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ELECTROCHEMICAL MEASUREMENTS AS A PROBE FOR THE INVESTIGATION OF THE STRUCTURE OF METAL CARBONYLS

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Summary

The relationship between structure and the formal electrode potential, E^0, for the oxidation of substituted metal carbonyls of the type $[M(CO)_{6-x}L_x]^{y+}$ has been investigated. E^0 values obtained in this work by cyclic voltammetry together with literature data, have been used to show that E^0 depends on x and y according to the relationship

$$E^0 = A + x\left(\frac{dE^0}{dx}\right)_L + 1.48\,y$$

where A is a constant dependent on the solvent and the reference potential and $(dE^0/dx)_L$ is a parameter characteristic of the ligand, L, which defines the shift in E^0 caused by the replacement of one CO ligand by one molecule of L. This relationship allows the estimation of E^0 for hexacoordinate carbonyls or, conversely, the use of electrochemical measurements as an aid to structure determination.

Introduction

Many spectroscopic techniques have been used in the investigation of the structure of metal carbonyl species and particular emphasis has been placed on the effect of structural changes on the relative energies of the molecular orbitals and the contribution of σ and π bonding to the metal—ligand bond. This paper shows that there is a significant quantitative relationship between the formal electrode potentials for the oxidation of a carbonyl and its structure in terms of the net charge on the species and the degree and type of ligand substitution, and, that electrochemical measurements provide additional and complementary information to that available from spectroscopic studies. Hexacoordinate metal carbonyls have been chosen for this study since the 17e oxidation products are generally more stable than their penta or tetra coordinated analogues and consequently the electrochemical oxidations are less complicated by following chemical reactions [1].

The formal electrode potentials for the oxidation of a series of metal carbonyl species

$$[M(CO)_{6-x}L_x]^{y+} - e \rightleftharpoons [M(CO)_{6-x}L_x]^{(y+1)+}$$

measured in the same inert solvent and versus the same reference electrode, should be a measure of the relative energies of their highest occupied molecular orbitals, (HOMO), provided that (*i*) the energies of the molecular orbitals are unperturbed by the removal of an electron from the HOMO and (*ii*) the change in free energy of solvation during the oxidation of $[M(CO)_{6-x}L_x]^{y+}$ to $[M(CO)_{6-x}L_x]^{(y+1)+}$ are approximately constant throughout the series; in practice these two restrictions are commonly met. Clearly the closest analogy to the electrochemical estimation of the energy of the HOMO will be spectroscopic techniques such as photoelectron spectroscopy [2] and in a limited number of cases charge-transfer band electronic spectroscopy [3]. The energy level of the HOMO clearly also determines much of the chemical behaviour of a metal carbonyl, e.g. the rates of disproportionation, homogeneous electron transfer reactions or electrophilic attack. Thus Dessy [4] has shown that the rate constants for attack by methyl iodide on a series of carbonyl anions show a linear correlation to the irreversible oxidation potential of these species.

The formal electrode potential E^0, may be conveniently measured by cyclic voltammetry provided the electrode reaction is reversible i.e. the heterogeneous electron transfer is fast, and, the one electron oxidation product is stable on the time scale of the experiment ($\tau_{1/2} > 10$ ms) and this was the technique and criteria used in this work.

Experimental

The instrumentation, the electrochemical cells and the purification of the acetonitrile has been described elsewhere [5]. $Cr(CO)_6$ and Cp_2Fe were obtained from BDH and $V(CO)_6$ from Alfa Inorganics. The species $[Cr(CO)_5(CH_3CN)]$ and $[Cr(CO)_4(CH_3CN)_2]$ were prepared from $Cr(CO)_6$ by UV irradiation in acetonitrile [6]. $[Cr(CO)_5Br]^-[Bu_4N]^+$, $[Mn(CO)_5Br]$ and $[Fe(CO)_4Br_2]$ were prepared by the established literature methods [7-9]. The species $[Mn(CO)_5(CH_3CN)]^+[BF_4]^-$ and $[Mn(CO)_5OCOCF_3]$ were prepared by our previously reported electrochemical [5] and direct air oxidation [1] of $Mn_2(CO)_{10}$ respectively.

Results

Cyclic voltammograms were run at several potential scan rates for solutions of each of the metal carbonyls [$\approx 5 \times 10^{-3}$ *M*] in acetonitrile tetrabutylammonium tetrafluoroborate; the working electrode was a bright platinum wire. For all the compounds discussed, except $[Fe(CO)_4Br_2]$, there was a range of potential scan rates for which the cyclic voltammogram for the primary oxidative process had the characteristics of a reversible one-electron oxidation reaction [10,11] and it was therefore possible to estimate from the voltammograms the

TABLE 1

FORMAL POTENTIALS FOR THE OXIDATION OF METAL CARBONYLS IN $CH_3CN/0.2\ M\ Bu_4NBF_4$, DETERMINED BY CYCLIC VOLTAMMETRY [a]

	E^0(V)		E^0(V)
$[V(CO)_6]^-$	−0.35	$Cr(CO)_6$	+1.12
$[Cr(CO)_4(NCCH_3)_2]$	+0.05	$[Mn(CO)_5Br]$	+1.55
$[Cr(CO)_5Br]^-$	+0.07		
$[Cr(CO)_5NCCH_3]$	+0.55		

[a] Potentials vs. the Cp_2Fe/Cp_2Fe^+ couple in this medium.

formal potentials for the couples $[M(CO)_{6-x}L_x]^{y+}/[M(CO)_{6-x}L_x]^{(y+1)+}$ in this medium. This data is reported in Table 1 versus the potential of the ferrocene/ferrocinium ion couple in the same solution. Later in this paper data reported in methylene chloride will be used [12]; this E^0 data is also quoted versus the same couple in methylene chloride.

Discussion

Treichel and coworkers [13] have noted a linear relationship between the number of isocyanide ligands and the half peak potentials, $E_{p/2}$, for the reversible oxidation of the manganese(I) complexes $[Mn(CO)_{6-x}(CNCH_3)]^+$; this data is replotted as E^0 vs. x in Fig. 1. The additive change in the oxidation potential with increasing x was attributed to the simple additive effect of the

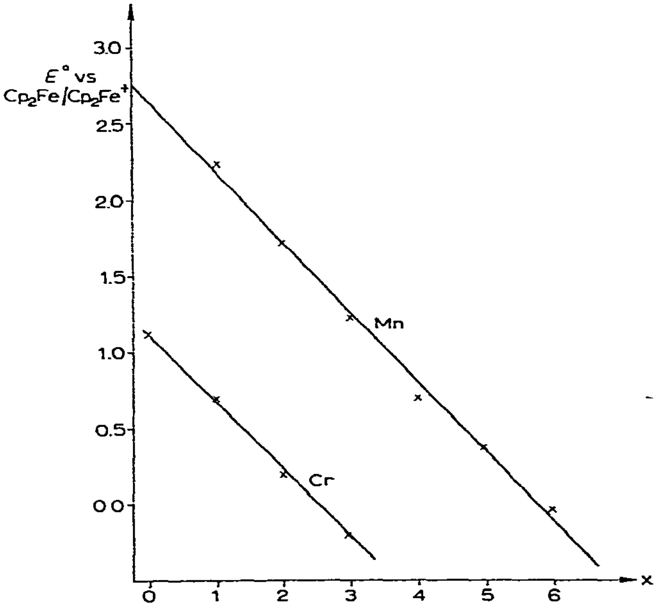

Fig. 1. Correlation of E^0 with x for the complexes $[Cr(CO)_{6-x}(CNCH_3)_x]$ and $[Mn(CO)_{6-x}(CNCH_3)_x]^+$.

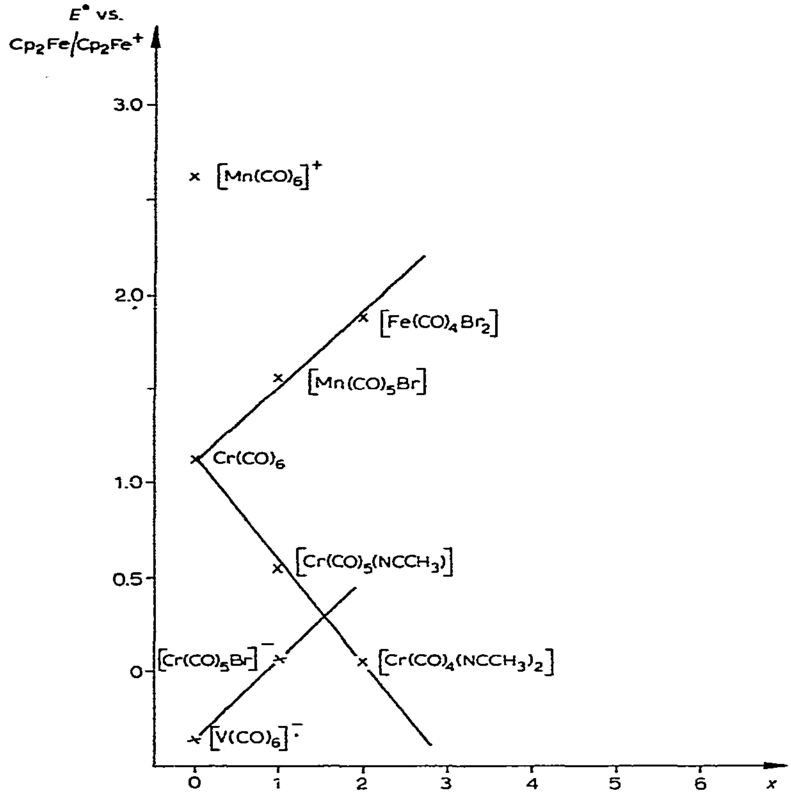

Fig. 2. Correlations of E^0 with x for two series of bromocarbonyls and the complexes $[Cr(CO)_{6-x}(NCCH_3)_x]$.

net inductive σ donor π acceptor characteristic of the isocyanide ligand on the energy of the HOMO, i.e. an increased electron density on the metal centre raised the energy of the HOMO and lowered the formal oxidation potential. Later McCleverty et al. [12] measured E_p^{ox} data for the oxidation of the isoelectronic series of complexes $[Cr(CO)_{6-x}(CNCH_3)_x]^0$ and arrived at similar conclusions. Their data together with our value of E^0 for $x = 0$ is also replotted on Fig. 1. It may be noted that the two lines are almost parallel and hence three conclusions can be drawn with respect to a ligand inductive parameter $(dE^0/dx)_{CNCH_3}$. For the isoelectronic series $[M(CO)_{6-x}(CNCH_3)_x]^{y+}$, the ligand parameter is independent of (*a*), the transition metal centre; (*b*), the net charge on the species and (*c*) the degree of substitution, x: (*a*) and (*b*) have not been previously noted. Fig. 2 shows E^0 vs. x plots for the series $[M(CO)_{6-x}Br_x]^0$ for M = Cr and $x = 0$, M = Mn and $x = 1$ and M = Fe and $x = 2$ and for $[Cr(CO)_{6-x}(NCCH_3)_x]^0$ with $x = 0, 1, 2$. Also shown is the E^0 vs. x plots for the isocharged pair $[V(CO)_6]^-$ and $[Cr(CO)_5Br]^-$. Again it is apparent that for such diverse ligands as acetonitrile and bromine the ligand parameters $(dE^0/dx)_L$ are independent of *a*, *b* and *c*. Hence it seems reasonable to estimate ligand inductive parameters for a range of further ligands even though data is available only for two 18e metal carbonyls of a hexacoordinate series.

TABLE 2

LIGAND PARAMETERS $(dE^0/dx)_L$ FOR A SERIES OF LIGANDS [a]

L	$(dE^0/dx)_L$
Br	+0.42
CO	0.00
$P(OC_6H_5)_3$	−0.19
$P(C_6H_5)_3$	−0.36
p-ClC_6H_4—NC	−0.37
p-MeC_6H_4—NC	−0.42
MeNC	−0.44
MeCN	−0.54
NH_3	−0.80

[a] Data for calculation of these parameters from this work and refs. 12, 13, 14.

TABLE 3

DIFFERENCE IN FORMAL OXIDATION POTENTIALS FOR ISOSTRUCTURAL COMPLEXES $[M(CO)_{6-x}L_x]^{y+}$ DIFFERING BY A NET CHARGE

Isostructural pair		$E^0_{II} - E^0_I = \Delta E^0$
I	II	
$[V(CO)_6]^-$	$Cr(CO)_6$	1.12 − (−0.35) = 1.47
$Cr(CO)_6$	$[Mn(CO)_6]^+$	2.62 − 1.12 = 1.50
$[Cr(CO)_5Br]^-$	$[Mn(CO)_5Br]$	1.55 − 0.07 = 1.48
$[Cr(CO)_5(CNCH_3)]$	$[Mn(CO)_5(CNCH_3)]^+$	2.24 − 0.71 = 1.53
$[Cr(CO)_4(CNCH_3)_2]$	$[Mn(CO)_4(CNCH_3)_2]^+$	1.73 − 0.20 = 1.53
$[Cr(CO)_3(CN\text{-}i\text{-}Pr)_3]$	$[Mn(CO)_3(CNCH_3)_3]^+$	1.24 − (−0.19) = 1.43

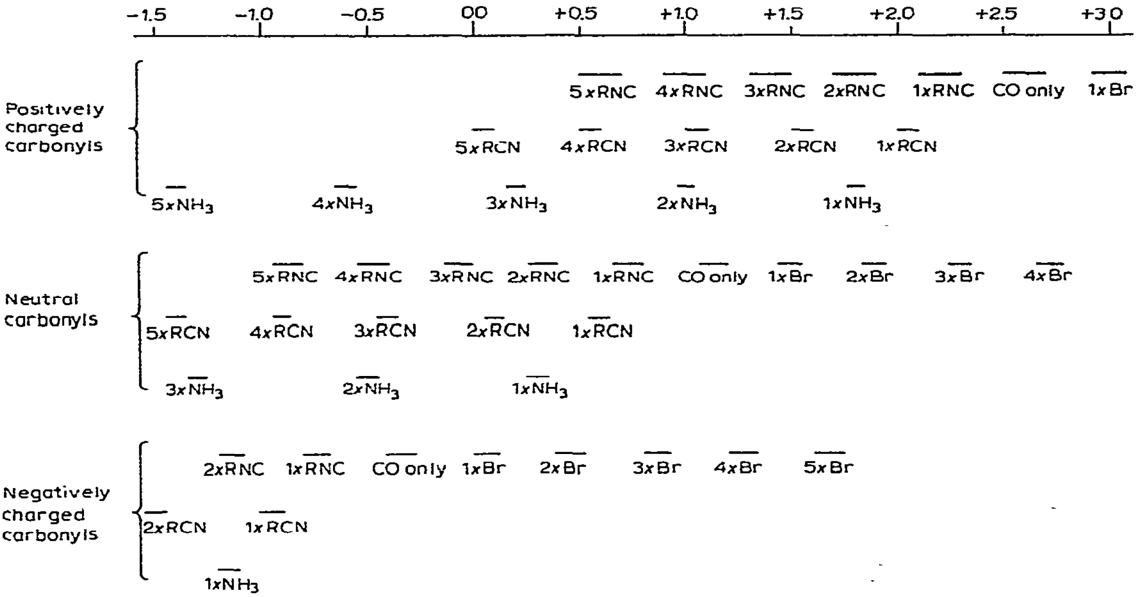

Fig. 3. Primitive correlation chart for determining the structure of hexacoordinate carbonyls from formal electrode potentials.

Table 2 shows $(dE^0/dx)_L$ parameters for ten ligands listed in order of net inductive effect. The order is consistent with the present understanding of transition metal—ligand bonding: the more electronegative ligands e.g. Br lower the energy of the HOMO i.e. increase the oxidation potential of a carbonyl whilst good donor ligands e.g. NH_3 behave in the opposite way.

The effect of the net charge on the carbonyl on the formal oxidation potential may be seen by considering the data for an isoelectronic and isostructural series such as $[V(CO)_6]^-$, $[Cr(CO)_6]^0$ and $[Mn(CO)_6]^+$ (the E^0 for the latter species may be estimated by extrapolating the data in Fig. 1 to $x = 0$). It can be seen from Fig. 3 that for each additional positive charge E^0 increases by ≈1.5 V. Table 3 shows the effect of charge for a set of further isostructural pairs and these confirm that the shift in formal potential $\Delta E^0 y$ is ≈1.48 V/net charge. Thus it would seem that the formal oxidation potential for these hexacoordinated 18e metal carbonyls may be estimated using the equation

$$E^0 = A + x\left(\frac{dE^0}{dx}\right)_L + 1.48\,y$$

where A is a constant which depends upon the solvent and reference potential, x is the degree of substitution of CO by the ligand L and y the net charge on the complex. In acetonitrile and using the potential of the ferrocene/ferrocinium couple as the reference potential, A has the value +1.12 V. The authors also believe that a similar equation would be appropriate for 18e carbonyls with two different substituent ligands $[M(CO)_{6-x-z}L_xL'_z]^{y+}$. Such equations might have a number of applications, for example the estimation of formal oxidation potentials for unstable carbonyls, the estimation of the stability of a carbonyl to air oxidation, the design of highly specific oxidising agents and the design of several carbonyls with the same electrode potential, i.e. isoenergetic HOMO species, so that structure—reactivity relationships could be studied independently of redox behaviour.

Conversely, the validity of equation 1 allows the use of the formal oxidation potentials, measured rapidly by cyclic voltammetry, as an aid to structure determination of hexacoordinate 18e carbonyl species. Since the E^0 value comments on the energy level of the HOMO and hence the net σ donor—π acceptor properties of the ligands, it is clear that in general the value of E^0 will depend upon steric factors as well as the net change, degree and type of substitution. As yet the body of E^0 data is insufficient to allow the drawing up of correlation charts comparable to those available for IR data. It is clear, however, that in principle a similar approach could be adopted and Fig. 3 shows a possible primitive correlation chart for hexacoordinated 18e carbonyls, relating E^0 to gross structural features.

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