THE ELECTROCHEMICAL OXIDATION OF (BENZYLIDENEACETONE) DICARBONYLTRIPHENYLPHOSPHITEIRON(0) COMPLEX IN DIMETHYLFORMAMIDE.

Assis V. Benedetti and Vania M. Nogueira

Instituto de Química de Araraquara,Universidade Estadual Paulista

Caixa Postal 174, 14800 - Araraquara (SP), Brasil

Eduardo J.S. Vichi and Edison Stein

Instituto de Química, Universidade Estadual de Campinas

Caixa Postal 6154, 13100 - Campinas (SP), Brasil

Abstract: The electrochemical oxidation of the title complex was studied by cyclic voltammetry, in DMF, at 25°C. The results suggest that the electrode process can be described by an ECE mechanism, i.e.,the species formed in the first oxidation step is highly unstable and its decomposition is assisted by the coordinating solvent.

In previous papers (1-3) we have described the preparation, structure and bonding properties of (benzylideneacetone)$Fe(CO)_2$ L (L= CO, phosphines, phosphites) complexes. One reason for investigating these compounds is that the electronic properties of the phosphorus ligands can help in understanding the nature of the iron-heterodiene bonding as well as the structure of the complexes in solution. The electron donor/acceptor properties of the $Fe(CO)_2$ L moieties are important in determining the "six-coordinated charater" of the formally five coordinated (diene) $Fe(CO)_2$L complexes (3,4). We are interested in the electrochemical behaviour of these compounds because it can provide additional information on the electronic properties of the metal into the complex.

The electrochemical reduction of (benzylideneacetone)$Fe(CO)_3$ was reported by El Murr et al (5). The authors observed that the product of the first step (monoelectronic and reversible) undergoes slow decomposition assisted by the solvent (THF) producing free benzylideneacetone (BDA) and the anion-radical $[Fe(CO)_3S_n]^{-\cdot}$(S=solvent). The anion-radical decomposes fastly in strongly coordinating solvents such as dimethylformamide (DMF). We here report the electrochemical oxidation of (BDA)$Fe(CO)_2P(OPh)_3$, as evidenced by cyclic voltammetry.

The electrochemical oxidation was performed at 25°C, in DMF containing $NaClO_4$ (0.5 M) as electrolyte. In the cyclic voltammetry experiments a platinum disk was used as working electrode and a platinum wire as auxiliary electrode. The potentials were measured against a Ag/Ag^+ (10^{-2} M) reference electrode. The oxidation of the complex occurs at +0.35 V, and the cyclic voltammograms were recorded before and after a controlled electrolysis at this potential. A platinum net was used as working electrode in the controlled potential electrolysis.
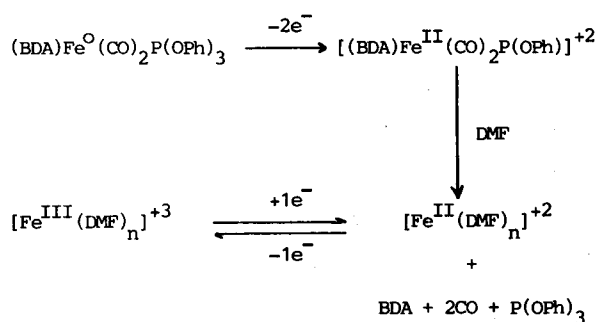
The cyclic voltammograms are shown in the Figure. Graph (a) is the voltammogram of the 0.50 M solution of $NaClO_4$ in DMF, recorded in the range of potentials from -1.5 to +1.0 V and scanning rate of 100 mV/s. Graphs (b) and (c) are the voltammograms of 1 mM solutions of (benzylideneacetone)$Fe(CO)_2P(OPh)_3$ in DMF, at scanning rate of 50 mV/s, recorded before the electrolysis at controlled potential. Graph (b) is the reppeating scanning voltammogram in the range of potentials from -1.5 to +0.40 V. The peak 2A appears only in the reppeated scanning and the pair 2A-2C is not observed when the scanning is inverted before the oxidation at +0.35 V (graph (c)).

After the controlled potential electrolysis at +0.35 V, which consumed 2.9 F/mol^{-1},the peak 1A disappears and only the 2A-2C pair is observed at a potential of -0.11 V, as shown in graph (d).The current ratio 2C/2A is 1.0 and the separation between the peaks is 60 mV, as expected for a one electron reversible process. The electrolysed solution at +0.35 V

was submited to a second electrolysis at -0.11 V, and 0.95 F/mol were consumed.

The current function for the 1A peak decreases with the scanning speed, suggesting that the electrode process can be described by an ECE mechanism (6), i.e., the species formed in the first oxidation step is highly ustable and its decomposition is assisted by the strongly coordinating solvent, DMF. One of the products of this decomposition is responsible for the 2A-2C pair of peaks. The analysis of the electrolysis products showed the presence of free BDA, identified by its infrared spectrum ($\nu_{C=O}$ at 1680 cm^{-1}), the presence of free Fe^{+3} and the absence of Fe^{+2}. When the solution resulting from the electrolysis at +0.35 V was electrolysed at -0.11 V, the presence of free Fe^{+2} was observed after a few hours. After bubling dioxygen and/or adding concentrated HCl to this solution the presence of Fe^{+3} was detected. Cyclic voltammetry of $Fe(NO_3)_2$, carried out in the same conditions, showed the same pair of peaks 2A-2C observed for (benzylideneacetone)$Fe(CO)_2P(OPh)_3$.

The results discussed above indicate that the global electrode process for the oxidation of (BDA)$Fe(CO)_2P(OPh)_3$ may be represented as in the Schemme.

$$(BDA)Fe^{O}(CO)_2P(OPh)_3 \xrightarrow{-2e^-} [(BDA)Fe^{II}(CO)_2P(OPh)]^{+2}$$

$$\downarrow DMF$$

$$[Fe^{III}(DMF)_n]^{+3} \underset{-1e^-}{\overset{+1e^-}{\rightleftharpoons}} [Fe^{II}(DMF)_n]^{+2}$$

$$+$$

$$BDA + 2CO + P(OPh)_3$$

<center>Schemme</center>

The assumed zero oxidation state for the iron in the (BDA)$Fe(CO)_2P(OPh)_3$ is further supported by Mossbauer spectroscopy (7).

References

1. B.F.G. Johnson, J. Lewis, G.R. Stephenson and E.J. S. Vichi, J.Chem.Soc., Dalton Trans.1978, 369.

2. E.J.S. Vichi, P.R. Raithby and M.Mc Partlin, J. Organomet.Chem. 1983, 256, 111.

3. E.J.S. Vichi, F.Y. Fujiwara and E. Stein, Inorg. Chem. 1985, 24, 286.

4. L. Kruczynski and J. Takats, Inorg. Chem. 1976, 15, 3140.

5. N. El Murr, M. Riveccie and P. Dixneuf, J. Chem. Soc., Chem. Commun. 1978, 552.

6. R. S. Nicholson and I. Shain, Anal. Chem. 1965, 37, 178.

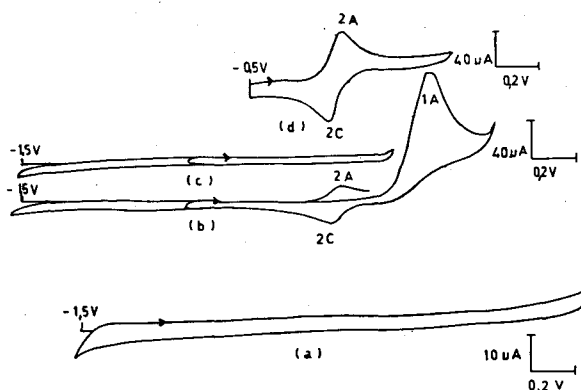7. E. J. S. Vichi, E. Stein and E. B. Saitovich, unpublished results.

Figure. Cyclic voltammograms of (a) solution of $NaClO_4$ (0.50M) in DMF, at 25°C and scanning rate of 100 mV/s; (b) and (c) solution of (BDA)$Fe(CO)_2P(OPh)_3$ in DMF (10^{-3}M), at 25°C and scanning rate of 50 mV/s, before the electrolysis at +0.35 V; (d) solution of (BDA)$Fe(CO)_2P(OPh)_3$ in DMF (10^{-3}M), at 25°C, and scanning rate of 50 mV/s, after the electrolysis at +0.35 V.