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Electrochemical Studies of [BrRe(CO)3(L)]-Type Rhenium(I) Polypyridine Complexes

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Têm-se determinado as propriedades eletroquímicas e espectroscópicas de vários complexos tricarbonil rênio(I), contendo ligantes polipiridínicos (2,2':6',2"-terpiridina (tpy), 4'-fenil-2,2':6',2"-terpiridina (ph-tpy), 4'-(4'''-piridil)-2,2':6',2"-terpiridina (py-tpy), 2',6'-di-2-quinolil-piridina (dq-py), e 2',6'-di-2-naftiridilpiridina (dn-py). Uma boa correlacão entre os valores de $E_{1/2}$ e E_{abs} foi encontrada, considerando as transições de mais baixa energia para os complexos preparados. Isso permite concluir que os mesmos orbitais moleculares estão envolvidos no processo eletroquímico de oxidação-redução e no processo da obsorção com transferência de carga entre o metal e o ligante. A compreensão das propriedades espectrais e redox desses complexos e suas correlações permitem confirmar as transições que ocorrem no espectro eletrônico.

The electrochemical and spectroscopic properties of several tricarbonyl rhenium(I) complexes containing polypyridine ligands (2,2':6',2"-terpyridine (tpy), 4'-phenyl-2,2':6',2"-terpyridine (ph-tpy), 4'-(4'''-pyridyl)-2,2':6',2"-terpyridine (py-tpy), 2',6'-di-2-quinolylpyridine (dq-py), and 2',6'-di-2-naphthyridylpyridine (dn-py) were determined. A good correlation between the redox potentials and E_{abs} was found upon considering the lowest energy transitions of the electronic spectrum for the prepared complexes. We conclude that the same molecular orbitals are involved in the electrochemical oxidation-reduction and in the metal-ligand charge-transfer absorption process for these species. The understanding of the spectral and redox properties of these complexes and their correlations permit the confirmation of the correct transitions in the UV-vis spectrum.

Keywords: *rhenium(I), polypyridine ligands, tricarbonyl*

Introduction

Rhenium(I) tricarbonyl complexes containing $[BrRe^{I}(CO)_3(L)]$-type polypyridine ligands (with L = bpy, tpy, and its derivatives) have been found to act as catalysts for the reduction of carbon dioxide in non-aqueous media to produce carbon monoxide, both photochemically[1] and electrochemically[2]. Recent studies have examined the reduction of CO_2 in a pure aqueous medium[3]. Variations in the structure of the heterocyclic ligands can produce considerable effects in the fundamental electronic structure of the complexes without significantly altering the energy of the excited state[4]. Electrochemical characterization of these systems can provide information concerning the molecular orbitals which participate in the mechanisms of intramolecular electron-transfer reactions[5]. The spectro-

scopic and electrochemical properties of these complexes permitted the correlation of the MLCT excited-state properties with ground-state properties[6], and have obvious applications in designing new species with particular redox energy and excited-state potentials and in checking assignments of observed charge-transfer energies in optical spectroscopy.

In this paper we report the electrochemical behavior of a series of monometallic rhenium(I) tricarbonyl complexes containing various substituted derivatives of 2,2':6',2"-terpyridine ligand (Fig. 1) in which bi-dentate bonding is suggested[7]. A good correlation was found considering the assignment of the lowest energy transitions for the new prepared rhenium(I) complexes. This shows that the same molecular orbitals are involved in the electrochemical oxidation-reduction and in the MLCT absorption process for these species.

Experimental

The polypyridine ligands 4'-phenyl-2,2':6',2"- terpyridine (ph-tpy), 4'-(4'''-pyridyl)-2,2':6',2"- terpyridine (py-tpy), 2',6'-di-2-quinolylpyridine (dq-py), and 2',6'-di-2-naphthyridylpyridine (dn-py) were synthesized by modification of the methods in the literature[8], and the complexes were formed by the general procedure described elsewhere[9].

Electronic absorption spectra were obtained on a Shimadzu UV-160 spectrophotometer using different solvents at ambient temperature. Electrochemical measurements were carried out on a classical three-electrode potentiostatic set-up consisting of a Bank-Wenking POS 73 potentiostat, a XY Linseis recorder model OS 17100, and a Gould oscilloscope model OS 4100. The working and auxiliary electrodes were a Pt disk electrode and a Pt wire, respectively. The reference electrode (SCE) was connected to the cell by a Vycor bridge with the corresponding solvent and supporting electrolyte. A 0.1 mol L^{-1} solution of purified and dried tetrabutylammonium perchlorate (TBAP) in CH_3CN was used as the supporting electrolyte.

Results and Discussion

The redox potentials relevant to the discussion are the ones derived from the processes involving the HOMO and LUMO. The HOMO consists of the d_π orbitals located on Re(I); the LUMO is predominantly the π^* orbital located on the polypyridine ligand. Thus, oxidation involves the removal of an electron from the d_π orbital on Re(I); reduction involves the addition of an electron to the π^* orbital on the polypyridine ligand.

As illustrated in Fig. 2 for $BrRe(CO)_3$(ph-tpy), all the complexes exhibit one reduction and two oxidation peaks during cyclic voltammetry in acetonitrile at 200 mV s^{-1}, corresponding to diffusion-controlled, one-electron processes, as established by linear $i_p/v^{1/2}$ *vs.* v dependence and by comparison of i_p/c values with those of well-known one-electron couples, *e.g.*, Fc^+/Fc[10] (i_p is the peak current measured by cyclic voltammetry at scan rate v; c is the sample concentration). Redox potentials, listed in Table 1, were measured against the ferrocenium/ferrocene couple (Fc^+/Fc) which was used as an internal standard.

In the - 0.4 to - 2.2 V *vs.* Fc^+/Fc range at v = 200 mV s^{-1} one quasi-reversible one-electron reduction peak was observed for the $BrRe(CO)_3$(tpy), $BrRe(CO)_3$(ph-tpy), and $BrRe(CO)_3$(py-tpy) complexes, with i_{pc}/i_{pa} values near 1 and ΔE_p values ($\Delta E_p = E_{pc} - E_{pa}$) which ranged from 80 to 100 mV. However, this peak is definitively irreversible in the $BrRe(CO)_3$(dq-py) and $BrRe(CO)_3$(dn-py) complexes.

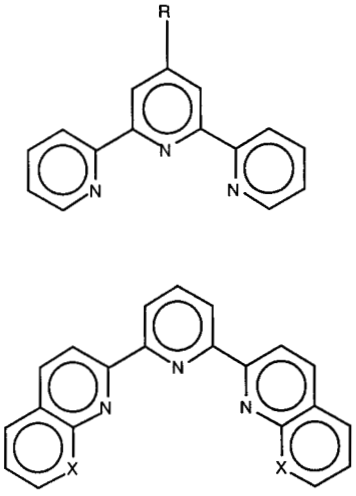

Figure 1. Polypyridine ligands: tpy (R=H), ph-tpy (R=phe), py-tpy (R=py), dq-py (X=CH), and dn-py (X=N).

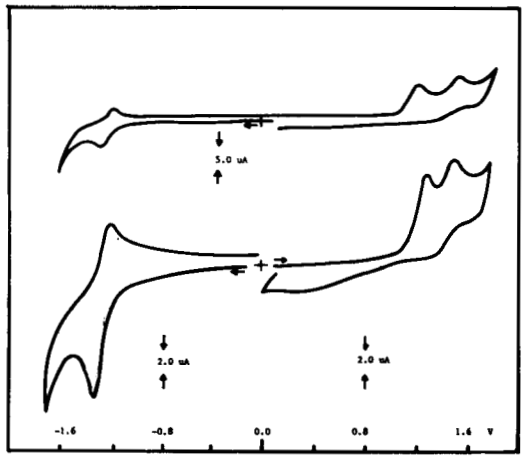

Figure 2. Cyclic voltammogram for $BrRe^I(CO)_3$(ph-tpy) in acetonitrile at 200 mV s^{-1} at 25 °C.

Table 1. Redox potentials and lowest energy transitions to the [BrRe(CO)3(L)]-type complex.

BrRe(CO)3(L) (L =)	redn		oxidn[a]		λ_{max}[e], nm	E_{abs}, eV
	E^{red} b (ΔE_p)[d]	i_{pc}/i_{pa}	E_{pc}^{I}	E_{pc}^{IIc}	(ε[f])	
1. (tpy)	E_{pc} - 1.78	1.16	0.76;	1.09	375	3.306
	E_{pa} - 1.68				(1820)	
	$E_{1/2}$ - 1.73					
	ΔE_p (100)					
2. (ph-tpy)	E_{pc} - 1.71	1.28	0.84;	1.05	387	3.204
	E_{pa} - 1.62				(1960)	
	$E_{1/2}$ - 1.67					
	ΔE_p (90)					
3. (py-tpy)	E_{pc} - 1.24	1.09	0.92;	1.10	373	3.322
	E_{pa} - 1.44				(2400)	
	$E_{1/2}$ - 1.34					
	ΔE_p (200)					
4. (dq-py)	E_{pc} -1.36	–	0.60;	1.07	357	3.479
	E_{pa} -				(900)	
	$E_{1/2}$ -					
	ΔE_p (i)					
5. (dn-py)	E_{pc} - 2.08	–	0.65;	0.94	415	2.988
	E_{pa} -				(840)	
	$E_{1/2}$ -					
	ΔE_p (i)					

[a] potentials in V (± 0.03 V) *vs.* Fc^+/Fc, in CH_3CN 0.1 mol L^{-1} of PTBA, ν = 200 mV s^{-1}; [b] $E_{1/2}^{red}$ = (E_{pc} - E_{pa})/2, where E_{pc} and E_{pa} are the peak cathodic and anodic current potentials, respectively; [c] irrev.; [d] $\Delta E_p = E_{pc} - E_{pa}$ in mV; [e] in CH_3CN 5 x 10^{-4} mol L^{-1} (± 0.5 nm); [f] in L $mol^{-1}cm^{-1}$.

Since the peak potential is sensitive to ligand variation, as reported for similar complexes[6a,6c,11], the peak can be attributed to a reduction of the polypyridine ligand, as illustrated in Eq. 1:

$$BrRe^{I}(CO)_3(L) + e^- \rightarrow [BrRe^{I}(CO)_3(L^{\bullet})]^- \quad (1)$$

in agreement with the fact that the LUMO is the energy level of the polypyridine ligand in these complexes[12].

All the complexes show two oxidation processes in the -0.4 to +1.4 V *vs.* Fc^+/Fc range. The first irreversible, one-electron peak must be associated with the metal-centered oxidation Re(II)/Re(I))[6b,13,14]. The most positive oxidation peak is difficult to assign to a given process due to the irreversibility of the initial oxidation.

The absorption spectra were similar to those of analogous Re(I) tricarbonyl complexes. A typical spectrum consisted of several strong UV bands, assigned as ligand-centered transitions. One broad band was observed in a lower energy region in every case, and this feature is assigned as a MLCT transition $d_\pi(Re^I) \rightarrow \pi^*(L)$ (Table 1) on the basis of intensity, position and solvent dependence[9a,15]. The positions of these low energy bands are also sensitive to the nature of the polypyridine ligand, shifting to longer wavelengths as the degree of the distortion ($BrRe(CO)_3$(tpy), $BrRe(CO)_3$(ph-tpy), and $BrRe(CO)_3$ (py-tpy) complexes), or the π delocalization ($BrRe(CO)_3$ (dq-py) and $BrRe(CO)_3$(dn-py) complexes) in the acceptor polypyridine ligand increases.

As this transition is produced by the oxidation of the metal and the reduction of the polypyridine ligand, it is possible to establish a relationship between the difference of the redox potentials ($\Delta E_{ox/red} = E_{1/2}^{ox} - E_{1/2}^{red}$) and the lowest energy band of the complexes[6a,6b]. However, the irreversibility of the first oxidation process means that $\Delta E_{ox/red} = E_{pa}^{ox,I} - E_{1/2}^{red}$. Figure 3 shows the correlation of the redox potentials with the low-energy MLCT absorption band of the complexes. The linear regression analysis gives the following relationship: $E_{abs} = 4.639 - 0.575\ (\Delta E_{ox/red})$ with r = 0.929; E_{abs} in eV and ΔE in V. This shows the

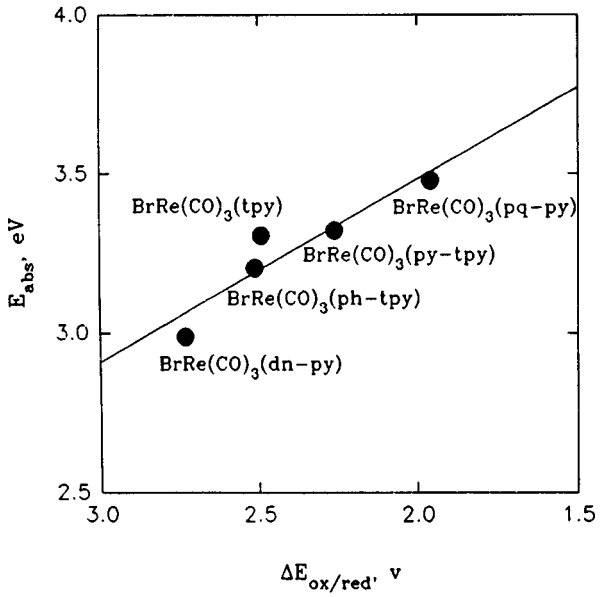

Figure 3. Plots observed of redox data *vs.* E_{abs} for BrRe(CO)3(L) complexes.

difference in energy which exists between the HOMO and the LUMO, and confirms the assignment of the MLCT transition to the lowest energy band in these complexes.

These results demonstrate that ligand substitution provides an effective means for controlling the nature, energy, and photodynamics of the lowest excited state of the complexes. More importantly, it shows that by varying the electronic nature of the polypyridine ligand, it is possible to adjust the ground- and excited-state properties.

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