Cationic (η^5-Cyclopentadienyl)(η^6-arene)iron(II) Catalyst for the Electroreduction of Nitrate Ion

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Summary The 19-electron complex radicals resulting from the one-electron reduction of the cationic precursors $[(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-arene})Fe^{II}]^+$ quickly reduce nitrate ions to ammonia in aqueous solutions.

Recent interest in chemically modified electrodes,[1] catalysis of electrochemical reductions,[2] and indirect coulometric titration[3] focuses attention on the use of organometallic redox couples in electrochemistry. Few metallic ions, complexed or not, are available as redox couples in aqueous media. We report here the use of the redox couples $[(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-arene})Fe^{II}]^+$– corresponding radical (equation 1), in the catalysis of the electroreduction of nitrate ions to ammonia, on a mercury electrode.

Suitable choice of arene[4] or starting ferrocene derivatives,[5] or regioselective ligand modification[6] permit the synthesis of various functional compounds. The very low standard potential of the couple (**1–2**) ($-1\cdot1$ to $-1\cdot5$ V, *vs.* standard

$$\text{(1)} + 1e \rightleftharpoons \text{(2)} \qquad (1)$$
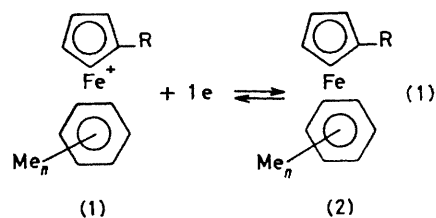
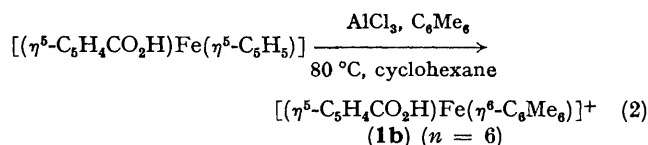a; R = H
b; R = COOH
$0 \leqslant n \leqslant 6$

hydrogen electrode) may be altered as required by ligand modification,[7] but it is more interesting to increase the stability of the corresponding neutral radical, a 19 electron-complex, by varying the number of methyl substituents on the arene ring; when hexamethyl benzene is used ($n = 6$) the neutral radical (**2a**) is insoluble and stable towards

TABLE. Rate constants k for the reoxidation of the reducing agent in catalytic electroreduction.[11]

Catalyst	Medium	Reducing agent	Substrate	k/mol^{-1} l s^{-1}
Na$_2$MoO$_4$	H$_2$SO$_4$ (0·2 N) Na$_2$SO$_4$ (0·2 M)	Mo^{3+}	NO$_3^-$	10^3
UO$_2$SO$_4$	HCl (0·01 N) KCl (0·1 M)	U^{3+}	NO$_3^-$	8×10^{6}[a]
(1b) $n = 6$	LiOH 0·1 N	(2b) $n = 6$	NO$_3^-$	4×10^2
"	pH 10·5	"	"	4×10^2
"	LiOH 0·1 N	"	NO$_2^-$	2×10^3
"	"	"	NH$_2$OH	$1·5 \times 10^2$
(1a) $n = 2$ (m-xylene)	"	(2a) $n = 2$	NO$_3^-$	3×10^2
(1a) $n = 0$	"	(2a) $n = 0$	"	2×10^2

[a] See J. Koryta, Coll. Czech. Chem. Comm., 1955, 20, 667.

decomplexation or dimerization in aqueous solutions.[8] For homogeneous conditions, the cationic carboxy compound (1b) ($n = 6$) is more suitable, synthesized by ligand exchange starting from the ferrocene-carboxylic acid, equation (2). The pure PF$_6^-$ salt of (1b) ($n = 6$) is easily

$$[(\eta^5\text{-}C_5H_4CO_2H)Fe(\eta^5\text{-}C_5H_5)] \xrightarrow[\text{80 °C, cyclohexane}]{\text{AlCl}_3, \ C_6Me_6}$$

$$[(\eta^5\text{-}C_5H_4CO_2H)Fe(\eta^6\text{-}C_6Me_6)]^+ \quad (2)$$
$$\text{(1b)} \ (n = 6)$$

obtained (yield 30%) after separation from the by-products $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6Me_6)]^+$ and $[(\eta^6\text{-}C_6Me_6)_2Fe]^{2+}$. In alkaline media the reducing agent (2b) is soluble, acting as a mediator transferring electrons from the electrode to the substrate. The pH must be kept above 10 to avoid reduction of CO$_2$H to CH$_2$OH.[6]

In the absence of other reducible substrates, the organometallic compounds (1) show a one-electron reduction wave. Cyclic voltammetry confirms that the process is reversible at a scanning voltage rate of 0·1 V s^{-1}. At very slow rates ($<$0·01 V s^{-1}) the corresponding radicals (2) are oxidised by water to regenerate the starting compounds (1), equation (3).

$$\text{(2)} + H_2O \rightarrow \text{(1)} + OH^- + \tfrac{1}{2}H_2 \quad (3)$$
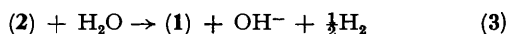
The very low potential of the redox couple is favourable for the electroreduction of small ions or molecules[2] which have a high standard potential. Nitrate ions are quickly reduced showing a polarographic catalytic wave increasing in height with nitrate concentration. The Table shows that the catalysts (1) are not as active as U^{III}[9] but are more specific than Mo^{III}[10] for nitrate reduction. The activity of the organometallic catalysts(1) is practically independent of the pH of the solution and of structural modification. The catalytic wave of the cationic compounds (1) can be

used for analytical determinations of nitrate ion in the range 10^{-3}—10^{-1} M.

Typically the catalyst (1b) ($n = 6$) (2×10^{-4} mol) is used for the controlled potential electrolysis of LiNO$_3$ (10^{-2} mol) in LiOH (0·1 N) at a mercury electrode ($-1·8$ V vs. standard calomel electrode). At the end of the electrolysis the polarogram of the solution shows the unaltered initial diffusion-controlled wave of the catalyst. Because of difficulties in the analysis and recovery of gaseous products, only the yield of ammonia is reported. Chemical and electrical yields for the reduction to ammonia, respectively 63 and 57%, show that an important part of the reaction leads to unanalysed products. However, formation of ammonia as the final product shows that the postulated intermediates in the reduction, resulting from successive one electron transfer steps (NO$_2$, NO$_2^-$, NO, NO$^-$, ·NHOH, NH$_2$OH, ·NH$_2$) are reduced either catalytically or at the electrode. The catalytic reductions of NO$_2^-$ and NH$_2$OH have been verified. As shown by the rate constants in the Table, estimated by Koutecky's procedure,[11] NH$_2$OH is slowly reduced, and hence it is detected as an intermediate during controlled potential nitrate reduction. N$_2$H$_4$, an intermediate which is also observed in solution, may result from the dimerization of the ·NH$_2$ radical. No other oxidisable or reducible species were detected in solution during electrolysis.

Other organometallic compounds having a low standard potential and high stability in aqueous solutions, such as $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ or $[(\eta^5\text{-}C_5H_5)_2TiOH]^+$, cannot be used as catalysts. They show very low activity for nitrate reduction in acidic media; the polarographic wave remains diffusion-controlled with increasing nitrate concentration. However, controlled potential electrolysis shows that slow reduction occurs in solution.

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