak current for the fluoride complex. This conceivably can be corrected by improving the original scheme and is currently under investigation.

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THE CATHODIC CLEAVAGE OF SOME PROTECTING GROUPS FROM AMINE AND THIOL DERIVATIVES

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The large molecule synthesis is totally dependent on the use and removal of protecting groups from amine and carboxylic acid groups and also sometimes from alcohols and thiols [1].

Electrochemical methods are known today to be convenient alternatives to deprotect molecules, because the control of the potential permits the selectivity between different protecting groups or even between the same group at different sites in the molecule. Thus, we have been concerned with the study of electrocleavage of some groups of interest for protection during the synthesis [2-5].

The benzyloxycarbonyl group is the most widely used group in peptide synthesis and it is known that the reduction of benzyloxycarbonyl derivatives of simple amines, aminoacids and peptides at vitreous carbon electrodes in *N,N*-dimethylformamide (DMF) only occurs at very negative potentials, approximately -2.8 V vs SCE.

This electrochemical procedure, however, has some experimental difficulties due to the very negative potentials.

For this reason, attempts were made to design substituted benzyloxycarbonyl groups where the role of the substituent is to shift the reduction potential to much less negative values.

In this paper we present the results obtained in the study of the cathodic cleavage of 4-chlorobenzyloxycarbonyl and 2,4-dichlorobenzyloxycarbonyl groups from the urethane derivatives of morpholine and of 4-picolyl group from thioethers at a vitreous