

ELECTROREDUCTION OF METHYLISOCYANIDE AT A LOW-OXIDATION
STATE IRON CENTRE

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Summary

Electroreduction of methylisocyanide to dimethylamine has been achieved by controlled potential electrolysis at the cathodic wave of trans-[FeH(CNMe)(Ph₂PCH₂CH₂PPh₂)₂][BF₄], in 0.2 M [Bu₄N][BF₄] / tetrahydrofuran and in the presence of phenol.

Introduction

Methylisocyanide (C≡NMe) is a recognized substrate of nitrogenase, being mainly reduced to methane plus methylamine (six electrons) and dimethylamine (four electrons); its activation is believed to proceed by coordination to a transition metal present at the active centre (Mo, V or Fe).

We have previously succeeded in achieving its chemical activation towards protonation (in particular to give those products) at some electron-rich d⁶ Mo, W or Re phosphinic sites [1], which are also able to bind N₂, but at the related (although less electron-rich) iron(II) centre trans-{FeH(dppe)₂}⁺ (dppe = Ph₂PCH₂CH₂PPh₂) such activation has not been detected [2] for the substrate.

However, we now report that electrochemical reduction of trans-[FeH(CNMe)(dppe)₂][BF₄] induces protonation at the isocyanide ligand which is then reduced to dimethylamine.

Results and discussion

In previous studies [3], we have investigated, by cyclic voltammetry (CV) and controlled potential electrolysis (CPE), the anodic behaviour of the hydride-isocyanide complexes $\text{trans-}[\text{FeH}(\text{CNR})(\text{dppe})_2][\text{BF}_4]$ ($\underline{1}$, R = alkyl or aryl), at a Pt electrode, and observed an anodically induced Fe-H bond cleavage (with proton loss) and metal fluorination, according to an ECEC - type mechanism, to give $\text{trans-}[\text{FeF}(\text{CNR})(\text{dppe})_2][\text{BF}_4]$ (R = Me). In the present work, we have investigated the cathodic behaviour of one of these complexes ($\underline{1}$, R=Me), in 0.2 M $[\text{Bu}_4\text{N}][\text{BF}_4]/\text{thf}$, also by CV and CPE, at a Pt-wire or -gauze electrode, respectively.

By CV, complex ($\underline{1}$, R = Me) undergoes a reversible cathodic wave at $E_{1/2}^{\text{red}}$ ca. -1.8 V vs. SCE (see Fig. 1). However, this wave becomes irreversible upon addition of phenol, and its current-function then exhibits a pronounced increase on lowering the scan rate (Fig. 2).

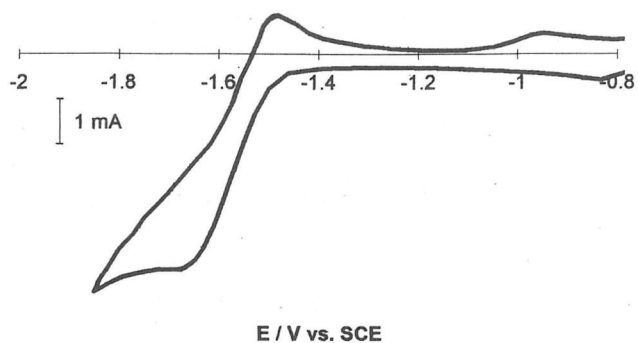


Fig. 1 - Cyclic voltammogram (cathodic scan, 200 mV s^{-1}) of $\text{trans-}[\text{FeH}(\text{CNMe})(\text{dppe})_2][\text{BF}_4]$ in 0.2 M $[\text{Bu}_4\text{N}][\text{BF}_4]/\text{thf}$, at a Pt wire electrode.

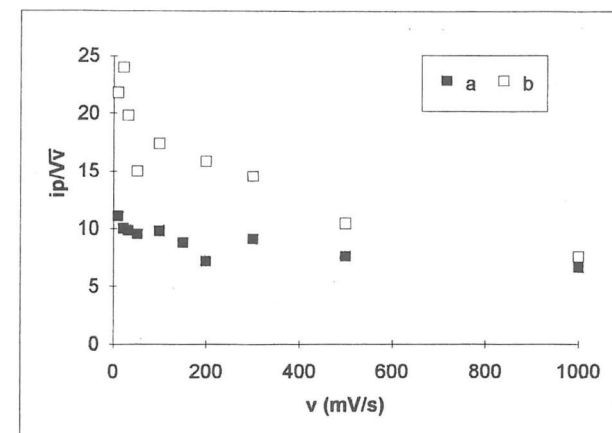
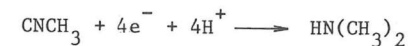


Fig. 2 - Variation of the current-function with the scan rate for the cathodic wave of $\text{trans-}[\text{FeH}(\text{CNMe})(\text{dppe})_2][\text{BF}_4]$, (a) in the absence and (b) in the presence of phenol. Current-function in arbitrary unit, and scan rate in mV s^{-1} .

Moreover, in the presence of a tenfold molar excess of phenol, the total charge transferred during the exhaustive cathodic CPE corresponds to 10 electrons per iron.

In addition, a spectrophotometric analysis (by using the 1-fluoro-2,4-dinitrobenzene test) of the electrolyzed solution indicated the formation of dimethylamine, derived from a 4e-reduction of the isocyanide (eq.), in ca. 35% yield relative to the metal (current efficiency of ca. 14%).



In the absence of phenol, the exhaustive CPE at the cathodic wave of the iron(II) complex corresponds to the transfer of two electrons/metal, possibly leading to the formation of an isocyanide-iron(0) species, a conceivable intermediate in the isocyanide reductive process.

In a related dinitrogen complex of iron(0), $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$ ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$), formed upon deprotonation of $[\text{FeH}(\text{N}_2)(\text{dmpe})_2]^+$ by KOBU^t , it was shown [4] that N_2 undergoes protic cleavage (e.g., by HCl) to ammonia. However, in contrast with this entirely chemical reduction of N_2 , the observed methylisocyanide reduction in our study followed an electrochemical route.

Final comments

This work indicates that an alkyl isocyanide ligand at an iron centre can undergo electrochemical activation towards protonation to give a dialkylamine, in a process which possibly involves the formation of a coordination iron(0) centre. Attempts to isolate and characterize intermediates in this process are under way.

The observed reduction of methylisocyanide to dimethylamine involves a 4-electron process which is also known to occur in nitrogenase. However, a 6-electron reductive pathway can also be followed in the enzymatic system, a situation which we have achieved previously [5] in the electrochemical reduction of CNMe at some thiomolybdate-derived centres, with formation of ammonia, methane and ethylene, involving the cathodic CN bond cleavage, a process which has not been detected at our iron system.

References

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IONIC INTERACTIONS IN PHOSPHATE AQUEOUS SOLUTIONS

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Abstract

Mean activity coefficients of NaCl have been calculated, by means of the Pitzer theory, in mixed solutions of NaCl and NaH_2PO_4 and of NaCl and Na_2HPO_4 , with ionic strength lower than 2 mol kg^{-1} , at 25°C . Electromotive force measurements, using a silver, silver chloride and a sodium ion selective electrodes, show nernstian response, in those mixed electrolyte solutions.

Introduction

In the study of mixed electrolyte solutions, the Pitzer approach separates arbitrarily between electrostatic and specific short-range interactions, and enables these, expressed as virial coefficients, to be calculated for single electrolyte solutions and applied to the analysis of mixtures [1]. Aqueous phosphate solutions are of great interest, mainly because phosphates are present in many natural waters, effluents and physiological fluids, being the sodium chloride the predominant electrolyte in some of them. The mean activity coefficient of NaCl has been calculated, by means of the Pitzer theory, in solutions of NaCl and NaH_2PO_4 and of NaCl and Na_2HPO_4 , and electromotive force measurements on the cell



have been used to study the response of the silver, silver chloride and sodium ion selective electrodes in those mixed electrolyte solutions.