Electrochemical Oxidation of Vaska Complexes, [Ir(CO)XL$_2$]

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Summary Electrochemical oxidation of complexes of the type [Ir(CO)XL$_2$] (X = monoanionic ligand, L = tertiary phosphine) in 0·1M Bu$_4$NClO$_4$–CH$_2$Cl$_2$ proceeds on Pt-electrodes as a diffusion controlled, irreversible one-electron process, indicating that in the redox addition processes atom transferability plays a more important role than the redox properties of the complex.

The oxidations of d^8 square-planar complexes of the type [IrX(CO)L$_2$] have been described as redox additions (see *e.g.* ref. 1) or as metal salt oxidations.[2] In redox addition processes the redox change is assisted by co-ordination, both processes proceeding presumably in a concerted way. The redox properties of the complex undergoing the redox addition would thus be expected to play an important role in the overall process. However, no information is available up to now on the mechanism of simple electron-transfer processes of Vaska complexes. We have therefore studied the electrochemical oxidation of the series of complexes $[IrCl(CO)L_2]$ (L = $PEtPh_2$, PEt_2Ph, PEt_3) and $[IrX(CO)(PPh_3)_2]$ (X = Cl, Br, I) at a rotating Pt electrode in a solution of Bu_4NClO_4 in CH_2Cl_2. Under these conditions it can be assumed that the electrode reaction would proceed as a simple electron-transfer process.

All the complexes mentioned underwent an irreversible, one-electron oxidation. The number of electrons transferred in the electrode process was determined by comparison of the limiting current of the complex with that of ferrocene; in the case of $[IrCl(CO)(PPh_3)_2]$ coulometric determination of the electron consumption gives a value of 0·95 F mol^{-1}. In all cases the limiting current was diffusion controlled and showed a linear dependence on complex concentration.

With $[IrCl(CO)(PPh_3)_2]$ the product of the electrochemical oxidation was studied by following the changes in the i.r. spectrum of the solution during preparative electrolysis on a large-area Pt-electrode under potentiostatic control. In the course of the oxidation the CO band of the original complex at 1965 cm^{-1} gradually diminishes and a new band at 2060 cm^{-1} appears. After passage of 0·95 F mol^{-1} the band at 1965 cm^{-1} disappears completely.†

The product of the electrochemical oxidation of $[IrCl(CO)(PPh_3)_2]$ must be considered, on the basis of the number of exchanged electrons, as an Ir^{II}-species (A) with ν_{CO} 2060 cm^{-1}. Solutions of (A) show no visible absorption bands nor any e.s.r. signal. An e.s.r. signal was not observed even when the preparative electrolysis was carried out directly in the cavity of the spectrometer. Species (A) is not electroactive. All this evidence indicates that species (A) is a dimeric Ir^{II} compound with a metal–metal bond (*cf.* Rh^{II} complexes[3]). Attempts to isolate species (A) in pure form from the reaction mixture for chemical identification were not successful.

TABLE I.

$E_{\frac{1}{2}}$ and n values of anodic waves corresponding to the oxidation of $[IrX(CO)L_2]$ complexes on a rotating Pt electrode ($E_{\frac{1}{2}}$ measured against saturated aqueous calomel electrode

X	L	n	$E_{\frac{1}{2}}$/V
Cl	PPh_3	1·00	1·12
Br	PPh_3	0·95	1·10
I	PPh_3	0·98	1·00
Cl	PPh_2Et	1·08	1·08
Cl	$PPhEt_2$	1·00	1·00
Cl	PEt_3	1·08	0·95

The complexes studied show a rather small influence of the composition of the co-ordination sphere upon the $E_{\frac{1}{2}}$ value (see Table). Even if the $E_{\frac{1}{2}}$ values measured are not thermodynamic quantities it can be concluded that under the given conditions the standard redox potential for the removal of the first electron and that for removal of the second differ considerably, the latter being much more positive than + 1 V. The d^7 system is obviously stabilized by dimerization, the second oxidation step, *i.e.* formation of the d^6 configuration requiring concerted co-ordination of additional ligands.

Comparison of these electrochemical data with those on redox addition indicate basic differences in the mechanism of electron transfer and atom transfer oxidations of the complexes studied. In the latter process the co-ordinating ability of the complex is obviously more important than its redox properties.

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† In some experiments, in addition to the band at 2060 cm^{-1} a band at 1722 cm^{-1} appears during the electrolysis, the origin of which has not been explained.

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[3] B. R. James and E. Ochiai, *Spectroscopy Letters*, 1972, **5**, 287.