CAPSULES
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Correlation of Redox Potentials with Frontier Orbital Energies

Purpose

When an electron is added to or removed from a molecule, the change in the energy of the system is due not only to the addition of an electron to an orbital (or removal of an electron), but also to changes in solvation energy, core orbital energy levels, and entropy. Therefore, there may not necessarily be direct correlation between the redox potentials of a series of closely related molecules (e.g., transition metal complexes with different phosphine ligands) and the energies of the frontier orbitals. However, for systems in which energy changes other than the variation of the energies of the frontier orbitals are constant for a series of compounds, then such correlation may occur. In this study, the correlation between the redox potentials and $E_{h\nu}$ values of a series of substituted alkyne molybdenum and tungsten complexes was examined.

Reference

Electronic Spectroscopy and Electrochemistry of Alkyne Dithiocarbamate Complexes of Molybdenum(II) and Tungsten(II), J.L. Templeton, R.S. Herrick and J.R. Morrow, Organometallics 3 (1984) 535-541.

Method

Cyclic voltammetry is the technique most commonly used for initial characterization of a redox system. The instrumentation required is relatively simple, and the redox potential can be readily estimated for most systems by calculating the average of the peak potentials on the forward and reverse scans.

Results

The molecular structure and the schematic energy level diagram used in this study are shown in ***F1*** (S-S=dithiocarbamate ligand). The frontier orbitals are derived from stabilization of the d_{xy}, d_{xz}, and d_{yz} orbitals by interaction with the π ligand orbitals. Since the HOMO (Highest Occupied Molecular Orbital) does not have a significant contribution from any alkyne π orbitals, varying the alkyne substituent should have little effect on the energy of the HOMO. In contrast, varying the alkyne substituent should affect the energy of the LUMO (Lowest Unoccupied Molecular Orbital), since the energy of the LUMO is determined by the strength of the anti-bonding interaction between the d_{xy} orbital and one of the alkyne π orbitals; for example, the presence of electron donating substituents on the alkyne ligands should raise the energy of the LUMO. The redox potentials and spectroscopic data reported in this study were interpreted according to a model in which changes in the energies of the visible transition and the redox potentials due to changing the alkyne substituent were attributed solely to variations in the energy of the LUMO.

It is important to note that a redox potential is the difference in energy between two ground states differing by one electron, whereas the energy derived from an absorption spectrum is a measure of the difference between a ground state and an excited state. Therefore, it is not guaranteed that there would a direct correlation between the energies from an absorption spectrum and redox potentials. Nevertheless, in this study, the changes in these two quantities brought about by changing the alkyne substituent is attributed solely to the change in the energy of the LUMO, and hence a correlation is reasonable.

All the complexes discussed in this study showed a one-electron reduction. The potential required for reduction (i.e., addition of an electron to the LUMO)

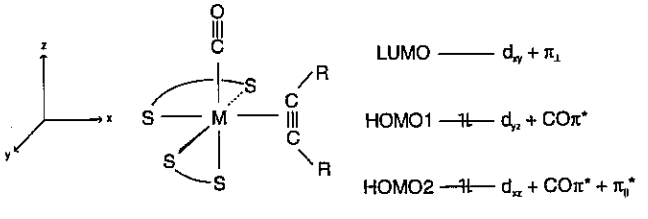

Figure 1. Schematic diagram of the frontier orbitals of M(CO)(RC2R)(detc) (M = Mo, W; detc = diethyldithiocarbamate).

RC_2R'	$E_{h\nu}$	$E^{0'}$
R = R' = CO_2Me(DMAC)	15870	-1.43
R = R' = PPh_2	15870	-1.59
R = R' = Ph	16130	-1.59
R = Ph, R' = H	16390	-1.65
R = R' = H	16340	
R = R' = CH_2OH	16670	
R = R' = Et	17150	
R = R' = Me	17390	-1.83
R = EtO, R' = H	17390	-1.87
R = NEt_2, R' = Me	18350	-2.14

Table 1. *$W(CO)(RC{\equiv}CR')(detc)_2$ Data*

RC_2R'	$E_{h\nu}$	$E^{0'}$
R = R' = CO_2Me(DMAC)	13890	
R = R' = $SiMe_3$	14080	-1.50
R = R' = Ph	14290	-1.39
R = Ph, R' = H	14390	-1.42
R = R' = H	14330	-1.46
R = CH_2Cl, R' = H	14600	-1.57
R = R' = Et	15150	-1.70
R = R' = Me	15150	-1.64
R = EtO, R' = H	15500	
R = NEt_2, R' = Me	17240	

Table 2. *$Mo(CO)(RC{\equiv}CR')(detc)_2$ Data*

and spectral data are shown in ***T1*** (for M = W), and ***T2*** (for M = Mo). In both tables, the complexes are listed in order of increasing $E_{h\nu}$. As would be expected, the smallest energy is found for an electron-withdrawing substituent, and the energy increases with increasing electron donation. For M = W, the same order is found for the redox potentials (more energy is required to add an electron to complexes with electron donating substituents). This is also shown in the plot of the redox potential vs. $E_{h\nu}$ ***(F2a)***. For M = Mo, the fundamental trend is the same, but the ordering of the redox potentials does not follow that of the absorption. This is reflected in more scatter in the correlation plot ***(F2b)***.

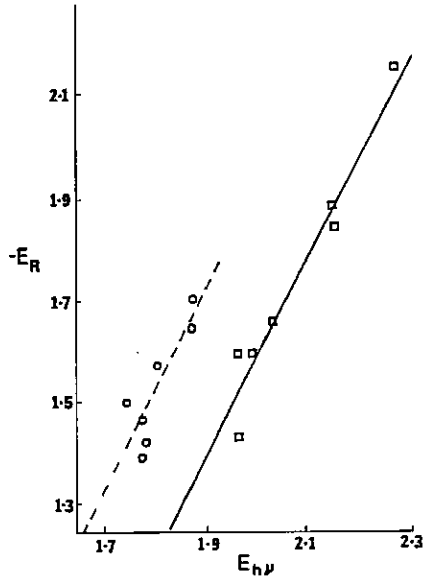

Figure 2. *Redox potential vs. $E_{h\nu}$ plots for $M(CO)(RC_2R)(detc)$ (M = Mo (o) or W (□)).*