Electrochemical Oxidation of Monosubstituted Chromium Carbonyl Complexes. Ligand and Solvent Effects

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The influence of basic aprotic solvents on the electrochemical oxidation of chromium carbonyl complexes [$Cr(CO)_5L$]{L = CO, PPh_3, $S(NC_4H_8O)_2$, $S[N(CH_2Ph)_2]_2$, HNC_4H_8O, $SC(NH_2)_2$, $SC(NHEt)_2$, or $SC(NMe_2)_2$} has been examined. The oxidation potentials (E_p^{ox}) depend on the solvent donor strength (*DN*), producing nearly linear relationships with intercepts and slopes determined fundamentally by the nature of L. The potentials estimated at *DN* = 0 for all studied complexes as well as the slopes $\Delta E_p^{ox}/\Delta DN$ (sensitivity of the potentials to the solvent) for the complexes with sulphur ligands are smooth functions of the π-acceptor capacity of the ligands expressed as the Graham π parameter. The results are discussed considering outer-sphere complex interactions.

Group 6 metal carbonyl derivatives are, because of their stability, relatively easy synthesis, and simple electroactivity,[1] suitable model compounds for studying the relationship between metal–ligand interactions and redox behaviour in organometallic compounds. In fact, electrochemical studies have been employed to investigate the nature of the bonding in carbonyl compounds, such studies being particularly useful to evaluate relative energies of molecular orbitals;[2,3] furthermore a linear relationship between oxidation potentials and highest occupied molecular orbital (h.o.m.o.) energies has been reported.[3] The redox properties of the Group 6 metal carbonyl derivatives are influenced considerably by a number of different factors. Thus, it has been established that the reduction and oxidation potentials for carbonyls of the type $[M(CO)_{6-x}L_x]^{y+}$ depend on the nature of the metal as well as on the degree of substitution and nature of the ligands L.[1–6] A quantitative relationship expressing the oxidation potentials as a linear function of the degree of substitution and on the total charge of the complex has been proposed.[5] In this relationship, a constant term which includes solvent effects has also been considered. The specific influence of the ligands L appears to be related to their π back-donation capacity.[2] The influence of the geometry in di- and tri-substituted carbonyl complexes has also been detected.[3,4,7]

As established by i.r. studies with hexacarbonylmolybdenum, the properties of the complexes are affected by formation of carbonyl–solvent outer-sphere complexes,[8] so that, similarly, significant solvent effects on the redox potentials are expected. Apart from the solvent effects considered in the relationship mentioned above,[5] there are also some studies about such effects on the redox behaviour of Group 6 metal carbonyl compounds: on the influence of the solvent donicity on the reduction of [$M(CO)_6$] (M = Cr, Mo, or W),[9] on the stabilization of carbonyl cation radicals in a solvent of low nucleophilicity such as trifluoroacetic acid,[10] on the effect of donor solvents on the reduction potential of *cis*-tetracarbonylbis(1,3-dimethylimidazolidin-2-ylidene)chromium(0),[11] and on the electrochemical behaviour of the hexacarbonyls [$M(CO)_6$] (M = Cr, Mo, or W) in a medium of high Lewis acidity containing $AlCl_3$.[12] However, we think that a somewhat more systematic study of these effects could contribute to a better knowledge of the redox properties of organometallic compounds. In this work we have therefore focused our attention on both the effect of various common organic aprotic solvents and the influence of the substituent on the electrochemical oxidation of a selected group of monosubstituted chromium carbonyl compounds of the type [$Cr(CO)_5L$].

Experimental

The chromium carbonyl complexes [$Cr(CO)_5L$] were synthesized from [$Cr(CO)_6$] and the respective ligand by a photochemical substitution method as previously reported.[13–15]

Solvents were purified according to the literature[16] and stored under argon protected from light. Tetraethylammonium perchlorate (teap), used as supporting electrolyte, was recrystallized twice from water and dried at 60 °C in vacuum. The water content of solvents and reagents was controlled by Karl-Fisher titrations.

Electrochemical data were obtained by cyclic voltammetry using a PARC model 370 electrochemistry system with a specially designed three-electrode glass cell, previously described.[17] The working electrode was a carbon glassy electrode, the counter electrode a platinum wire, and the reference electrode an aqueous saturated calomel electrode (s.c.e.). In order to cancel the effects of the uncompensated ohmic potential drop (*iR*) and the liquid junction potentials, peak potentials were measured at the first-cycle voltammogram with respect to bis(biphenyl)chromium(I)/(0) used as a solvent-independent internal reference system.[18]

Results

The electrochemical oxidation of a series of chromium pentacarbonyl complexes [$Cr(CO)_5L$] listed in Table 1 was studied by cyclic voltammetry in different solvents at room temperature. A first-cycle voltammogram typical of the studied complexes is reproduced in Figure 1.

The potentials of the oxidation peaks for a scan rate of 0.3 V s^{-1} are reported in Table 1; the dependence of these potentials on the substituent as well as on the solvent is illustrated in Figure 2.

Typical electrochemical parameters usually used as criteria[19] for reversibility are shown in Tables 2 and 3. The differences between the oxidation and reduction potentials, ΔE_p, are in almost all the cases *ca.* 60 mV, such differences being similar to those for the internal standard. Although in solvents with high donor strength small variations of the ratios i_p^{red}/i_p^{ox} are observed, indicating a slight increase of the degree of reversibility with increasing scan rate, the mean values of the ratios are, within the experimental error, almost always *ca.* 1.0. According to all these criteria, the electrochemical oxidation of the studied complexes can be considered to be a reversible diffusion-controlled one-electron process.

Although all studied complexes are stable in weakly basic

Table 1. Voltammetric oxidation peak potentials of chromium carbonyl complexes $[Cr(CO)_5L]$ in various basic aprotic solvents

		Oxidation potentials[a,b] of complexes with L							
Solvent[c]	*DN*[d]	CO	PPh_3	$S(NC_4H_8O)_2$	$S[N(CH_2Ph)_2]_2$	HNC_4H_8O	$SC(NH_2)_2$	$SC(NHEt)_2$	$SC(NMe_2)_2$
$MeNO_2$	2.7	2.295	1.905	1.660	1.660	1.640	1.410	1.390	1.375
$PhNO_2$	4.4	2.375	1.940	1.635	1.625	1.635	1.420	1.390	1.405
PhCN	11.9	2.255	1.885	1.670	1.655		1.385	1.370	1.385
MeCN	14.1	2.220	1.900	1.650	1.645	1.610	1.380	1.350	1.370
pc	15.1	2.225	1.910	1.595	1.600	1.635	1.405	1.375	1.400
Me_2CO	17.0	2.210	1.910	1.620	1.630	1.610	1.390	1.370	1.410
$PO(OMe)_3$	23.0	2.160		1.530	1.515	1.630	1.365	1.385	1.430
dmf	26.6			1.480	1.470	1.600	1.370	1.350	1.415
dma	27.8			1.505	1.505	1.635	1.355	1.380	1.420
Me_2SO	29.8						1.355	1.400	1.435
dea	32.2						1.360	1.390	1.450

[a] Oxidation peak potential (E_p^{ox}/V) *vs.* bis(biphenyl)chromium(I)/(0). [b] Potentials were measured to ±5 mV. [c] Abbreviations: pc = propylene carbonate, dmf = *N*,*N*-dimethylformamide, dma = *N*,*N*-dimethylacetamide, dea = *N*,*N*-diethylacetamide. [d] Donor numbers of the solvents from ref. 14.

Table 2. Cyclic-voltammetric data for $[Cr(CO)_5L]$ in acetonitrile in the potential scan rate (υ) range 0.1—0.5 V s^{-1}

L	i_p^{red}/i_p^{ox} [a,b]	ΔE_p[a]/mV	$i_p^{ox}\upsilon^{-\frac{1}{2}}[\text{complex}]^{-1}$ [c]/ μA $s^{\frac{1}{2}}$ $V^{-\frac{1}{2}}$ dm^3 $mmol^{-1}$
CO	0.94	70	290.0
PPh_3	1.02	75	45.0
$S[N(CH_2Ph)_2]_2$	1.12	65	288.0
Morpholine	0.85	80	287.0
Thiourea	0.96	70	172.9
$SC(NHEt)_2$	1.07	70	126.0
$SC(NMe_2)_2$	1.02	80	150.0
Bis(biphenyl)-chromium(I)/(0)[d]	1.01	70	133.3

[a] Mean value from five different scan rates. [b] Estimated error ±0.05. [c] Obtained from the slopes of the plots i_p^{ox} *vs.* $\upsilon^{\frac{1}{2}}$[complex]. [d] Reference compound.

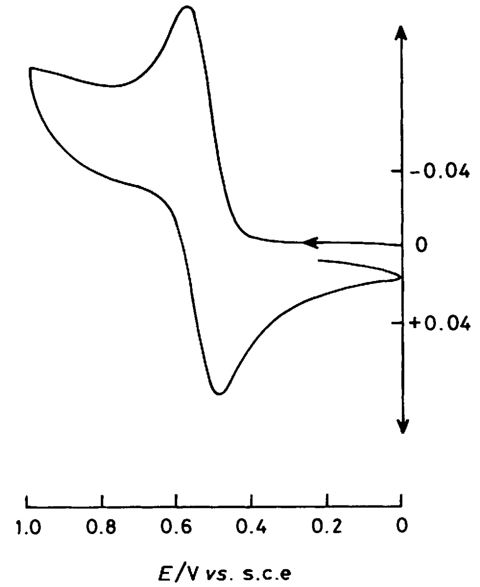


Figure 1. Cyclic voltammogram corresponding to the oxidation of $[Cr(CO)_5\{SC(NH_2)_2\}]$ in nitromethane (0.1 mol dm^{-3} teap) at a glassy carbon electrode (potential scan rate 0.5 V s^{-1})

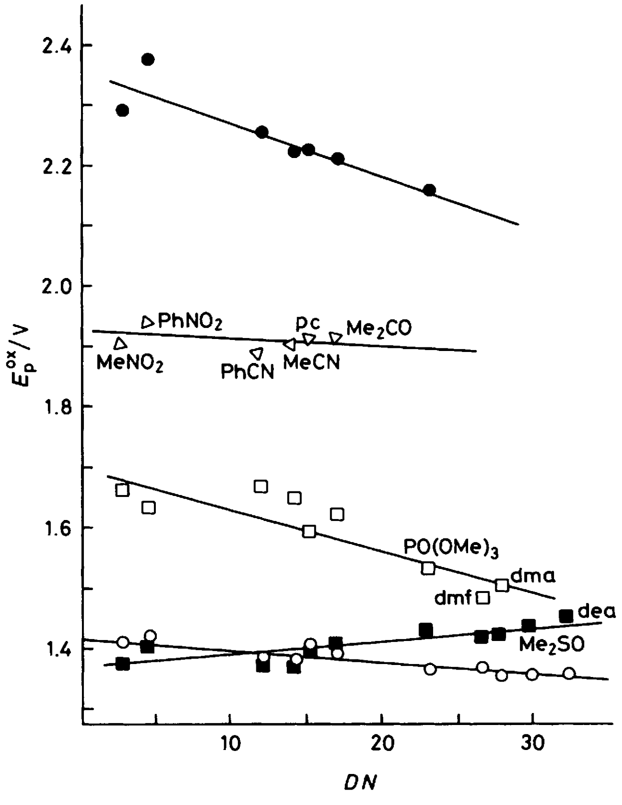


Figure 2. Dependence of the oxidation potentials of complexes $[Cr(CO)_5L]$ on the donor strength of the medium: L = CO (●), PPh_3 (Δ), *N*,*N'*-thiodimorpholine $[S(NC_4H_8O)_2]$ (□), thiourea $[SC(NH_2)_2]$ (○), tetramethylurea $[SC(NMe_2)_2]$ (■)

media, some of them decompose in strong donor solvents, thus restricting the working basicity range of the medium.

The complexes are also soluble in non-polar solvents so that the i.r. spectra could be obtained in n-hexane, except for the thiourea complex which was measured in $CHCl_3$. In most cases the CO stretching modes *A*, *E*, and B_1 were observed. The π Graham parameter used in Figures 3 and 5 was calculated according to the equations $\Delta k_1 = \sigma + 2\pi$ and $\Delta k_2 = \sigma + \pi$, where k_1 and k_2 are Cotton–Kraihanzel[20] force constants. In the cases of the complexes with morpholine and

Table 3. Cyclic voltammetric data for $[Cr(CO)_5\{SC(NH_2)_2\}]$ in different solvents in the potential scan rate range 0.1—0.5 V s^{-1}

Solvent	i_p^{red}/i_p^{ox} [a,b]	ΔE_p[a]/ mV	ΔE_p/[a,c] mV	$i_p^{ox}v^{-\frac{1}{2}}[complex]^{-1}$ [d]/ $\mu A\ s^{\frac{1}{2}}\ V^{-\frac{1}{2}}\ dm^3\ mmol^{-1}$
$MeNO_2$	0.99	70	70	126.9
$PhNO_2$	0.99	80	70	107.9
PhCN	0.98	80	80	94.7
MeCN	0.96	70	60	172.9
pc	1.02	80	80	64.7
Me_2CO	0.99	70	65	162.7
$PO(OMe)_3$	1.01	80	75	68.3
dmf	0.93	85	75	125.8
dma	0.95	70	65	101.3
Me_2SO	1.08	80	75	53.6
dea	0.82	75	75	79.7

[a] Mean value from five different scan rates. [b] Estimated error ±0.05. [c] Reversible internal reference system bis(biphenyl)chromium(I)/(0). [d] Obtained from the slopes of the plots i_p^{ox} *vs.* $v^{\frac{1}{2}}$[complex].

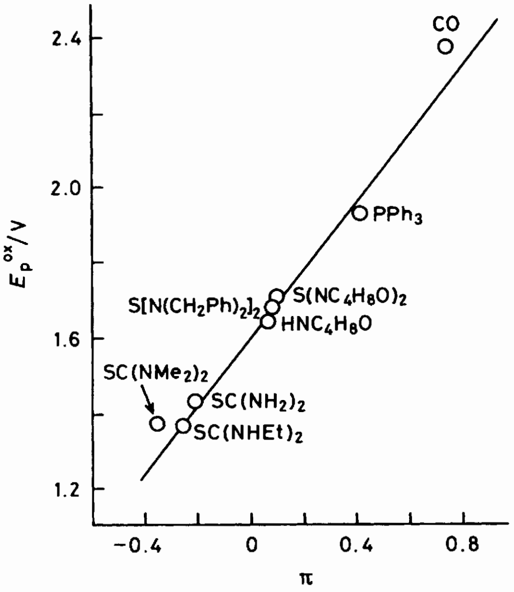


Figure 3. Relationship between the oxidation potential of $[Cr(CO)_5L]$ complexes in an inert medium (*DN* = 0) and the Graham π parameter (ref. 24)

triphenylphosphine, B_1 was not observed and the force constants were calculated by an iterative method.[21]

Discussion

The oxidation of hexacarbonylchromium, previously described as corresponding to the formation of the cation radical $[Cr(CO)_6]^+$, stable on the time-scale of many seconds,[22] shows a voltammetric pattern similar to that observed for the complexes $[Cr(CO)_5L]$ studied here (Figure 1), According to their i.r. spectra, the complexes $[Cr(CO)_5L]$ show approximately the same structures in every solvent studied and, by considering the reversibility observed for their electrochemical oxidations, a similar structure is also expected for the cation radicals.

Furthermore, the oxidation potentials depend on the ligand L as well as on the solvent, being especially influenced by the solvent basicity as can be clearly observed in Figure 2. The approximately linear relationship between the oxidation potentials and the donor strength of the solvents (*DN*),[23] however, permits estimation of the potential at *DN* = 0, *i.e.* the potential of the complexes in an inert medium, and thus to analyse separately the effect of the ligand L.

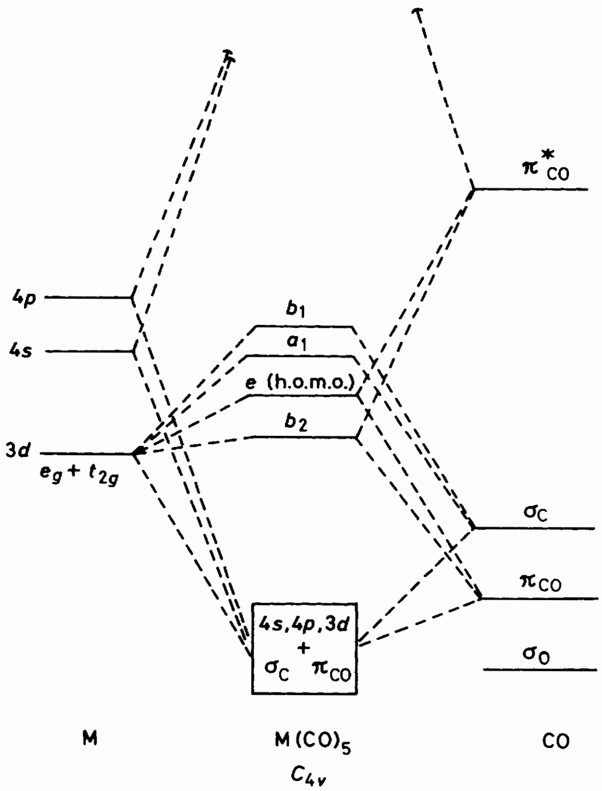


Figure 4. Qualitative molecular orbital diagram for $[Cr(CO)_5L]$

Such effects can be better understood by considering the influence of the nature of the ligand on the limiting structures given below, usually applied to describe carbonyl compounds.

$$\underset{\textbf{(I)}}{\overset{\delta+\qquad\delta-}{O{\equiv}C{-}M{-}L}}\qquad\qquad\underset{\textbf{(II)}}{O{=}C{=}M{-}L}$$

The relative weights of the structures (I) and (II) in the description of a given species are strongly influenced by the nature of L. The contribution of structure (I) increases with increasing π-acceptor capacity of L, diminishing the electron density at the metal atom and thus making the oxidation of the compound more difficult. In Figure 3 the dependence of the oxidation potentials (extrapolated to *DN* = 0) on the Graham π parameter[24] can be observed. This parameter, considered as a measure of the π-acceptor capacity of the ligand L in the complex, is obtained from the i.r. spectra in an inert solvent.[20] Contrarily, no correlation of the oxidation potentials with the Graham σ parameter[24] was observed (correlation coefficient $r = 0.33$) and the correlation with the average values of the force constants, $(4k_2 + k_1)/5$, considering the overall effects is less good ($r = 0.93$) than that taking into account only the π-acceptor characteristics of the ligands ($r = 0.99$). The relationship shown in Figure 3 agrees with the above explanation and moreover, the fairly linear correlation obtained offers the possibility to estimate the acceptor capacity of the ligands by electrochemical methods.

The preponderance of the π metal–ligand interaction for determining the oxidation facility of the complexes can be better understood by considering the qualitative molecular orbital diagram shown in Figure 4. This scheme, being obtained by

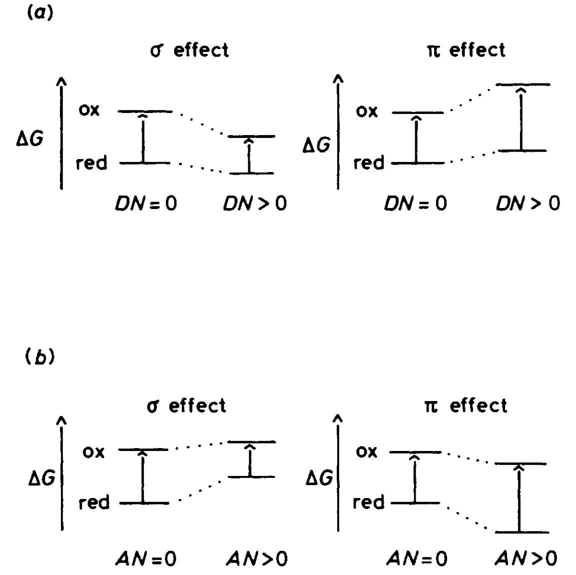


Figure 5. Scheme of the solvent effect on the relative stability of the oxidized and reduced forms of the $[Cr(CO)_5L]$ complexes considering two components σ and π (σ and π 'effects'). (*a*) Effect of a donor medium (DN = donor number); (*b*) effect of an acceptor medium (AN = acceptor number)

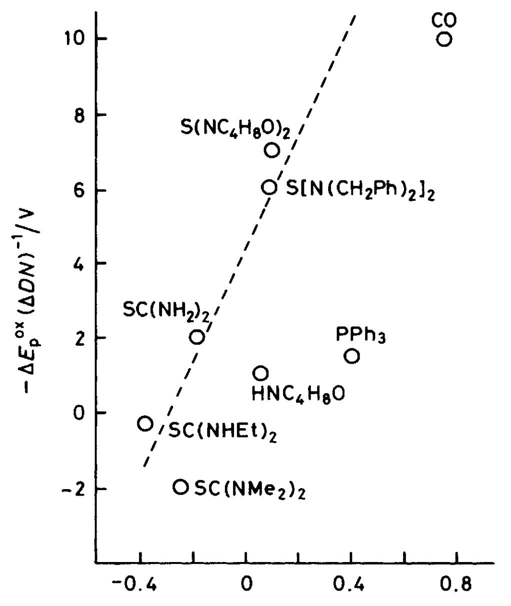
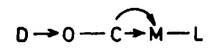


Figure 6. Effect of the π-acceptor capacity of sulphur ligands L (expressed as the Graham π parameter[24]) on the sensitivity to the solvent donicity ($\Delta E_p^{ox}/\Delta DN$ from Figure 2) for $[Cr(CO)_5L]$ complexes

mixing orbitals of the fragment $M(CO)_5$[25] with σ and π orbitals of a hypothetical ligand L, clearly indicates that the energy of the h.o.m.o. and, consequently, the oxidation potential depends fundamentally on the energy of the π-acceptor orbitals of the ligand. The foregoing analysis also agrees with the importance of the degree of π back-donation in the M–CO bond on the redox properties observed for the Group 6 metal carbonyls, $[M(CO)_6]$.[9] An increase of the π back-donation capacity of the metal facilitates the reduction and makes the oxidation of the compound more difficult.

The interaction of the carbonyl compounds with donor solvents can be understood by considering the contribution of the polar structure (**I**) to the hybrid. With increasing π-acidity of L, the partial positive charge on the oxygen atom increases, thus enhancing the possible outer-sphere interactions of the complex with the medium and also enhancing the sensitivity of the oxidation potentials to the solvent. The outer-sphere interaction of the carbonyl with a nucleophilic medium should produce electronic rearrangements like those described by the interaction diagram (**III**) giving rise fundamentally to two effects:



$$D \rightarrow O - C \rightarrow M - L$$

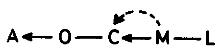
(**III**)

(*i*) a reinforcement of the OC → M bond, a 'σ effect', which could be considered as a stabilizing effect for the system; and (*ii*) a weakening of the π back-bonding M → CO bond, a 'π effect', which should destabilize the carbonyl species.

The contribution of these effects to the free energy of the reduced as well as of the oxidized form of the carbonyl complexes is graphically described in Figure 5. As observed in this Figure, in a nucleophilic medium the oxidized form of the complex would always be preferentially affected. The relative contribution of the σ and π effects to the actual solvent influence on the species depends on the degree of back-donation in the OC–M bond and therefore on the nature of the ligand L. For derivatives with a good π-acceptor ligand L a preponderance of the stabilizing σ effect will occur; thus a lowering of the oxidation potential with increasing solvent donicity is expected. For compounds with ligands with low π-acceptor capacity, the interactions with strong donors (Figure 5) will lead to positive values of the slope $\Delta E_p^{ox}/\Delta DN$. The experimental results fully support these conclusions. As shown in Figure 2, tetramethylthiourea shows a slightly positive influence of the donor solvents on the potential, similar to that found for *cis*-tetracarbonylbis(1,3-dimethylimidazolidin-2-ylidene)-chromium(0),[11] meanwhile for other compounds with somewhat stronger π-acceptor ligands negative slopes are observed. Furthermore, for those complexes with sulphur ligands, the sensitivity to the solvent (slopes $\Delta E_p^{ox}/\Delta DN$) appears to be, as shown in Figure 6, a linear function of the π-acceptor capability of the ligands.

Although we have focused our attention on effects of the medium on the oxidation of these complexes, the same analysis should be valid for the corresponding reduction processes. In this case, however, the contribution of the π effect to the actual influence of the donor solvent will be relatively greater than that for the oxidation process because of the greater degree of π back-bonding in species with the metal in lower oxidation states. The solvent would affect more the neutral than the reduced species, thus a decrease of the reduction potential with increasing solvent donor strength would be expected. The solvent effects on the electrochemical reduction of the Group 6 metal carbonyls have been studied, a diminution of the reduction potentials with increasing solvent basicity[9] indeed being observed. Although a mechanism assuming the formation of substituted species of the type $[M(CO)_5S]^{\cdot -}$ (S = solvent, M = Cr, Mo, or W) has been proposed,[9] the formation of outer-sphere complexes could be an alternative explanation for the reduction of $[M(CO)_6]$ in the different solvents.

Although in the experiments described in this work the donor strength of the solvent appears to be the most important property of the medium for determining both the oxidation and reduction potentials, the acceptor properties of the same solvents cannot be totally neglected.[26] The i.r. spectra of some metal carbonyl and nitrosyl compounds[8] show in fact that the strength of the C–O bond depends principally on the acceptor (A) properties of the medium, ν(C–O) frequencies decreasing with increasing solvent acceptor number according to diagram (**IV**).



(**IV**)

The influence of the acceptor properties of the medium has not been detected in our experiments, it is probably masked by the predominantly donor nature of the solvent. However, the relatively high dispersion observed in the correlation of the oxidation potentials reported for a number of carbonyl compounds in dichloromethane[2] (a solvent with virtually zero donicity but relatively high acceptor properties[26]) with the Graham π parameter estimated from the i.r. spectra of the compounds* could be the consequence of the interaction of the complex with the acceptor medium.

The relevance of the outer-sphere mechanism for the interaction of metal carbonyls with acceptor solvents [Figure 5(*b*)] can be appreciated in the oxidation of the carbonyls $[M(CO)_6]$ (M = Cr, Mo, or W) in a molten salt system composed of an aluminium chloride–*N*-ethylpyridinium bromide melt and benzene.[12] The oxidation potentials of the carbonyls in a strong acceptor medium are markedly more positive than those in donor solvents and, unlike in the oxidation of these carbonyls in acetonitrile occurring in a narrow potential range around 1.5 V *vs.* s.c.e., the potentials show a notorious dependence on the nature of the metal; the greater the back bonding degree, the stronger the effect of the medium.

Acknowledgements

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* Graham π parameters were estimated from C–O frequencies and force constants for the respective $[M(CO)_5L]$ complex from the data of: ref. 6, ref. 13, and G. M. Bodner, *Inorg. Chem.*, 1975, **14**, 2694.