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ELECTROCHEMICAL STUDY OF $[Fe(NO)_2I]_2$ AND $Fe(NO)_2IPPh_3$ IN DMF AND EVIDENCE FOR THEIR COMPLETE IONIZATION

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Summary

$[Fe(NO)_2I]_2$ and $Fe(NO)_2IPPh_3$ are completely ionized in DMF; the resulting $Fe(NO)_2{}^+$ and $Fe(NO)_2PPh_3{}^+$ can be reduced at a mercury electrode giving rise to the neutral $Fe(NO)_2$ which is known to be a powerful catalyst.

Introduction

The search for inexpensive and selective catalysts in homogeneous solution attracts great interest. Two routes to active catalytic species derived from transition metal compounds are available: a) in situ preparation by elimination of appropriate ligands to generate reactive entities; and b) production of unusual oxidation states of the central metal coupled with a change in its coordination number in order to provide new bonding possibilities for the species whose reactions are to be catalyzed. Both of these methods can be initiated in a controlled way by electrochemical procedures.

Route b is currently exploited in this laboratory for some ruthenium complexes [1], while route a has been attempted with Fe and Co compounds [2].

The recent publication of a short note [3] on the electrochemical study of the generation and fate of iron dinitrosyl, a powerful catalyst for C–C bond formation from dienes, prompted us to present some preliminary results on related systems which have been studied in a different solvent. The purpose is to throw light on the different behaviour of the title compounds in different media.

Experimental

$[Fe(NO)_2I]_2$ and $Fe(NO)_2IPPh_3$ were prepared by the literature procedures [4]. Conductance measurements in DMF were carried out with an Amel Mod. 131 Conductometer at 10^3 Hz. An air-tight thermostatted cell (cell constant = 0.573 cm) was used. Polarographic measurements were performed with an Amel Mod. 462 potentiostat. Voltammetric experiments with a hanging mercury electrode were made

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with an Amel Mod. 448 polarograph with Ag/AgCl, Me_4NCl(sat.) in DMF as reference electrode. All measurements were made at 25 ± 0.2°C.

Results

Conductance measurements

$[Fe(NO)_2I]_2$ showed strong ionic conductivity in DMF in the concentration range 5×10^{-5} to $10^{-3}M$; the equivalent conductance data are shown in Fig. 1. They follow the Onsager limiting equation with $\Lambda_\infty = 340$ ohm^{-1} cm^{2}mol^{-1}. Assuming that the complex is fully dissociated according to:

$$[Fe(NO)_2I]_2 = 2\, Fe(NO)_2{}^+ + 2\, I^-$$

and with Λ_∞ for iodide ion in DMF (52 ohm^{-1} cm^{2}mol^{-1}), one obtains $\Lambda_{\infty[Fe(NO)_2{}^+]} = 118$ ohm^{-1} cm^{2}mol^{-1}. With this figure and the value of the Stokes iodide radius,

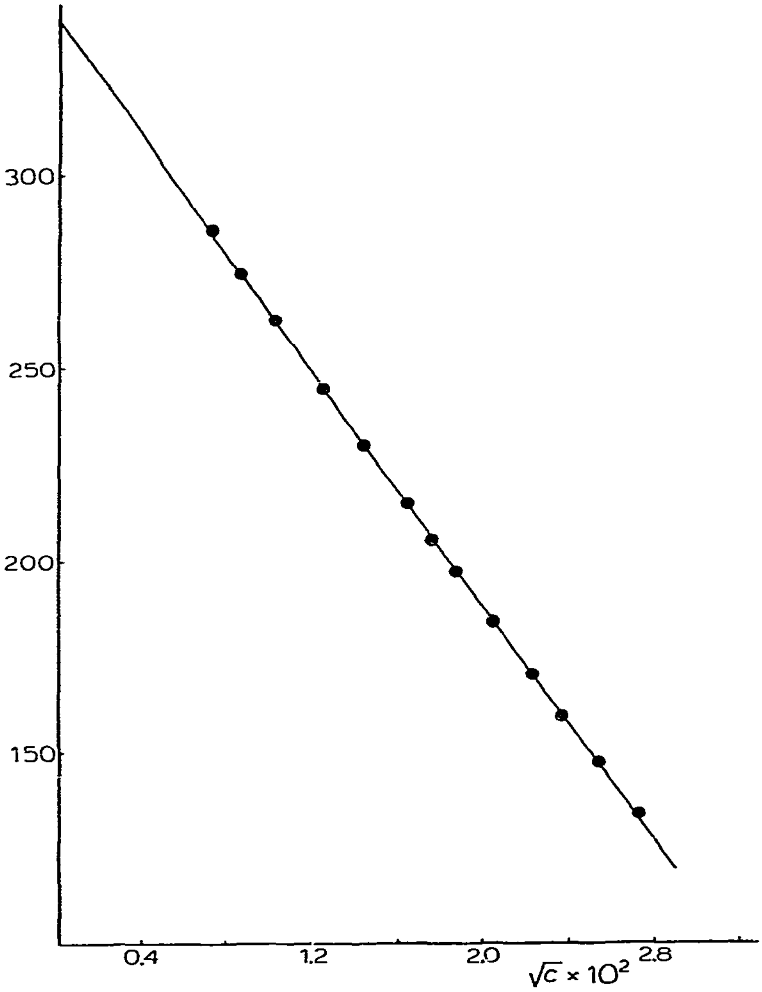

Fig. 1. Conductometric data for $[Fe(NO)_2I]_2$ in DMF.

$r_s = 2.0$ Å, the Walden rule allows evaluation of the $Fe(NO)_2^+$ radius, i.e. 0.9 Å. This value is compatible with the crystallographic data for the moiety $Fe(NO)_2$ inferred from the structural data for $[Fe(NO)_2I]_2$ [5]. It seems reasonable, then, despite the uncertainties in the Walden rule, to conclude that the dimer is completly dissociated and ionized in solution, giving bare $Fe(NO)_2^+$ ions.

The conductance measurements for $Fe(NO)_2IPPh_3$ do not at present have quantitative significance because of the presence of the impurities of PPh_3 and $Fe(NO)_2(PPh_3)_2$, which are very difficult to remove from the main product.

Polarographic and voltammetric measurements

The solutions of the title compounds are sensitive towards air and oxidizing agents, giving iron oxides and nitrogen dioxide as main products. The rate of the decomposition increases with the ionic strength of the solution, providing further evidence for a decomposition involving ionic species. It was also ascertained that mercury in contact with the solution of these compounds did not appreciably influence the decomposition rate, which is, however, greatly enhanced by traces of either metallic iron or iodine. Unfortunately, the latter substances are slowly formed even in solutions stored under nitrogen at low temperature. For these several reasons only freshly prepared solutions were studied. The polarograms of the two com-

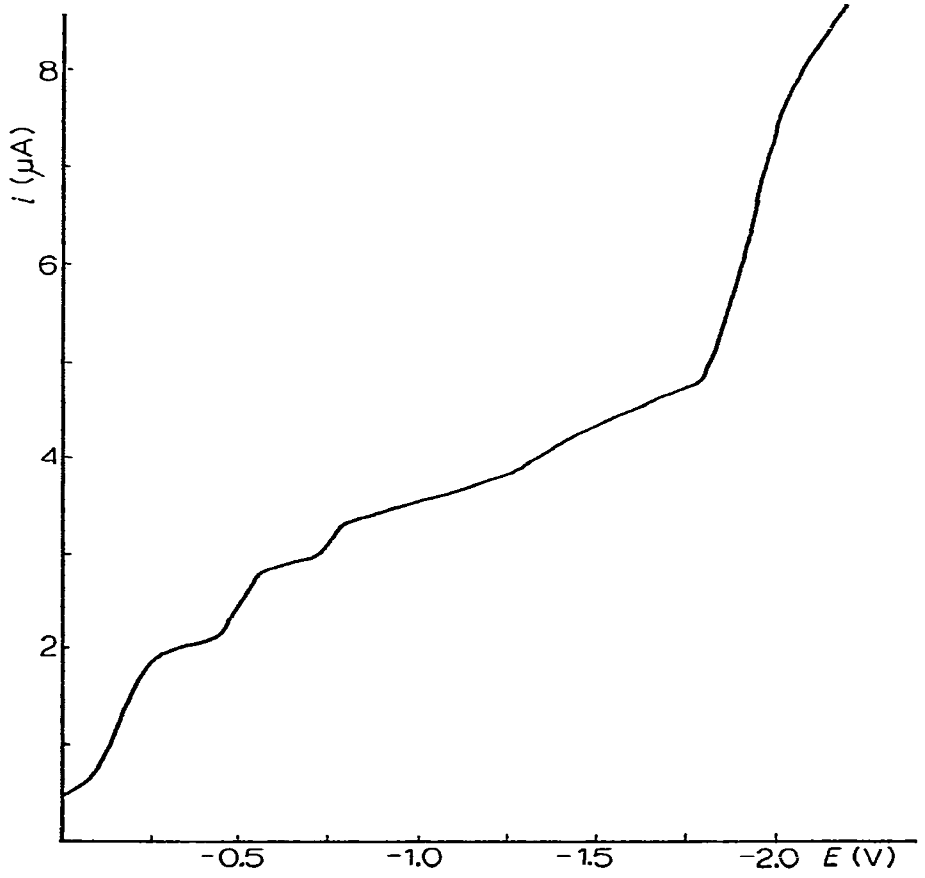

Fig. 2. Polarogram of a 1.25×10^{-3} M solution of $[Fe(NO)_2I]_2$ in DMF with 0.1 M TEAP.

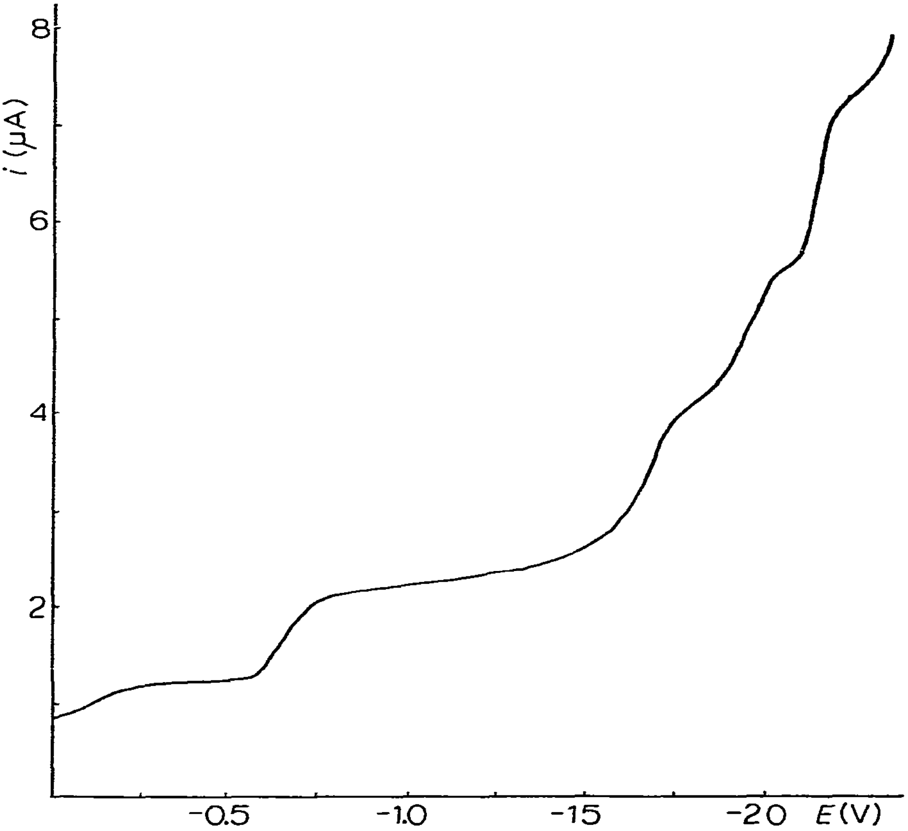

Fig. 3. Polarogram of a 10^{-3} *M* solution of $Fe(NO)_2IPPh_3$ in DMF with 0.1 *M* TEAP.

pounds, in the potential range from 0 to -2.4 V, are shown in Figs. 2 and 3. Both of them show a finite reduction current even at 0 V. Its origin was ascertained from measurements in the range -0.1 to $+1.0$ V (Fig. 4), where both compounds show two oxidation waves at the same potential; they are due to oxidation of mercury in presence of free I^- ions, as ascertained from independent measurements with solutions of KI in DMF *. The coincidence of the $E_{1/2}$ with those for the KI solutions at the same bulk concentration of I^- provides further evidence that the two compounds are completely ionized in solution. It must be deduced, then, that the finite current at 0 V is due to the reduction of HgI_4^{2-} formed at the surface of the electrode according to the following sequence:

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* KI in DMF gives two oxidation waves at $+0.095$ and $+0.48$ V. The first follows the equation $E = c + (RT/2F)\ln(i/(i_d - i)^4$, with $E_1/_2$ depending on the bulk concentration of I^- according to $E_{1/2} = c' - (3RT/2F)\ln i_d$. This is compatible with the reaction

$Hg + 4\,I^- = HgI_4^{2-} + 2e^-$

The second wave, presumably involving the formation of HgI_3^-, is irrelevant to the present discussion.

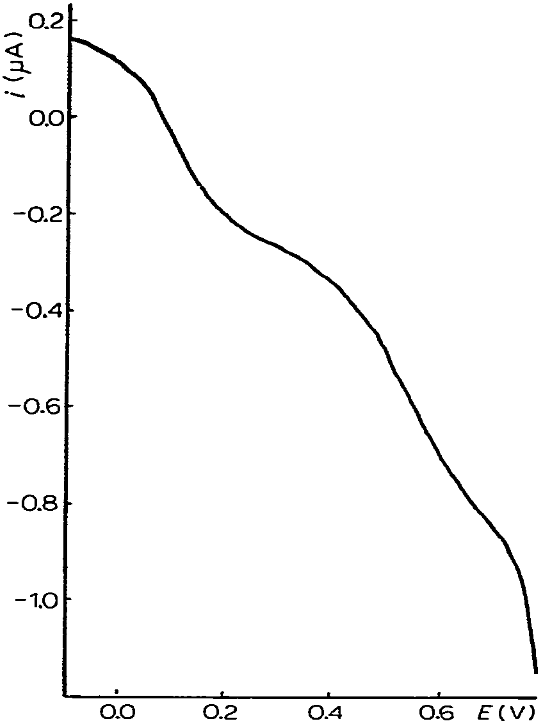

Fig. 4. Polarogram of a 10^{-3} *M* solution of $Fe(NO)_2IPPh_3$ in DMF with 0.1 *M* TEAP.

$$\left.\begin{array}{l} 1/2\,[Fe(NO)_2I]_2 \rightleftarrows Fe(NO)_2^+ + I^- \\ Fe(NO)_2IPPh_3 \rightleftarrows Fe(NO)_2PPh_3^+ + I^- \\ \text{or} \\ Fe(NO)_2IPPh_3 \rightleftarrows Fe(NO)_2PPh_3^+ + I^- \\ \qquad \searrow\nwarrow \qquad\qquad \swarrow\nearrow \\ \qquad\qquad Fe(NO)_2^+ + I^- + PPh_3 \end{array}\right\} \qquad (1)$$

$$Hg + 4I^- + 2\,Fe(NO)_2^+\ (\text{or } 2\,Fe(NO)_2PPh_3^+) \rightleftarrows HgI_4^{2-} + 2\,Fe(NO)_2 \qquad (2)$$

$$HgI_4^{2-} + 2\,e^- \rightleftarrows Hg + 4\,I^- \qquad (3)$$

The reaction sequence eq. 1–3 is compatible both with free I^- ions and the finite current at 0 V, given by eq. 3. If the process represented by eq. 2 were missing, the total current at 0 V would be zero due to the sequence:

$$Hg + 4\,I^- \rightleftarrows HgI_4^{2-} + 2\,e^- \qquad (2')$$

$$HgI_4^{2-} + 2\,e^- \rightleftarrows Hg + 4\,I^- \qquad (3')$$

The usual analysis of the first wave showed that in both compounds a monoelectronic reversible process is involved, due to reactions 4 and 5, respectively:

$$Fe(NO)_2^+ + e^- \rightarrow Fe(NO)_2\ (E_{1/2} = -0.15\ \text{V}) \qquad (4)$$

$$Fe(NO)_2PPh_3^+ + e^- \rightarrow Fe(NO)_2PPh_3\ (E_{1/2} = -0.62\ \text{V}) \qquad (5)$$

A small wave at -0.15 V is also present for the phosphine derivative. Addition of this to the main wave at -0.62 V gives a total current comparable to that of the unsubstituted compound at the same bulk concentration. It can be concluded, then, that further dissociation of the PPh_3 derivative as in eq. 1, contributes to the total reduction process. However, this dissociation is relatively slow as shown by the kinetic character of the corresponding wave at -0.15 V. The same wave for the unsubstituted compound is purely diffusive.

The low value of the corresponding values of $E_{1/2}$, compared to that for Fe^{2+} (-0.98 V), is mainly due to the high electron affinity of the low valence Fe^{I} stabilized by the two nitrosyl groups, and presumably, also to lack of solvation. On the other hand, the potential shift of ca. -0.4 V upon insertion of a PPh_3 ligand is compatible with the empirical rule previously observed [2a] for different iron nitrosyl compounds, involving a shift of -0.6 V per PPh_3 ligand introduced.

A further wave, at -1.93 V, is common to both compounds and to $Fe(NO)_2(PPh_3)_2$ previously studied [2a]. As a possible reduction of Fe^{2+}, NO (-0.6 V) or polynuclear species [2a] was ruled out is was concluded that either $Fe(NO)_2$ or $Fe(NO)_2(DMF)_2$ might be responsible. This is also in agreement with the appearance of the reduction wave of free PPh_3 for the substituted compound at -2.14 V, as a result of the fast dissociation of $Fe(NO)_2PPh_3$.

Finally, the nature of the wave at -0.53 for $[Fe(NO)_2I]_2$ and at -1.68 V for its PPh_3 derivative have not been ascertained.

Voltammetric experiments on a stationary mercury electrode have shown, as

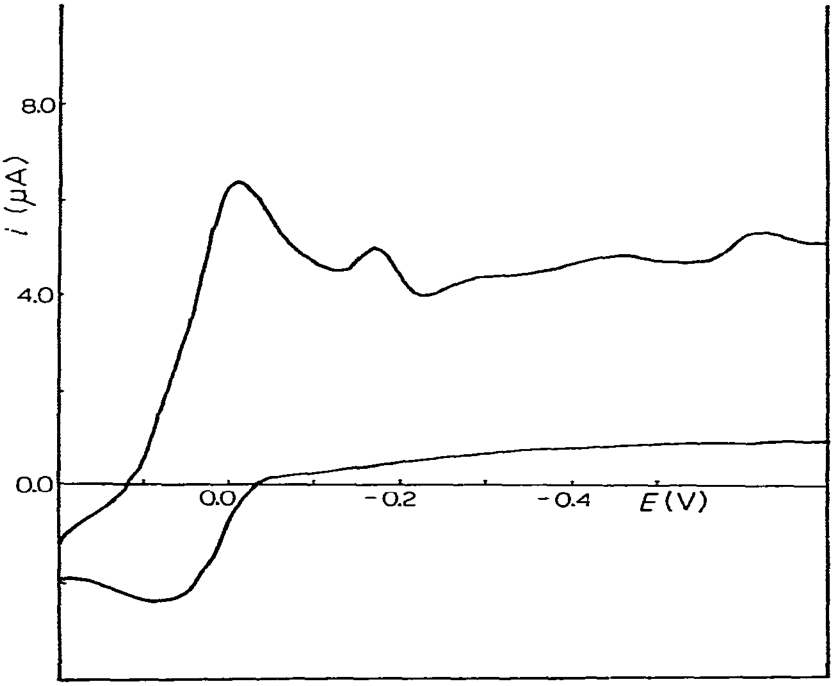

Fig. 5. Voltammogram of a 10^{-3} *M* solution of $[Fe(NO)_2I]_2$ in DMF with 0.1 *M* TEAP; $v = 0.1$ V/s; prepolarization time = 48 s at +0.2 V.

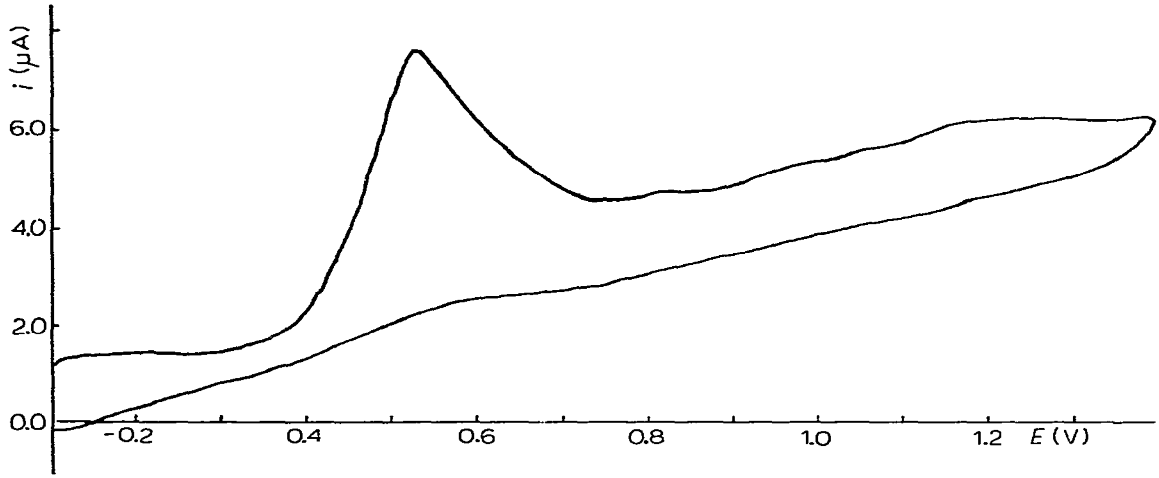

Fig. 6. Voltammogram of a 10^{-3} *M* solution of $[Fe(NO)_2I]_2$ in DMF with 0.1 *M* TEAP; $v = 0.1$ V/s; prepolarization time = 48 s at −0.1 V.

expected, a strong influence of the prepolarization time, at a potential positive to that of $Fe(NO)_2{}^+$ reduction, on the whole shape of the *i*-*V* curves. In Fig. 5 is shown a voltammogram of $[Fe(NO)_2I]_2$ after a prepolarization time of 48 s at 0.2 V. The main reversible peak, at −0.01 V, is due to the reduction of $HgI_4{}^{2-}$ formed according to eq. 3. The peak at −0.17 V is due to the reduction of $Fe(NO)_2{}^+$. In this case also, independent experiments with KI in DMF confirmed the previous conclusions.

Other peaks observed in the cathodic branch are kinetic in nature and require further investigation. It should be mentioned however, that a voltammogram of $[Fe(NO)_2I]_2$ at an electrode maintained for 48 s at −0.1 V showed (Fig. 6) a main peak at −0.53 V, corresponding to the unknown polarographic wave. This suggests that the peak may be due to some species not fully coordinated with DMF.

Conclusions

Comparison of the present results with those in THF [3] reveals a marked difference in the behaviour of the compounds in different solvents. It is apparent that in a solvent with a higher dielectric constant the compounds dissociate and ionize completely, giving rise to different electroactive species. In contrast with the results in THF, not all the reducible species contain halogen atoms in the inner coordination sphere of the complexes. The neutral species $Fe(NO)_2$ or $Fe(NO)_2(Sol.)_n$, reducible at the most negative potential, is common to both solutions. For the same reasons, the anodic behaviour of these compounds is different in the two solvents. In fact, free halogen ions give oxidation waves at less negative potentials under our conditions, paralleling the behaviour of free halogens in solution.

However, the different reduction mechanism should not give rise to different catalytic activity since the active species is the neutral $Fe(NO)_2$. This aspect of the problem is being currently investigated.

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