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Solvent Effects on VIb Metal Carbonyls Oxidation and Reduction Potentials

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The electrochemical behaviour of $M(CO)_6$, $\{M_2(CO)_{10}\}^{2-}$, $\{M_2H(CO)_{10}\}^-$ and $M(CO)_5S$ (M = Cr, Mo, W) has been studied [1] on mercury or platinum electrodes in several solvents S (acetonitrile, AN; propylene carbonate, PC; Acetone, A; N,N-dimethylformamide, DMF and dimethylsulfoxide, DMSO) characterized by a wide range of donor numbers [2]. The experimental study has been focused on the following main factors:

i) In a given solvent, the effect of the metal on the reduction potentials ($E_{1/2}^{cath}$), from $Cr(CO)_6$ to $W(CO)_6$.

ii) For each of the three $M(CO)_6$ complexes, the solvent effects on $E_{1/2}^{cath}$.

iii) For a given metal carbonyl, in a given solvent, the effect on $E_{1/2}^{cath}$ of substituting the ligand CO by solvent molecule(s).

The main results are the following:

1) In a given solvent, changing the metal M in $M(CO)_6$ induces a positive shift of $E_{1/2}^{cath}$, from $Cr(CO)_6$ to $W(CO)_6$, all other parameters being held constant. Also, the first monoelectronic oxidation of $M(CO)_6$ requires increasing energy from $Cr(CO)_6$ to $W(CO)_6$. These results may qualitatively be ascribed to an increasing metal to ligand π back-donation, from $Cr(CO)_6$ to $W(CO)_6$.

2) For a given metal M, the reduction of $M(CO)_6$ is facilitated as the donor number DN of the solvent increases. On the contrary, the reduction potential does not parallel the acceptor number AN of the solvent.

3) Gradual substitution of CO by CH_3CN in $W(CO)_6$ facilitates the oxidation and makes the reduction more difficult (except for $W(CO)_5(CH_3CN)$. This is fully consistent with the fact that CH_3CN is a weaker π acceptor than CO.

In conclusion, it is possible to rationalize these effects in terms of metal-to-carbon π back-bonding whose reinforcement results in a facilitated reduction and in a hindered oxidation, from $Cr(CO)_6$ to $W(CO)_6$. Also, the influence of the donor number of the solvent upon the $E_{1/2}^{cath}$ supports the reduction scheme previously proposed [1] for $M(CO)_6$, where the stable species, $M(CO)_5S$, results from the coordination of $M(CO)_5^{\cdot}$ to the solvent S. In such a reaction indeed, a strengthened coordination of S on the metal is expected as DN of S increases, the consequence of which is to facilitate the reduction process, as observed experimentally.

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Complexes of Bipositive Metal Ions from Vanadium(II) to Copper(II) with Tris(3,5-dimethyl-1-pyrazolylethyl)amine

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Metal complexes of polypyrazolyl ligands have been found to provide significant examples of bioinorganic models [1]. As a part of a general investigation on this class of complexes [2], the study of compounds of the bipositive ions from vanadium(II) to copper(II) with the potentially tetradentate ligand tris(3,5-dimethyl-1-pyrazolylethyl)amine(TPy-EA) has been undertaken.