THE ELECTROCHEMICAL OXIDATION OF HETERODIENECARBONYL-IRON (O) COMPLEX WITH DIFFERENT LIGANDS.

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The electrochemical oxidation of complexes of the $|(bda)\ Fe(CO)_2L|$ type with bda = benzylideneacetone, L = CO, PPh_3, $P(OPh)_3$, PEt_3 and Pcy_3 was studied by cyclic voltammetry, controlled potential electrolysis and chronoamperometry in dimethylformamide, DMF 0.5M $NaClO_4$. A platinum disk, with 0.18 cm^2 of area was used as working electrode in the cyclic voltammetry experiments. For the controlled potential electrolysis, the working electrode was a platinum network and for the chonoamperometry, a vitreous carbon disk with 0.07cm^2 of area was used. An Ag/Ag^+ (10^{-2}M), DMF 0.5M $NaClO_4$ electrode was used as a reference electrode[1] and a platinum wire as auxiliary electrode. All tests were made at 25°C, using a threee electrode conventional cell and previously purified chemical substances[1]. The electrochemical measurements were made with a FAC MOD. 200A potentiostat, and UNIVERSAL RAMP GENERATOR FAC MOD. 201A and a HP 7090A MEASUREMENT PLOTTING SYSTEM recorder.

The figure shows the cylcic voltammograms for the 1.10^{-3}M solution of the $|(bda)\ Fe(O)\ (CO)_2\ P(OPh)_3|$ complex at different conditions. This illustrates the electrochemical behavior of all compounds. For all the complexes, the 2a peak appears only in the repetitive scanning and stays even at v>500 $V.s^{-1}$ and -50°C. The

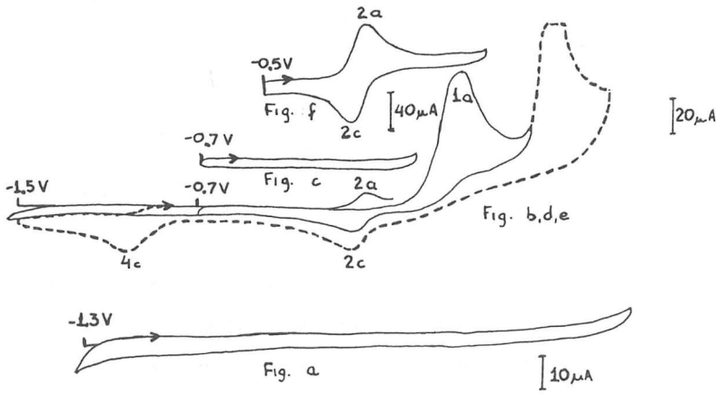

Figure. Cyclic voltammograms for (a) solution of $NaClO_4$ (0.5M) in DMF, at 25°C and sweep rate, v = 0.1V.s^{-1}; (b) and (c) solution of |(bda) Fe(O) $(CO)_2P(OPh)_3$| (10^{-3}M) in DMF, at 25°C and v = 0.05V.s^{-1}, before the electrolysis at +0.35V; (d) ibid. (b) and (c) after electrolysis at + 0.35V.

separation of the 2a/2c pair of peaks is 60mV and the peak current ratio is unitary. This pair of peaks is the only observed after the exhaustive electrolysis at the 1a potential peak and they were ascribed to the Fe^{3+}/Fe^{2+} solvated pair. The analysis of the electrolysis products showed the presence of free bda, identified by its infrared spectrum ($\bar{\nu}_{C=O}$ at 1680 cm^{-1}) and by its ultra-violet spectrum (band at 280nm). The peak was ascribed to the Fe(O) complex → → Fe(II) complex oxidation. The 3a peak correponds to the oxidation of the CO adsorbed on the platinum originated from the composition of the complex oxidized form. The number of electrons obtained from the controlled potential electrolysis depends on the potential of the 1a peak, being almost 3 for complexes with L = CO and $P(OPh)_3$ and lower for the others. The results here described suggest a complex electrode process with chemical decomposition reaction of the oxidized form.

The chronoamperometry was used to detemine the complex diffusion coefficients an the decomposition constant rate of the oxidized form. The experiments were repeated for at least six (6) times in every potential condition at a fixed time. The background current was taken away in the calculation[2].

The table shows the parameters obtained from the cyclic voltammograms and chronoamperograms for the |(bda) $Fe(O)(CO)_2L$| compounds at 25°C.

L	E_p^a/mV	$Dx10^6$/cm^2.s^{-1}	k_f/s^{-1}	ΔHNP^3/MV
CO	+550	2.7	12	-
$P(OPh)_3$	+310	6.3	50	875
PPh_3	+35	5.0	30	573
PEt_3	-30	5.5	~100	111
Pcy_3	+120	-	-	35

The results seem to indicate the following mechanism for the electrode global process:

$$|(bda)\ Fe^{o}(CO)_2L| \underset{1a}{\overset{-2e^-}{\rightleftharpoons}} |(bda)\ Fe''(CO)_2L|^{2+} \xrightarrow{k_f} 2\ CO + L + bda + |Fe'''(DMF)_n|^{3+}$$

$$-e^- + e^- \quad (2c)/(2a)$$

$$|Fe''(DMF)_n|^{2+}$$

$$(3a) \downarrow -ne^-$$

products

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