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Charge-Transfer Processes in (4-Nitrobenzoate)Re(CO)$_3$(azine)$_2$ Complexes. Competitive Reductions of 4-Nitrobenzoate and Azine in Thermally and Photochemically Induced Redox Processes

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The photochemically and thermally induced redox reactions of the (4-nitrobenzoate)Re(CO)$_3$ (azine) (azine = 1,10-phenanthroline, 2,2'-bipyridine, and (4-phenylpyridine)$_2$) were investigated by flash photolysis and pulse radiolysis. Processes characterized as intramolecular charge transfers from coordinated azine radicals to the 4-nitrobenzoate ligand and vice versa were observed in a 1-100 μs time scale by pulse radiolysis. In photochemical experiments, the conversion among metal to ligand charge-transfer excited states, i.e., from the Re to azine to the Re to 4-nitrobenzoate charge-transfer excited state, involves intermediates with lives of picoseconds. A mechanism for the conversions that incorporates intraligand excited states is discussed.

Introduction

Early works about the photochemistry of Re(CO)$_3$(azine)$_2$X compounds, where X = halide and (azine)$_2$ = (4-phenylpyridine)$_2$, 2,2′-bipyridine, or 1,10- phenanthroline derivatives, have shown that photophysical and photochemical properties are largely associated with either or both MLCT$_{\mathrm{azine}\leftarrow\mathrm{Re}}$ and IL$_{\mathrm{azine}}$ excited states.[1,2] In these excited states the azine functions as an electron acceptor, i.e., in a MLCT$_{\mathrm{azine}\leftarrow\mathrm{Re}}$ state, or undergoes changes in its electronic configuration, i.e., in a Il$_{\mathrm{azine}}$ state, similar to those undergone by a free ligand.[1a] Biradical intermediates, Re(CO)$_3$(azine$^{\bullet-}$)(azine$^{\bullet+}$)X, were detected in irradiations that populated electronic states above the lowest MLCT$_{\mathrm{azine}\leftarrow\mathrm{Re}}$.[3] In most of these Re compounds X functions as an "expectator ligand".[4] However, conversions between ^{3}MLCT and ^{3}LLCT excited states appear to control the rate of the luminescence in some Re compounds where X is a dimethylaniline derivative.[5]

Photoprocesses where charge is transferred in parallel from Re to X and azine ligands should be observable paths when, in principle, X is as good or better an electron acceptor as the azine ligand. For example, a one-electron reduction potential from −1.5 to −2.0 V is spanned by the series (azine)$_2$ = (4-phenylpyridine)$_2$, 2,2′-bipyridine, or 1,10-phenanthroline derivatives. The moderately oxidant 4-nitrobenzoate anion 4-O$_2$-NC$_6$H$_4$CO$_2$$^-$ with a reduction potential $\epsilon_0 = -0.3$ to -0.4 V vs NHE, behaves as an electron acceptor in the coordinated-radical-mediated reduction of Co(NH$_3$)$_5$(4-O$_2$CC$_6$H$_4$NO$_2$)$^{2+}$, eq 1.[6]

$$\mathrm{Co^{III}(NH_3)_5(4\text{-}O_2CC_6H_4NO_2)^{2+}} \xrightarrow[-\ \mathrm{Ox}]{+\ \mathrm{Red}} \mathrm{Co^{III}(NH_3)_5(4\text{-}O_2CC_6H_4NO_2^{\bullet})^{+}} \quad (1)$$

$$\{\mathrm{Red} = \mathrm{CO_2}^{\bullet-},\ \mathrm{Ox} = \mathrm{CO_2}\}\ \text{or}\ \{\mathrm{Red} = {}^{\bullet}\mathrm{CH_2OH},\ \mathrm{Ox} = \mathrm{CH_2O} + \mathrm{H^+}\}$$

The slow conversion of the coordinated-radical intermediate to the Co(II) product, eq 2, has been ascribed to the "poor electron permeability" of the carboxylate group coordinated to Co(III).[6b] The lack of overlap between orbitals, the donor (radical) π and the acceptor (metal) σ^*, and/or a large reorganization energy associated with a change in the geometry of the ligand upon reduction were considered possible reasons for the slow reaction rate.[6b] In regard to the Re(I) photophysics, these factors should favor the observation of a charge transfer to the 4-nitrobenzoate ligand by various photochemical and thermal mechanisms. Such redox processes were investigated with (4-nitrobenzoate)Re(CO)$_3$(azine)$_2$ complexes prepared in this work.

$$\mathrm{Co^{III}(NH_3)_5(4\text{-}O_2CC_6H_4NO_2^{\bullet})^{+}} \rightarrow \mathrm{Co^{II}(NH_3)_5(4\text{-}O_2CC_6H_4NO_2)^{+}} \quad (2)$$

Experimental Section

Flash-Photochemical Procedures. Two different flash photochemical apparatus were used for the investigations of reaction kinetics and transient spectra in a time domain of 20 picoseconds to a 100 microseconds.[7,8] Processes occurring in more than several nanoseconds,

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[1] For a review of the subject prior to 1995, see: (a) Ferraudi, G.; Feliz, M.; Wolcan, E.; Hsu, I.; Moya, S. A. Guerrero, J. *J. Phys. Chem.* **1995**, *99*, 4929 and references therein. (b) Lees, A. J. J. *Chem. Rev.* **1987**, *87*, 711. (c) Geofrey, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

[2] Abbreviations: isoquinoline, isoq; quinoline, q; 1,10-phenanthroline, phen; pyridine, py; 4-phenylpyridine, 4-Phpy; 4-cyanopyridine, 4-CNpy; ligand-to-ligand charge-transfer state, LLCT; ligand-to-metal charge-transfer state, LMCT; metal-to-ligand charge-transfer state, MLCT; ligand-centered state, IL; metal-centered (ligand field) state, LF.

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were investigated with a flash photolysis apparatus described elsewhere.[8] In these experiments, 10-ns flashes of monochromatic light were respectively generated with a Nd:YAG (Quanta Ray) or an excimer (Lambda Physik) laser. A mode-locked Nd:YAG (Quantel) laser was used for the generation of 20 ps pump (354 nm) and probe (400−700 nm) light pulses.[7] The probe of optical events was set at instants ranging from several hundred picoseconds in advance to the pump to several nanoseconds following the pump by means of a computer-controlled optical delay. Photochemical-induced changes on the sample's optical density, OD, were recorded with a spectrograph and a dual multichannel analyzer. In this detection system, two spaces inside the reaction cell were probed, but only one of them spatially overlapped with the pump. The effect of the temperature on the rate of the luminescence was investigated by placing photolytes in cells with cylindrical geometries.[1a] The cells were located in a transparent finger of a Suprasil Dewar flask. Solutions for the photochemical work were deaerated with streams of ultrahigh-purity N_2 before and during the irradiations. Concentrations of the complexes were adjusted, i.e., optical densities less than or equal to 0.1 at 355 nm with a 2 mm optical path, to result in homogeneous concentrations of photogenerated intermediates within the volume of irradiated solution.

Pulse-Radiolytic Procedures. Optical pulse radiolysis measurements were carried out with a system and procedures similar to those described earlier.[9] Thiocyanate dosimetry was carried out at each Experimental Section. In this procedure, the output signal of a secondary emission monitor was calibrated against $(SCN)_2^-$ concentrations produced in the radiolysis cell by the electron pulse. A flow system was used to ensure that fresh solution was brought to the reaction cell between electron pulses. Solutions for the irradiation were prepared by adding the solid compounds to liquids previously deaerated with streams of O_2-free gases, i.e., N_2O and N_2. Radiolyses with ionizing radiation of CH_3OH and CH_3OH/H_2O mixtures have been reported elsewhere in the literature.[10,11] These studies have shown that pulse radiolysis can be used as a convenient source of e^-_{solv} and $^{\bullet}CH_2OH$ radicals according to eq 3. Since these products have large reduction potentials, i.e., −2.8 V vs NHE for e^-_{solv} and −0.92 V vs NHE for $CH_2OH^{\bullet}$, they can be used for the reduction of coordination complexes and for the study of electron-transfer reactions. The yield of e^-_{solv} in CH_3OH ($G \approx 1.1$) is about a third of the G value in the radiolysis of H_2O ($G \approx 2.8$).[11] In solutions where e^-_{solv} was scavenged with N_2O,[12] the $^{\bullet}CH_2OH$ radical appears to be the predominant product (yield > 90%) of the reaction between CH_3OH and OH.

$$\begin{array}{lcccccc}
 & CH_3O\bullet + H^+ & & & {}^{\bullet}CH_2OH + CH_3OH & & \\
 & \uparrow & & & \uparrow + CH_3OH & & \\
\rightarrow & CH_3OH^+ & + & e^-_{solv} & + CH_3O\bullet + H^+ & & (3) \\
 & & & \downarrow + CH_3OH + N_2O & & & \\
 & & \bullet CH_2OH + N_2 + OH^- & & & &
\end{array}$$

Steady-State Irradiations. The luminescence of the Re(I) complexes was investigated in an SLM Aminco 8100 interfaced to a Dell 333P microcomputer.[1a] The spectra were corrected for differences in instrumental response and light scattering. Solutions were deaerated with O_2-free nitrogen in a gastight apparatus before recording the spectra.

Materials. The Re(I) complexes, $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(azine)_2$, where $(azine)_2$ = bipy, phen, and (4-phenpy)$_2$, were prepared by some modifications of literature procedures.[14] A given $(azine)_2$ complex, $Re(CO)_3(azine)_2X$ (X = Cl, Br), was reacted with $Ag(4\text{-}O_2NC_6H_4CO_2)$, the silver salt of 4-nitrobenzoate. Small fractions of solid $Ag(4\text{-}O_2NC_6H_4CO_2)$, in the form of a fine powder, were added to a warm solution of the Re(I) complex (2 or 5 g) in CH_3CN (100 cm^3) until the materials were in a 1:1 stoichiometry. This mixture was stirred overnight while kept in the dark and at room temperature. The Re(I) complex in the CH_3CN solution was precipitated by adding pentane after removal of the other product, solid AgX, by filtration. Since some of the precipitated Re(I) complexes were collected with several percents of impurities, they had to be purified by column chromatography on Al_2O_3. The Re complexes were easily eluted, by comparison to the impurities, with $CH_3OH/CHCl_3$ mixtures. Pure Re(I) complexes were collected by rotoevaporation of several chromatographic fractions. Elemental analyses and UV−vis and IR spectra were used for the characterization of the materials and to ascertain their purity. Anal. Calcd for $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(azine)_2$, where $(azine)_2$ = phen: C, 42.86; N, 6.82; H, 1.96; O, 18.16. Found: C, 42.70; N, 6.90; H, 1.89; O, 18.20. Calcd for $(azine)_2$ = bipy: C, 40.54; N, 7.09; H, 2.04; O, 18.90. Found: C, 39.90; N, 6.99; H, 1.99; O, 18.98. Calcd for $(azine)_2$ = (4-Phpy)$_2$: C, 51.47; N, 5.62; H, 2.97. Found: C, 50.50; N, 5.47; H, 2.94. Double displacement reactions of $Na(4\text{-}O_2NC_6H_4CO_2)$ with $AgClO_4$ or $Ag(CF_3SO_3)$ were used for the preparation of Ag $(4\text{-}O_2NC_6H_4CO_2)$. Complexes $Re(CO)_3(azine)_2X$ (X = Cl, Br), were available from previous work.[1a,3] The sodium salt was prepared by titrations of Aldrich $4\text{-}O_2NC_6H_4CO_2H$ with NaOH. Other materials were reagent grade and used without further purification.

Results

Displacements of charge from one ligand to another, following thermal- or photoinduced reductions of one of them, were observed with $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(azine)_2$ compounds. Experimental observations about the steady-state luminescence and time-resolved of processes in excited and ground states are communicated below.

(a) Optical Properties. Given the large differences between the reduction potentials of the azine ligands and $4\text{-}O_2NC_6H_4CO_2^-$, an optical absorption band associated with a charge-transfer transition from Re to $4\text{-}O_2NC_6H_4CO_2^-$ could be expected somewhere in the vis−near-IR wavelengths. However, the absorption spectra of the $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(azine)_2$ and related $ClRe(CO)_3(azine)_2$ complexes are similar with differences, in the UV, due to intraligand transitions of coordinated 4-nitrobenzoate.

The emission spectra of the Re complexes exhibited dependencies on the wavelength of excitation, solvent, and temperature when they were irradiated at wavelengths within the lowest-energy absorption band, $\lambda_{exct} > 300$ nm. For example, the emission spectrum of $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(bipy)$ in deaerated CH_3CN exhibited a maximum at 600 nm and a shoulder at 540 nm when it was irradiated at 350 nm, Figure 1. Relative to this emission spectrum, a bathochromic shift of the 600 nm maximum and quenching of the intensities around the 540 nm shoulder resulted when irradiations were carried out at 395 nm. Excitation spectra recorded by monitoring the luminescence at 680, 540, and 500 nm also showed that features in the luminescence are related to two electronic states; both populated when irradiations of $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(bipy)$ are limited to $\lambda_{exct} > 300$ nm. The effect of the temperature, i.e., when it

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(14) Extended Hückel calculations have been carried out on $Re(CO)_3L_2Cl$ (L = py, 4-Phpy, 4-CNpy, q, isoq) complexes.[3,15] These calculations show that the HOMO is mostly a Re-centered molecular orbital and that the LUMO is mostly an azine-centered molecular orbital. Other filled π orbitals near but of lower energies than the HOMO and empty π^* orbitals near but at higher energies than the LUMO are largely centered on the azine ligands. In the LCAO wave functions for these $\pi$and π^* MOs, Re orbitals, i.e., 5d, 6s, and 6p, appear weighted by very small coefficients, $\alpha^i \leq 0.05$. Based on these observations filled orbitals of $4\text{-}O_2NC_6H_4CO_2^-$ can be expected at lower energies than the HOMO.

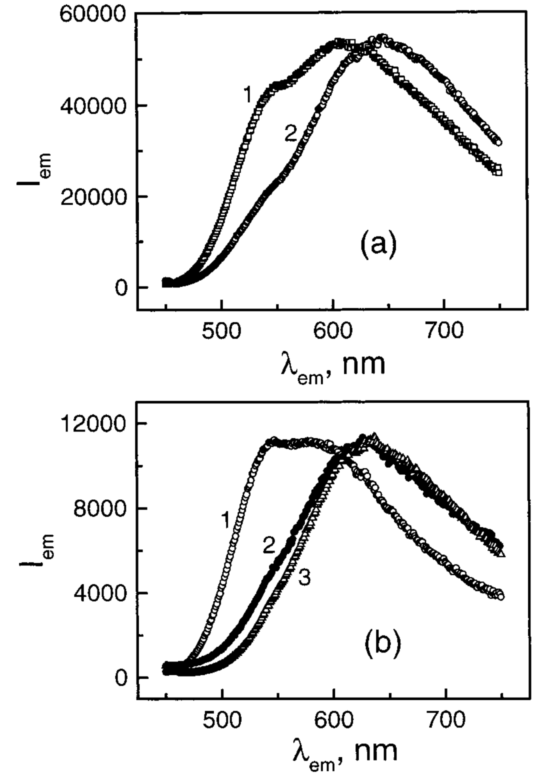

Figure 1. Emission spectra of $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(bipy)$ in various medium conditions. (a) Spectra recorded in 350 nm irradiations of the complex in deaerated CH_3CN at 273 K, with $\lambda_{exc} = 350$ nm (1) and $\lambda_{exc} = 395$ nm (2). (b) Spectra recorded at 298 K in CH_3CN (1), CH_2Cl_2 (2), and CH_3OH (3) with $\lambda_{exc} = 350$ nm.

is reduced from 298 to 273 K, appears to be similar to a change in the wavelength of irradiation. Moreover, differences among the emission spectra in various solvents are more complex than those resulting from a simple rigid shift of the spectral envelope. By comparison to $(4\text{-}O_2NC_6H_4CO_2)\text{-}Re(CO)_3(bipy)$, a weaker luminescence was exhibited by $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(4\text{-}phpy)_2$ and smaller dependencies on the wavelength of excitation, on the solvent, and temperature were observed with $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(phen)$.

(b) Flash-Photochemical Observations. The luminescence kinetics of 4-nitrobenzoate Re(I) complexes, investigated by 355 nm flash photolysis of their deaerated solutions, revealed dual emissions that were differentiated by means of their spectra and/or corresponding lifetimes. Emission lifetimes are listed in Table 1 together with results from the decay of transient optical absorptions. The weakest and usually longer-lived component of the optical density decay could not always be measured by flash photolysis with sufficient accuracy; single values are reported in those instances.

Two well-defined single exponentials, each with a characteristic lifetime, could only be measured at different monitoring wavelengths in flash photolysis of $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3\text{-}(4\text{-}phpy)_2$. In the other two Re(I) complexes, a single-exponential fit to emission and optical density decay traces, collected at wavelengths from 320 to 670 nm, deviated from the data. By contrast, no such deviations were observed with a double-exponential fit, $A\ \exp(t/\tau_1) + B\ \exp(t/\tau_2)$, a photophysical behavior that has been previously observed with other Re(I) complexes.[1a] In such a double-exponential fit, typical values of χ^2 were less than or equal to 10^{-4}. Attempts to separate these two component by using different solvents and temperatures were unsuccessful.

Table 1. Lifetimes of Transients Observed by Flash-Photolysis and Flash-Fluorescence in Deaerated Solutions of $(4\text{-}O_2NC_6H_4CO_2)\text{-}Re(CO)_3(azine)_2$ Complexes

		$\tau\ (\lambda_{ob})^a$	
$(azine)_2$	solvent	lifetimes of OD changes	luminescence lifetimes
$(4\text{-}phpy)_2$	CH_3CN	25 (350 nm); 390 (680 nm)	
	CH_2Cl_2	264 (370 nm); 150 (600 nm)	313 (470 nm); 90 (640 nm)
2,2′-bipy	CH_3CN	25 (400 nm); 430 (450 nm)	25 (680 nm, 298 K); 440 (520 nm, 298 K) 25 (680 nm, 273 K); 430 (520 nm, 273 K)
	CH_2Cl_2	20 (400 nm)	
	benzene	18 (400 nm); 170 (450 nm)	28 (680 nm); 210 (520 nm)
1,10-phen	CH_3OH	20 (400 nm)	20 (680 nm); 156 (520 nm)
	CH_3CN	20; 157[b]	80; 274[b]
	CH_2Cl_2	80; 274[b]	80; 247[b]
	benzene	90; 380[b]	87; –[b]
	chlorobenzene	127; 300[b]	110; 317[b]

[a] Lifetimes in ns were measured at 298 K unless otherwise stated. [b] Lifetimes from a double-exponential fit of the experimental data.

Since lifetimes (Table 1) for the luminescence and transient optical absorptions are similar, spectra measured by flash photolysis under those experimental conditions can be ascribed to the emissive excited states of the Re complexes. Inspection of transient spectra recorded from 20 ns to 2 μs in 355 nm flash irradiations of the 4-phpy, bipy, and phen complexes reveals that, of the two excited states that resulted in the double exponential decay, one must have an absorption band with maxima near 500 nm. Similar absorption bands were observed in the spectra of $MLCT_{azine\leftarrow Re}$ excited states of complexes, $XRe(CO)_3(azine)_2$, where the 4-nitrobenzoate ligand has been replaced by halides (X = Cl, Br). The other excited state, the longest lived of the two, should have a strong absorption band at ca. 300 nm and a much smaller one near 400 nm in order to account for the spectral features. It must be noted that the positions of these bands coincide with those previously observed in the spectra of the 4-nitrobenzoate radical, $4\text{-}O_2NC_6H_4CO_2^{\bullet -}$, free and coordinated to Co(III).[6]

Appropriate spectral changes between 450 and 670 nm for a study of the 20 ps to 2 ns photophysics were found only in the 4-phpy complex, Figure 2. The 355 nm flash irradiation of $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(4\text{-}phpy)_2$ in deaerated CH_3CN resulted in a prompt change of the absorption spectrum that was later followed by further spectral changes at longer times. A resemblance was observed between the prompt photogenerated spectrum of $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(4\text{-}phpy)_2$ photolyses and the spectrum of $MLCT_{azine\leftarrow Re}$, observed in a similar experiment with $ClRe(CO)3(4\text{-}phpy)_2$. While no further spectral changes were observed between 20 ps and 2 ns with $ClRe(CO)_3(4\text{-}phpy)_2$, the experiment with $(4\text{-}O_2NC_6H_4CO_2)Re(CO)_3(4\text{-}phpy)_2$ shows that a prompt photogenerated spectrum changes into the same observed (above) to decay in more than 20 ns. These experimental observations covering from ps to μs had to be rationalized in terms of a minimal mechanism, eq 4–7, of greater complexity than is usually required with other related Re(I) complexes. The excited-state CT_1 in eq 4 accounts for

$$XRe(CO)_3L_2 + h\nu \rightarrow CT_1 \qquad (4)$$

$$CT_1 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} I \qquad (5)$$

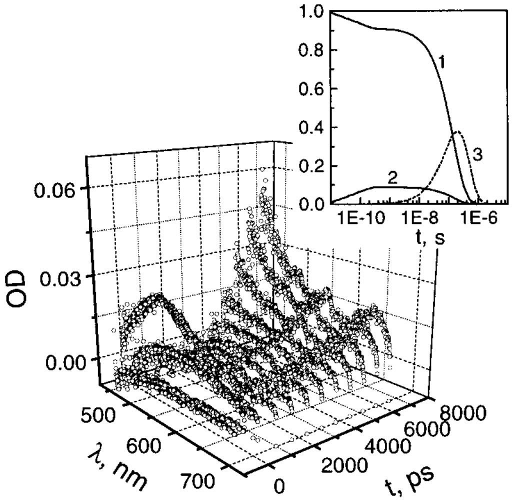

Figure 2. Time-resolved spectra recorded in 353 flash irradiations of (4-O$_2$NC$_6$H$_4$CO$_2$)Re(CO)$_3$(4-phpy)$_2$ in deaerated CH$_3$CN. The insert shows traces calculated for the excited-state CT$_1$ (1), an intermediate I (2), and the excited-state CT$_2$ (3), of the mechanism discussed elsewhere in the text.

$$\mathrm{I} \xrightarrow{k_6} \mathrm{CT}_2 \tag{6}$$

$$\mathrm{CT}_i \xrightarrow{k_7,\,k_8} \mathrm{XRe(CO)_3L_2};\ i = 1, 2 \tag{7}$$

the prompt photogenerated spectrum in the picosecond flash photochemical experiments, e.g., similar to the MLCT$_{\mathrm{azine}\leftarrow\mathrm{Re}}$ in flash photolyses of ClRe(CO)$_3$(4-phpy)$_2$. A lifetime of 5 to 1 ns could be assigned to a relaxation of the equilibrium, eq 5, between CT$_1$ and a precursor, I, of the long-lived excited-state CT$_2$. Conversion of I into CT$_2$ through an irreversible process, eq 6, allows the excited states CT$_i$, $i = 1, 2$, to undergo radiative and radiationless relaxations to the ground state, eq 7, with (experimentally observed) different lifetimes. While assignments of I and CT$_2$ will be deferred to the Discussion, the result of modeling the photophysical behavior of (4-O$_2$NC$_6$H$_4$CO$_2$)-Re(CO)$_3$(4-phpy)$_2$ is considered here. The dependence of the CT$_i$, $i = 1, 2$, and I concentrations, eq 8−10, on time was expressed as

$$[\mathrm{CT}_1] = [\mathrm{CT}_1]_{t_0}\frac{(K + \exp^{-(k_5 + k_5)t})}{(1 + K)}\exp^{-(k_7 + (k_6/K))t} \tag{8}$$

$$[\mathrm{I}] = [\mathrm{CT}_1]_{t_0}\frac{(1 - \exp^{-(k_5 + k_{\bar{5}})t})}{(1 + K)}\exp^{-(k_7 + (k_6/K))t} \tag{9}$$

and

$$[\mathrm{CT}_2] = [\mathrm{CT}_1]_{t_0}\frac{k_6K}{Kk_8 - k_6 - Kk_7}[\exp^{-(k_7 + k_6/K)t} - \exp^{-k_8t}] \tag{10}$$

where $[\mathrm{CT}_1]_{t_0}$ is the flash photogenerated concentration of CT$_1$ and $K = k_{\bar{5}}/k_5$. Such concentrations were calculated (Figure 2) by introducing experimentally measured lifetimes into each species analytical form of the integated rate law. The later mathematical expressions were obtained as solutions of the Laplace transform method applied to a complete set of differential rate-law equations for the species in eq 4−7. In this treatment, the lifetime for the relaxation of the equilibrium, eq 5, was associated with $k_5 + k_{\bar{5}}$.

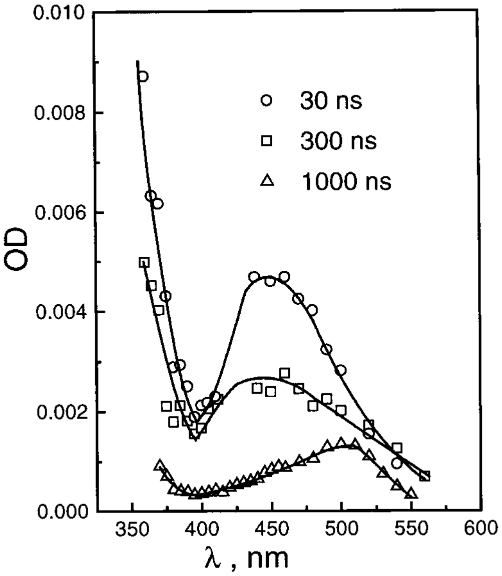

Figure 3. Transient spectra recorded in flash irradiations of (4-O$_2$-NC$_6$H$_4$CO$_2$)Re(CO)$_3$(bipy) in deaerated solutions of TEOA (0.05 M) in CH$_3$CN.

In deaerated solutions of CH$_3$CN, TEOA in concentrations equal to or larger than 0.01 M quenched the luminescence of the Re(I) complexes. Time-resolved spectra, recorded in flash irradiations ($\lambda_{\mathrm{exc}} = 354$ nm) of 10^{-4} M (4-O$_2$NC$_6$H$_4$CO$_2$)-Re(CO)$_3$(bipy) and 0.05−1 M TEOA in CH$_3$CN, revealed that two species resulted from the excited state quenching; one ($\lambda_{\max} = 500$ nm) longer lived than the other ($\lambda_{\max} = 450$), Figure 3. A lifetime dependent on the TEOA concentration was measured for the disappearance of the intermediate with an absorption at 400 nm.

(c) Coordinated Radicals Generated via Pulse-Radiolysis. The coordinated 4-nitrobenzoate radical was produced by reducing (4-O$_2$NC$_6$H$_4$CO$_2$)Re(CO)$_3$(azine)$_2$, (azine)$_2$ = (4-phpy)$_2$ or bipy, with pulse-radiochemically generated $^{\bullet}$CH$_2$OH radicals. In N$_2$O-saturated CH$_3$OH solutions of these Re(I) complexes, the decay of $^{\bullet}$CH$_2$OH in 5.8 μs coincides with the appearance of the (4-O$_2$NC$_6$H$_4$CO$_2$$^{\bullet}$)Re(CO)$_3$(azine)$_2$,

$$\begin{aligned}&(4\text{-}\mathrm{O_2NC_6H_4CO_2})\mathrm{Re(CO)_3(azine)_2} + {}^{\bullet}\mathrm{CH_2OH} \rightarrow \\ &\quad (4\text{-}\mathrm{O_2NC_6H_4CO_2}^{\bullet})\mathrm{Re(CO)_3(azine)_2} + \mathrm{CH_2O} + \mathrm{H}^+\end{aligned} \tag{11}$$

a species with an absorption maximum at 295 nm, Figure 4a. Most of the $^{\bullet}$CH$_2$OH radical appears to decay, however, by dimerization and disproportionation reactions and only a small fraction (~$^1/_6$) by this reaction with (4-O$_2$NC$_6$H$_4$CO$_2$)Re(CO)$_3$-(azine)$_2$. Additional spectral changes were observed between 450 and 600 nm at longer times, i.e., 20−200 us. Their first-order reaction kinetics, independent of Re(I) complex concentration, and the positions of the new optical absorptions suggest some minor intramolecular electron transfer from the coordinated 4-nitrobenzoate radical to the azine ligand. The solvated electron pulse, radiochemically generated in solutions of CH$_3$-OH saturated with N$_2$, reduced (4-O$_2$NC$_6$H$_4$CO$_2$)Re(CO)$_3$-(azine)$_2$ mainly at the azine site producing its characteristic spectrum (absorptions between 450 and 620 nm). These coordinated pyridinium radicals were unstable and disappear, Figure 4b, by generating the coordinated 4-nitrobenzoate radical in a longer (15−150 μs) time scale. It must be noted that interconversion among these radicals suggests that transient species, (4-O$_2$NC$_6$H$_4$CO$_2$$^{\bullet}$)Re(CO)$_3$(azine)$_2$$^-$ and (4-O$_2$NC$_6$H$_4$-

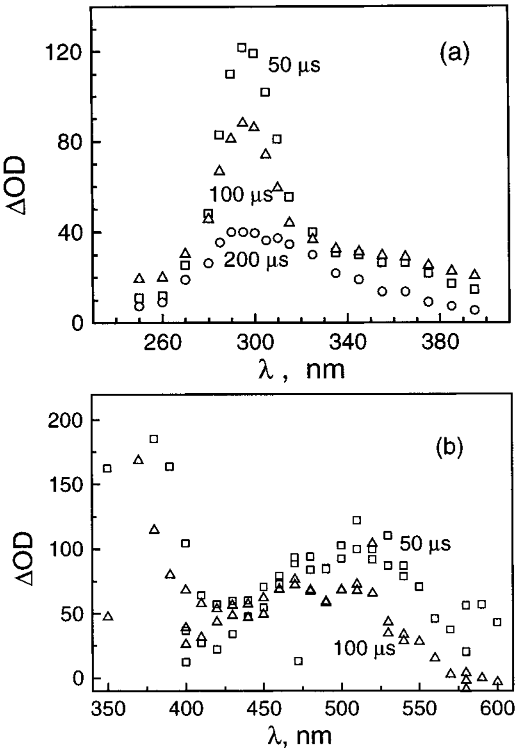

Figure 4. Spectra recorded in pulse radiolysis of (4-$O_2NC_6H_4$-CO_2)Re$(CO)_3$(4-phpy)$_2$ in N_2O-saturated CH_3OH (a) and N_2-saturated CH_3OH (b).

CO_2)Re$(CO)_3$((azine)$_2^{\bullet}$)$^-$ coexist in equilibrium, eq 12.

$$(4\text{-}O_2NC_6H_4CO_2^{\bullet})\mathrm{Re}(CO)_3(\mathrm{azine})_2^{-} \rightleftarrows (4\text{-}O_2NC_6H_4CO_2)\mathrm{Re}(CO)_3((\mathrm{azine})_2^{\bullet})^{-} \quad (12)$$

Discussion

A common feature in the photophysics of the 4-nitrobenzoate complexes of Re(I) in Table 1 is that two excited states result from irradiation at wavelengths of the lowest energy absorption band, i.e., between 340 and 380 nm. Comparison of the time-resolved optical spectra and luminescence of these complexes with those of related materials XRe$(CO)_3$(azine)$_2$[1] (X = Cl, Br, and (azine)$_2$ = (4-phenylpyridine)$_2$, 2,2′-bipyridine, 1,10- phenanthroline) helped to characterize one of these two excited states as a metal-to-ligand (Re to azine) charge-transfer state, $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$. Neither the luminescence nor the transient spectrum associated with the other excited state agrees with that expected for an intraligand state, IL, of the azine ligand, i.e., states which alone or in competition with the $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$ determine the photophysics of numerous Re(I) complexes.[1] Since absorption bands in the spectra of the excited state and the 4-nitrobenzoate radical appear at similar wavelengths, some localization of electric charge in the 4-nitrobenzoate ligand must ensue in such an excited state, i.e., the one expected for a $\mathrm{MLCT}_{\mathrm{NO_2Bzt}\leftarrow\mathrm{Re}}$ charge-transfer excited sate. The luminescence kinetics, discussed below, supports this spectroscopic assignment vs one of an intermediate with a coordinated radical similar to those detected in pulse radiolysis.

Time-resolved measurements of the (4-$O_2NC_6H_4CO_2$)Re-$(CO)_3$(azine)$_2$ luminescence, several ns after the laser irradiation, show the two MLCT excited states decaying with two very different lifetimes. A mechanism, eqs 4−7, that rationalizes these experimental observations and the spectral changes in the picosecond domain must consider equilibration of the $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$ with a precursor, I, of the $\mathrm{MLCT}_{\mathrm{NO_2Bzt}\leftarrow\mathrm{Re}}$. Photophysical schemes which solely consider the irreversible conversion of one state into the other or a thermal equilibration between $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$ and $\mathrm{MLCT}_{\mathrm{NO_2Bzt}\leftarrow\mathrm{Re}}$ fail to account for the kinetics of the luminescence and/or absorptions from ps to μs. In this regard, the appearance of the $\mathrm{MLCT}_{\mathrm{NO_2Bzt}\leftarrow\mathrm{Re}}$ spectrum several ns after the $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$ was produced by the absorption of light can be related to relaxation of the equilibrium between $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$ and I. A plot of the calculated concentrations of I, $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$ and $\mathrm{MLCT}_{\mathrm{NO_2Bzt}\leftarrow\mathrm{Re}}$ as a function of time shows that the concentration of I rises and decays long after an equilibration between I and $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$ has been reached.

The displacement of charge mediated by I, from azine to 4-nitrobenzoate, is a much faster process, eq 4−7, than the equilibration observed between two ground-state radical-like species, eq 12, in pulse radiolysis. This observation suggests that the exchange of the electron between ligands in the ground-state radical-like species is kinetically hindered. One possible reason for this behavior is the wrong symmetry of vacant high-energy Re(I)-centered orbitals above the ligand-centered LUMO, i.e., a condition leading to a small electronic coupling.[14,15] An internal conversion of the $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$ to the $\mathrm{MLCT}_{\mathrm{NO_2Bzt}\leftarrow\mathrm{Re}}$ can be regarded as a process close to a ligand-to-ligand charge transfer, i.e., nearly devoid of the metal center participation. Based on the reasons presented above for transformations between radical-like species, eq 12, such an internal conversion should be much slower than radiationless relaxations of the MLCT excited states. It must be noted that, in the $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$, the metal-centered HOMO is partially occupied and possesses the correct symmetry for overlapping π orbitals in the 4-nitrobenzoate and azine ligands.[14] On an empirical basis, this cannot be a sufficient condition for rapid exchange because an intermediate I, eqs 5−7, is also required in the excited state conversion. An additional feature is that a partially occupied HOMO opens paths from the $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$ to the $\mathrm{MLCT}_{\mathrm{NO_2Bzt}\leftarrow\mathrm{Re}}$ through intraligand and LLCT excited states involving one-electron electronic transitions. In their absence, low-probability simultaneous promotions of two electrons are required, e.g. those entailing electronic density centered at the Re. An interesting feature of the mechanism is that these various steps in the $\mathrm{MLCT}_{\mathrm{azine}\leftarrow\mathrm{Re}}$ to the $\mathrm{MLCT}_{\mathrm{NO_2Bzt}\leftarrow\mathrm{Re}}$ conversion are exoergonic by about several tenths of a Volt, i.e., they exhibit a considerable driving force toward the $\mathrm{MLCT}_{\mathrm{NO_2Bzt}\leftarrow\mathrm{Re}}$.

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